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Mechanism of Intramolecular Energy Transfer in Rare Earth Chelates as Revealed by Infrared Absorption Measurements

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The purpose of this paper is to clarify the mechanism of intramolecular energy transfer from the triplet state of the ligand to the excited levels of the central ion in rare earth chelates. As to seven kinds of samarium β-diketonates, the frequency of infrared absorption due to the stretching vibration of the chelate bond, $\tilde{\nu}_{\mathrm{MO}}$, and the manner of energy transfer are investigated. The probability of energy transfer is estimated from the ratio of the intensity of the samarium emission to that of the ligand phosphorescence, $I_{\mathrm{Sm}}/I_{\mathrm{ph}}$. The overlap integral, S, between the ligand phosphorescence spectrum and the samarium absorption spectrum is obtained. It was found that a linear relation roughly holds between $\log\{(I_{\mathrm{Sm}}/I_{\mathrm{ph}})/S\}$ and $\tilde{\nu}_{\mathrm{MO}}$. On the basis of this fact, one is led, by making some arguments, to the conclusion that intramolecular energy transfer is dominated by the resonance mechanism due to the exchange interaction of the π electron system of the ligand triplet state with the f electron system of the central rare earth ion.

In chelates of rare earths such as europium, intramolecular energy transfer takes place from the ligand to the central rare earth ion, and consequently luminescence of line spectrum due to the f–f transition of the rare earth ion is emitted. The manner and mechanism of this intramolecular energy transfer process has been recently studied by a number of investigators. This has attracted interest also from the viewpoint that these chelates are important as laser materials.

In our previous paper,[1] we have elucidated that after absorption from the ground state to the excited singlet state of the ligand relaxation takes place to the triplet state of the ligand, and then energy is transferred to the central rare earth ion. The purpose of this paper is to clarify the mechanism of this energy transfer process. It is considered that the nature of the chelate bond is closely connected with the efficiency of the energy transfer process. The strength and electron density of the chelate bond will be widely changed with the change of the ligand. This would be strongly reflected to the manner of infrared absorption due to the vibration of the chelate bond. Therefore, it would be useful, for clarifying the mechanism of energy transfer, to investigate the correlation of the efficiency of intramolecular energy transfer with the frequency of the infrared absorption of the chelate bond.

The infrared absorption of metal chelates has been studied by several investigators. Nakamoto and Martell[2] calculated the frequency of the stretching vibration of chelate bond for transition metal acetylacetonates by the normal-coordinate analysis, and made the assignment of observed infrared absorption bands. Misumi and Iwasaki[3] also carried out the normal-coordinate analysis for acetylacetonates of various rare earths, and stated that the force constants for the stretching of rare earth-oxygen (M–O) bond are nearly proportional to the reciprocal values of M–O bond length.

Previously, we have investigated[4] the correlation between the manner of the temperature quenching of the emission of chelated europium ion and the frequency of the M–O bond stretching vibration for seven kinds of europium β-diketonates. It was found in general that the higher the frequency of the M–O bond vibration is, the less quenched the europium emission is with increasing temperature. It was reported by Bhaumik[5] that both the intensity and the lifetime of the emission of chelated europium ion decrease with increasing temperature from 77°K, but that the intensity starts to decrease at lower temperatures than the lifetime does. For instance, in the case of europium

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[1] Y. Matsuda, S. Makishima and S. Shionoya, This Bulletin, **41**, 1513 (1968).

[2] K. Nakamoto and A. E. Martell, *J. Chem. Phys.*, **32**, 588 (1960).

[3] S. Misumi and N. Iawsaki, This Bulletin, **40**, 550 (1967).

[4] S. Shionoya, Y. Matsuda, M. Morita and S. Makishima, a contributed paper at Internatl. Conf. Luminescence, Budapest, 1966, p. 9–84; in press in Proc.

[5] M. L. Bhaumik, *J. Chem. Phys.*, **40**, 3711 (1964).

dibenzoylmethide, the intensity starts to decrease at 120°K while the lifetime at 220°K. Similar tendencies were observed for the other europium chelates. From these facts it is suggested that the manner of the temperature quenching is mainly dominated by the temperature dependence of the non-radiative process taking place in the ligand part before intramolecular energy transfer occurs. Then, our results as mentioned above are regarded as indicating that for those europium chelates in which the temperature quenching hardly occurs, the efficiency of intramolecular energy transfer is high and also the frequency of absorption bands due to the M–O bond stretching vibration is high. This was thought to imply that the shorter the M–O bond length is, the higher the efficiency of energy transfer becomes. It was, however, difficult for europium chelates to estimate quantitatively the efficiency of intramolecular energy transfer. If it could be done, it would present more useful information for clarifing the mechanism of intramolecular energy transfer.

