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Energy Transfer from the Triplet Excited States of Aromatic Molecules to Chromium(III) Complexes

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The quenching efficiencies of five tervalent chromium complexes on the phosphorescence of erythrosin and benzil have been compared at the temperatures of dry ice and liquid nitrogen. The results were well explained in terms of the collisional energy transfer. It was observed that aromatic ligands enhanced the rate of the energy transfer even if the triplet energy of the donor was lower than that of the ligands.

It is well known that the triplet excited states of the aromatic compounds are quenched by some paramagnetic transition metal complexes. Porter and Wright, however, observed no relation between the magnetic susceptibilities of quenchers and the rate constants of the quenching processes of the triplet states, they classified the paramagnetic substances into the following three groups on the basis of the quenching rate constants[1]:

1) simple molecules (NO, O_2) having unpaired electrons in the 2p orbital,

$$k \sim 10^{10}\ \text{M}^{-1}\,\text{sec}^{-1},$$

2) transition metal complexes having unpaired electrons in the 3d orbitals,

$$k \sim 10^{7}\ \text{M}^{-1}\,\text{sec}^{-1},$$

3) rare earth metal complexes having unpaired electrons in the 4f orbitals,

$$k \sim 10^{5}\ \text{M}^{-1}\,\text{sec}^{-1}.$$

These results, which were partly confirmed by Linschitz and Pekkarinen,[2] showed that the quenching of the triplet excited states could not be attributed to the enhancement in the intersystem crossing of the triplet state caused by the inhomogeneous field of the paramagnetic molecule, but only to the overlapping beween the orbitals of the triplet state and the quencher.

Linschitz and Steel found that the aromatic ligands in transition metal chelates accelerated the rate of the quenching as well as the rate of the redox reaction between metal complexes, and supposed that the quencher transiently formed a charge-transfer complex with the triplet state, in which the intersystem crossing was increased.[3]

An alternative mechanism—electronic energy transfer—in the quenching of the triplet states was proposed by Hammond and his co-worker.[4] Their proposal seems to be supported by the fact that overlapping of the orbitals of the two reactants allows an energy transfer from the triplet state to quencher if the energy level of the acceptor is lower than that of the donor.[5] Hammond and his co-worker hesitated to insist on the importance of the energy transfer on the quenching process, however, because the triplet state of anthracene, whose energy is very low (42.6 kcal/mol), is still very efficiently quenched by all the complexes investigated, $Fe^{III}(acac)_3$,[*2] $Cu^{II}(acac)_2$, $Cr^{III}(acac)_3$, $Ni^{II}(dpm)_2$,[*3] *etc.*[6]

The purpose of this work is to make clear the quenching mechanism of the triplet states in the presence of a transition metal complex, the tervalent chromium complex. The effect and the role of the aromatic ligands of chromium complexes in the quenching were investigated, too. Independent work along these lines has also been done by Forster and his co-workers.[7]

Experimental

Procedure. Figure 1 schematically illustrates the simple apparatus for measuring the emission spectra. A quartz cell 10 mm in diameter was cooled with dry ice or liquid nitrogen. Solutions of 6×10^{-4} M erythrosin in 90% ethanol were illuminated at 534 mμ, while those of 2×10^{-2} M benzil were illuminated at 365 mμ. In order to avoid the scattering of the excitation light,

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[*1] Presented at the Symposium on Photochemistry of the Chemical Society of Japan, Sendai, October,1968.

1) G. Porter and M. R. Wright, *Discus. Faraday Soc.*, **27**, 18, (1959).

2) H. Linschitz and L. Pekkarinen, *J. Am. Chem. Soc.*, **82**, 2411, (1960).

3) C. Steel and H. Linschitz, *J. Phys. Chem.*, **66**, 2577, (1962).

4) G. S. Hammond and R. P. Foss, *ibid.*, **68**, 3739, (1962).

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

[*2] acac: acetylacetonate ion.

[*3] dpm: dipivaloylmethanate ion.

6) A. J. Fry, R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4781, (1966).

7) D. J. Binet, E. L. Goldberg and L. S. Forster, *J. Phys. Chem.*, **72**, 3017, (1968).