It is known that samarium β-diketonates show both the samarium emission and ligand emission, although europium β-diketonates show only the europium emission. Therefore, in case of samarium chelates, it would be possible to estimate the efficiency of energy transfer from the relation between the intensity of the ligand emission and that of the samarium emission. In this paper, as to seven kinds of samarium β-diketonates, infrared absorption due to the vibration of the chelate bond and the manner of intramolecular energy transfer are investigated.

In rare earth chelates, the absorption spectra of the ligand parts show no significant difference in comparison with those of the free ligand molecules,[1] and also the emission spectra of the chelated rare earth ions are very similar to those of the free ions in solutions. Furthermore, energy transfer from the ligand to the rare earth ion is suggested to occur only in a short range, on the basis of the fact, reported by us,[1] that energy transfer does not take place if β-diketone is not coordinated to the rare earth ion in solution. From these facts, the ligand π electron system, *i. e.* energy donor, is considered to interact very weakly with the f electron system of the rare earth ion, *i. e.* energy acceptor. Therefore, it would be inferred that the theory of intermolecular energy transfer due to the resonance mechanism in condensed systems, as developed by Förster[6] and further by Dexter,[7] is also applicable to the intramolecular energy transfer in the present case. It is, therefore, necessary, for discussing the problem along this inference, to take the energy overlap of the ligand triplet level with the excited levels of the chelated rare earth ion into consideration. This energy overlap is estimated from spectral measurements. As will be described below, it has been revealed that the intramolecular energy transfer is governed by the resonance mechanism due to the exchange interaction between the ligand and the central rare earth ion.

Experimental

1) Samples. Hexa-coordinated β-diketonates of samarium were used in this investigation, although octa-coordinated ones were used by many other investigators. The reason is that octa-coordinated chelates are dissociated in solutions so that errors might be caused. The chelates used are listed with their abbreviations in Table 1. These samples were prepared by the following methods.

TABLE 1. LIST OF SAMARIUM β-DIKETONATES, $R_1 \cdot CO \cdot CH_2 \cdot CO \cdot R_2$, USED IN THIS INVESTIGATION

Chelates	Abbreviation	R_1	R_2
Samarium acetylacetonate	SmAA	CH_3	CH_3
Samarium trifluoroacetylacetonate	SmTAA	CF_3	CH_3
Samarium benzoylacetonate	SmB	CH_3	C_6H_5
Samarium trifluorobenzoylacetonate	SmBFA	CF_3	C_6H_5
Samarium dibenzoylmethide	SmD	C_6H_5	C_6H_5
Samarium thenoyltrifluoroacetonate	SmTTA	CF_3	C_4H_3S
Samarium furoyltrifluoroacetonate	SmFTA	CF_3	C_4H_3O

a) SmAA, SmTAA, SmB, SmBFA: About 100 m*l* of xylene solution containing 5 g of β-diketone was refluxed with the stoichiometric quantity of metallic sodium untill all the quantity of sodium had reacted. The precipitate was filtered and was washed with *p*-xylene, benzene and ether in this order. The product, *i. e.* sodium β-diketonate, was dried by air. Aqueous solution of samarium chloride was mixed with aqueous solution of sodium β-diketonate. The precipitate, *i. e.* octa-coordinated chelate, was filtered and washed several times with water. The product was recrystallized in acetone-water, and then was dried under vacuum for 20 hr at 80—100°C in order that it is converted to hexa-coordinated chelate.

b) SmD: The octa-coordinated chelate was prepared by the ordinary piperidine method at first. This was kept under vacuum for 24—30hr at 150°C to obtain hexa-coordinated chelate.[8]

c) SmTTA, SmFTA: Aqueous solution of samarium nitrate was added to toluene solution containing about 30% excess ligand in a separatory funnel. About 50% excess piperidine was added to the solution. This was then shaken and was separated into aqueous and toluene solutions. Normal pentane was added to the toluene solution. The precipitate was collected, and

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[6] Th. Förster, *Ann. Phys.*, **2**, 55 (1948).

[7] D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

[8] R. E. Whan and G. A. Crosby, *J. Mol. Spectry.*, **8**, 315 (1962).

recrystallized in toluene-pentane. The product, *i. e.* octa-coordinated chelate, was kept under vacuum at 120—150°C for 20 hr to obtain hexa-coordinated one.

2) Optical Measurements. *a) Infrared Absorption Spectra.* The measurement was made with a Hitachi EPI-2 infrared spectrophotometer with an NaCl or KBr prism for NaCl or KBr region, respectively, by means of the KBr disk method.

b) Emission Spectra. The measurement was made at liquid nitrogen temperature for methanol-ethanol (1 : 3) solutions of the chelates with the concentration of 5×10^{-3} M. A Kipp & Zonen prism double monochromator and an EMI 9558QB photomultiplier were used. As the exciting light, the 365 mμ line obtained from a 1 kW high pressure mercury lamp combined with a Bausch & Lomb grating monochromator was used.

c) Emission Lifetime. An Edgerton FX-3 type xenon flash lamp (energy: 1 joule/pulse, duration: 2μsec) with an ultraviolet-pass filter was used as the exciting light source. The response of an RCA 931A photomultiplier was fed to an oscilloscope, and decay curve was photographed. All the measuremens were made for methanol-ethanol (1 : 3) solutions of the concentration of 1×10^{-3} M at liquid nitrogen temperature.

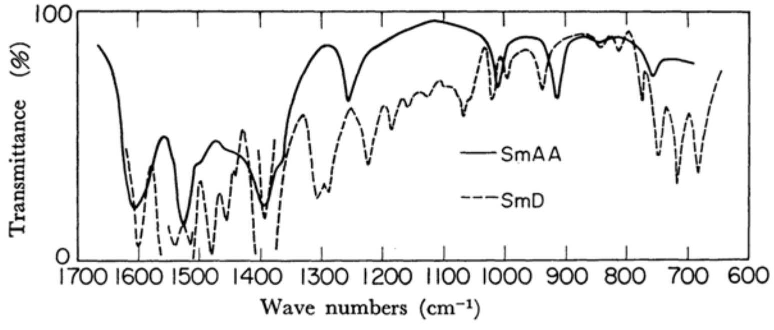
Results and Discussions

Infrared absorption spectra were measured for seven kinds of samarium β-diketonates listed in Table 1. As examples, the spectra of SmAA and SmD are shown in Fig. 1.

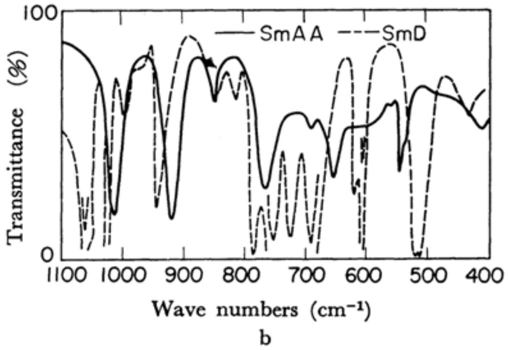
The assignment of infrared absorption bands for metal acetylacetonate was made, as mentioned already, by several investigators. The theoretical assignment was given first by Nakamoto and Martell[2] for transition metal acetylacetonates. Misumi and Iwasaki[3] carried out a similar calculation for rare earth acetylacetonates. Liang *et al.*[9] also carried out a similar analysis for EuAA. It was pointed out by both of these authors that in rare earth chelates an absorption band in a region of 400 to 450 cm^{-1} is mainly due to the M–O bond stretching, and that another absorption band located at the second place counted from the short wavelength side in a region of 1500 to 1700 cm^{-1} is mainly due to the C–O bond stretching. The assignment for other rare earth β-diketonates was made empirically on the basis of the calculation for acetylacetonate.

Misumi and Iwasaki[3] showed for acetylacetonates of various rare earth ions that the larger the atomic number of the central ion is, the higher the frequency of the absorption band due to the M–O bond stretching is. We measured the frequency of this band in six kinds of β-diketonates, other than acetylacetonates, of lanthanum, samarium, europium and gadolinium, and found that this kind of tendency also holds.

The observed frequency of the absorption bands due to the M–O and C–O bond stretching, $\tilde{\nu}_{MO}$



a



b

Fig. 1. Infrared absorption spectra of SmAA and SmD, a) obtained by NaCl prims, and b) by KBr prism.

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[9] C. Y. Liang, E. J. Schimitschek, D. H. Stephens and J. A. Trias, *J. Chem. Phys.*, **46**, 1588 (1967).

and $\tilde{\nu}_{CO}$, for seven kinds of samarium β-diketonates are given in Table 2. The frequency for the M–O bond stretching changes with the change of R_1 and R_2 in β-diketonates. Namely, the value of $\tilde{\nu}_{MO}$ becomes smaller in the order of $C_6H_6 \rightarrow CF_3 \rightarrow CH_3$. On the other hand, the value of ν_{CO} does not show such a systematic change.

TABLE 2. INFRARED ABSORPTION FREQUENCY DUE TO M–O AND C–O BOND STRETCHING, $\tilde{\nu}_{MO}$ AND $\tilde{\nu}_{CO}$, RATIO OF THE INTENSITY OF SAMARIUM EMISSION TO THAT OF LIGAND PHOSPHORESCENCE, I_{Sm}/I_{ph}, OVERLAP INTEGRAL BETWEEN LIGAND PHOSPHORESCENCE SPECTRUM AND SAMARIUM ABSORPTION SPECTRUM, S, AND $(I_{Sm}/I_{ph})/S$, FOR SEVEN KINDS OF SAMARIUM β-DIKETONATES

	$\tilde{\nu}_{MO}$(cm^{-1})	$\tilde{\nu}_{CO}$(cm^{-1})	I_{Sm}/I_{ph}	S	$(I_{Sm}/I_{ph})/S$
SmBFA	438	1530	1.00	0.630	0.444
SmD	430	1538	0.819	0.229	1.00
SmB	433	1523	0.573	1.00	0.160
SmFTA	432	1522	0.242	0.477	0.142
SmTTA	417	1538	0.0296	0.486	0.0170
SmTAA	420	1534	0.0105	0.191	0.0154
SmAA	409	1520	0.00617	0.296	0.00581

Samarium β-diketonates show, under the excitation by ultraviolet light, the emission due to the f–f transitions in the chelated samarium ion, the fluorescence from the excited singlet state of the ligand and the phosphorescence from the triplet state of the ligand. As an example, the emission spectrum of SmAA at liquid nitrogen temperature is given in Fig. 2.

We observed[1] that there is no significant difference between the phosphorescence spectra of lanthanum and gadolinium chelates which do not show the emission of the central ions. This fact indicates that the ligand triplet state is hardly affected by changing the central ion. In Fig. 2, the spectrum of the total ligand emission is separated into the phosphorescence and the fluorescence by referring to their spectra in lanthanum and gadolinium chelates.

The decay times for the samarium emission in seven kinds of samarium β-diketonates were measured by picking a part arround 600 mμ in the spectra up with color filters. It was found that the decay times are in a range of 25 to 35 μsec. The decay times for the phosphorescence were measured for a part arround 490 mμ in the spectra. Those of SmB, SmD and SmBFA were 5, 5 and 7μsec, respectively. For other samarium chelates the measurement could not be made because of low intensities of their phosphorescence.

We reported, as mentioned above, that in rare earth chelates the transfer of excitation energy takes place from the triplet state of the ligand to the excited levels of the chelated rare earth ion. For the samarium chelates studied the probabilities of non-radiative transition within the samarium excited levels would be nearly equal among each other at liquid nitorgen temperature, since there is no significant difference among the lifetimes of the samarium emission. If the transition probability from the triplet state to the ground state of the ligand does not change among these chelates, the probability of intramolecular energy transfer should be proportional to the intensity ratio of the samarium emission to the ligand phosphorescence, I_{Sm}/I_{ph}. However, the transition probability from the triplet to ground state of the ligand cannot be measured for samarium chelates, because of the reason that the lifetime of the triplet state of

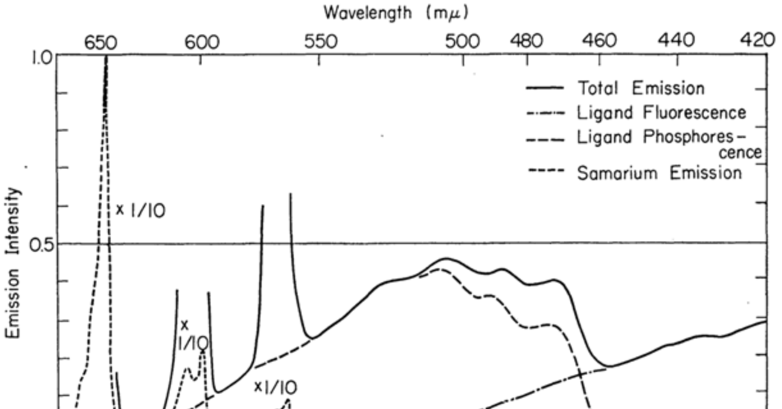

Fig. 2. Emission spectrum of SmAA at liquid nitrogen temperature. The total emission is separated into ligand fluorescence, ligand phosphorescence and samarium emission. "×1/10" indicates that emission intensity is reduced to one tenth.

samarium chelate is made shorter by the occurrence of intramolecular energy transfer, so that one can not estimate the transition probability from the observed lifetime of the phosphorescence. In the gadolinium β-diketonates, however, intramolecular energy transfer does not occur. Therefore, for seven kinds of gadolinium chelates, the ligands of which are the same as those of samarium chelates under study, the lifetime of the phosphorescence was observed, and was found to be in a range of 35 to 45μsec.

From this it may be considered that these samarium β-diketonates have nearly equal transition probabilities from the triplet to ground state of the ligand. Therefore, the probability of intramolecular energy transfer is regarded to be proportional to $I_{\mathrm{Sm}}/I_{\mathrm{ph}}$. The observed values are given in Table 2. Here, I_{Sm} and I_{ph} were obtained, respectively, from the areas of the spectra for the samarium emission and the ligand phosphorescence.

It is clearly observed from the table that the transfer efficiency is enhanced by the fluorination of the ligand or by the enlargement of the conjugate system. Further from the observation of the table, it is very roughly said that in these seven kinds of samarium chelates the larger the value of $I_{\mathrm{Sm}}/I_{\mathrm{ph}}$ is the higher the frequency of $\tilde{\nu}_{\mathrm{MO}}$ is, although there are some exceptions. As for the frequency of $\tilde{\nu}_{\mathrm{CO}}$ such a tendency is more obscure.

Since it is inferred, as mentioned already, that the resonance between the π electron system in the ligand and the f electron system in the rare earth ion might be responsible for energy transfer, one has to take the overlap between the spectrum of the phosphorescence from the triplet state of the ligand and that of the absorption of the rare earth ion into consideration for discussing the mechanism of the intramolecular energy transfer. Therefore, the overlap integral, S, as expressed by the following equation was estimated,

$$S = \int I_{\mathrm{ph}}(E)\,\alpha(E)\,\mathrm{d}E, \qquad (1)$$

where $I_{\mathrm{ph}}(E)$ is the phosphorescence spectrum and $\alpha(E)$ is the absorption spectrum of the chelated samarium ion, both being normalized as

$$\int I_{\mathrm{ph}}(E)dE=1 \text{ and } \int \alpha(E)\,dE=1.$$

Since the absorption spectra of the chelated samarium ions in the chelates used could not be measured because of their very small absorption coefficient, the absorption spectrum of $\mathrm{SmCl_3}$ solution was used as a substitute. The absorption and emission spectra of $\mathrm{SmCl_3}$ in ethanol solution with the concentration of 1 M are shown in Fig. 3. The absorption measurement was made with a Cary model 14 spectrophotometer at room temperature. This shows an emission spectrum similar to that of the chelated samarium ion; that is, the positions of the emission peaks differ only by 0.006—0.009 eV from those of the chelated samarium ion. The band-width of the phosphorescence spectrum of samarium β-diketonates is about 0.4 eV as seen from Fig. 2. The peak position of the phosphorescence spectrum depends markedly on the kind of the ligand in samarium β-diketonates. It differs at least by 0.25 eV among the seven chelates studied. Therefore, the slight difference of the samarium emission spectra between the chelates and chloride is negligible in comparison with the difference of the phosphorescence spectra. From these facts, it is reasonable to use the absorption spectrum of samarium chloride as a substitute for that of the chelates. The results for S thus estimated are given in Table 2. The values are expressed by normalizing the largest value to be unity.

As is well known Förster[6)] investigated the theory of intermolecular energy transfer by resonance mechanism. Dexter[7)] developed the theory further to the case where the resonance due to various types of interactions take place. In the case of energy transfer due to exchange interaction, which occurs when energy donor and acceptor are located in close ranges, the probability of transfer, P_t, is approximately given by[7)]

$$P_t = \text{const. } S \exp(-2R/L), \qquad (2)$$

where R is the donor-acceptor distance, L is the

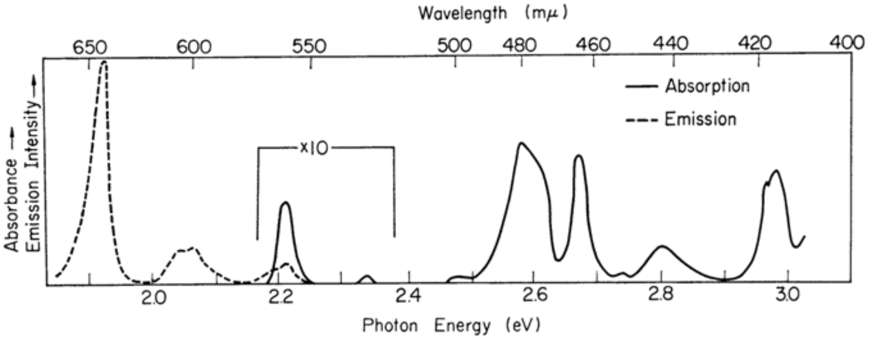

Fig. 3. Absorption spectrum at room temperature and emission spectrum at liquid nitrogen temperature of $\mathrm{SmCl_3}$ in ethanol solution. "×10" indicates that absorbance is ten times magnified.

effective average Bohr radius for the excited and unexcited states of donor and acceptor and S is the overlap integral as defined by Eq. (1). The exponential term of this equation represents the magnitude of the spacial overlap of the wave functions of donor and acceptor.

I_{Sm}/I_{ph} is, as described above, proportional to the probability of intramolecular energy transfer. It was found, after some graphical trial, that a linear relation roughly holds between the values of $\log\{(I_{Sm}/I_{ph})/S\}$ and $\tilde{\nu}_{MO}$ as shown in Fig. 4. Namely,

$$I_{Sm}/I_{ph} \propto P_t = a\,S\exp(b\,\tilde{\nu}_{MO}), \tag{3}$$

where a and b are constants.

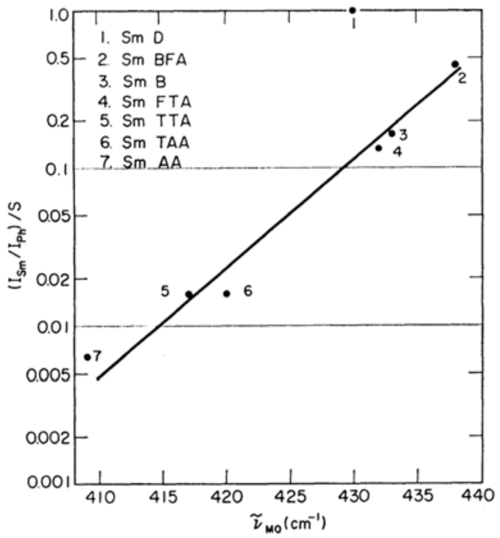

Fig. 4. Plotting of $\tilde{\nu}_{MO}$ *vs.* $(I_{Sm}/I_{ph})/S$ (in logarithmic scale) for seven kinds of samarium β-diketonates.

Let us examine how this experimentally obtained equation is correlated with Eq. (2), the theoretical one for the case of energy transfer due to the exchange interaction. The reduced mass relating with $\tilde{\nu}_{MO}$ in Eq. (3) has the same value for all chelates studied, since M is always samarium. Therefore, $\tilde{\nu}_{MO}$ is proportional to the square root of the force constant of the M–O bond stretching, $\sqrt{k_{MO}}$. Since all the observed values of $\tilde{\nu}_{MO}$ are located in a small range of frequency, *i. e.* in 409 to 438 cm^{-1}, $\tilde{\nu}_{MO}$ can be approximately replaced by k_{MO}. Then, Eq. (3) can be rewritten as,

$$P_t = a'S\exp(b'\,k_{MO}), \tag{4}$$

where a' and b' are constants. It was confirmed that if the plot of $\tilde{\nu}_{MO}{}^2$ *vs.* $\log\{(I_{Sm}/I_{ph})/S\}$ is made, a rough straight line as in Fig. 4 is obtained.

Several authors studied the correlation of the force constant of chelating bond with the bond length and also with the electron density at the bond. Misumi and Iwasaki³⁾ reported, as mentioned already, that k_{MO} is nearly proportional to the reciprocal value of the M–O bond length for various rare earth acetylacetonates, if the sum of the ionic radii of oxygen and rare earth ion is taken as the bond length. For the acetylacetonates they studied, the bond length is in the range of 1.43 to 1.56 Å, and $\tilde{\nu}_{MO}$ in the range of 420 to 432 cm^{-1}. The observed values of $\tilde{\nu}_{MO}$ shown in Table 2 change from 409 to 438 cm^{-1}. The M–O bond length in this case, therefore, would be regarded to change a little more widely than the case reported by Misumi and Iwasaki. It would be likely that in various samarium chelates the real length of the M–O bond changes by the change of ligand. Since k_{MO} would be affected by the M–O bond length, r_{MO}, one may assume that the correlation between k_{MO} and r_{MO}, as reported by Misumi and Iwasaki, also holds in this case in which the ligand, but not the central ion, is changed. Since the change of r_{MO} in various samarium chelates is limited only in a narrow range, the inverse proportion of k_{MO} to r_{MO} can be replaced by a simpler dependence, in other words, k_{MO} may be regarded to decrease linearly with the increase of r_{MO}.

Nakamoto *et al.*[10] showed that k_{MO} of transition metal β-diketonates is increased, if the electron density at oxygen in chelate bond is increased by the substitution of R_1 and R_2. Taking it into consideration that k_{MO} is increased with the increase of the electron density at oxygen and also with the increase of electronegativity of the central ion, one can assume that k_{MO} is increased with the increase of electron donation from oxygen to the central ion in chelate bond. The increase of the electron donation would cause the reduction of the bond length.

From the above-mentioned discussion, one may say that k_{MO} is decreased approximately in proportion to the increase of r_{MO}. Therefore Eq. (4) can be rewritten as,

$$P_t = a''S\exp(-b''\,r_{MO}), \tag{5}$$

where a'' and b'' are constants. This equation is equivalent to Eq. (2).

This indicates that the theory of intermolecular energy transfer due to the exchange interaction can be applied also to intramolecular energy transfer in the chelate system. In other words, this indicates that the intramolecular energy transfer under discussion is dominated by the resonance mechanism due to the exchange interaction of the π electron system of the ligand triplet state with the f electron system of the central rare earth ion.

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[10] K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Am. Chem. Soc.*, **66**, 346 (1962).

Summary and Conclusion

In order to clarify the mechanism of intramolecular energy transfer in rare earth chelates, the correlation of the efficiency of energy transfer with the frequency of the infrared absorption of the chelate bond was investigated. It is known that this energy transfer takes place *via* the triplet state of the ligand. Seven kinds of samarium β-diketonates as shown in Table 1 were used, since samarium chelates show both the samarium emission and ligand emission so that they are more suitable for the present investigation than the chelates of other rare earths. The probability of intramolecular energy transfer was estimated from the ratio of the intensity of the samarium emission to that of the ligand phosphorescence. It is inferred that the theory of intermolecular energy transfer due to the resonance mechanism would be also applicable to the intramolecular energy transfer in the present case. To make discussion along this inference, the overlap integral between the ligand phosphorescence spectrum and the samarium absorption spectrum was estimated.

It was found that an experimental relation as expressed by Eq. (3) roughly holds among the probability of intramolecular energy transfer, the frequency of infrared absorption due to the stretching vibartion of the chelate bond and the overlap integral. By some arguments it was shown that this equation is equivalent to the theoretical equation, Eq. (2), expressing the probability of energy transfer by the resonance mechanism due to the exchange interaction. In conclusion, one can say that intramolecular energy transfer in rare earth chelates is dominated by the resonance mechanism due to the exchange interaction of the π electron system of the ligand triplet state with the f electron system of the central rare earth ion.

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