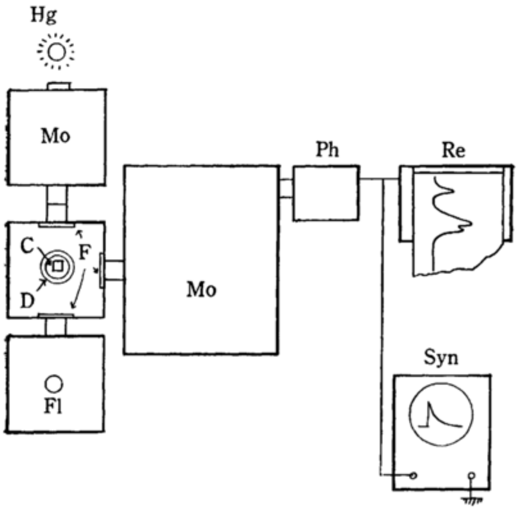

Fig. 1. A schematic diagram of the apparatus for measuring spectra and life-times of emission. Hg: mercury lamp, Mo: monochromator, C: quartz cell, F: filters, D: Dewar's vessel, Fl: flash lamp, Ph: photomultplier 7102, Re: recorder, Syn: synchroscope.

a glass filter, Toshiba UV-D2, was set in front of the cell for the benzil solution, and a Toshiba VY-42 filter for the erythrosin solution. The emission spectra were recorded with a LER-10A recorder (Yokogawa Co.).

To measure the emission life-time, a flash lamp was used with 4-71 Corning filter for the erythrosin solution and a UV-D2 filter for the benzil solution. The solutions were thoroughly degassed by six bulb-to-bulb distillations *in vacuo*.

Materials. Benzil was recrystallised three times from ethanol, erythrosin, from water. Three chromium(III) complexes——$NH_4[Cr^{III}(NCS)_4(NH_3)_2]\cdot\frac{3}{2}H_2O$, $K_3[Cr^{III}(NCS)_6]\cdot 4H_2O$, and $NH_4[Cr^{III}(NCS)_4\cdot(\text{aniline})_2]\cdot\frac{3}{2}H_2O$——were prepared by the usual method.[8] $Cr^{III}(acac)_3$ was prepared by the method of Cooperstein.[9] Cr^{III}(8-oxyquinolinate)$_3$ was obtained by warming chromium(III) chloride and 8-hydroxyquinoline in 2N acetic acid.

Ethanol was dried over calcium oxide; then it was refluxed with silver nitrate and distilled.

Results and Discussion

I) The emission and the absorption spectrum of 6×10^{-4} M erythrosin solution are shown in Fig. 2. The emission peaks at 17.9 and 14.3 kK can easily be assigned to the fluorescence and the phosphorescence respectively, the life-times of the latter being 0.63 msec at −72°C and 0.91 msec at −196°C.

Figure 3 shows the emission spectrum of the 2×10^{-2} M benzil solution at −72°C. The fluorescence at 20 kK is weak and the phosphorescence, with peaks at 14.5, 16.0, and 17.6 kK, is much stronger, with the life-time of 0.67 msec. Elevating the temperature made the phosphorescence as weak as the fluorescence.

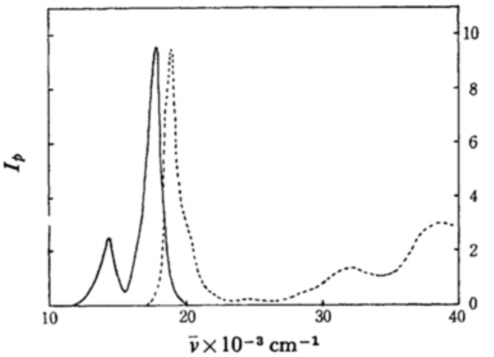

Fig. 2. Absorption spectrum and emission spectrum of erythrosin.

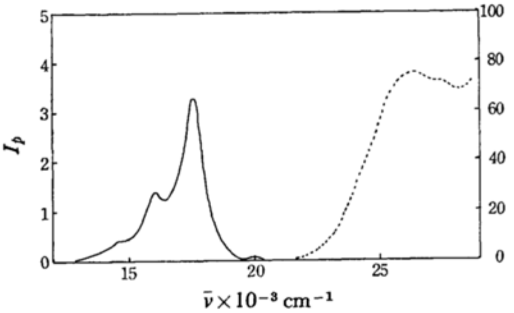

Fig. 3. Absorption and emission spectra of benzil.

The phosphorescences of some chromium(III) complexes which had no fluorescence were observed at −196°C. For $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, $NH_4[Cr^{III}(NCS)_4(\text{aniline})_2]$, and $K_3[Cr^{III}(NCS)_6]$, the phosphorescences were found at −72°C. Table 1 shows the levels of the phosphorescent states of the aromatic compounds and the chromium(III) complexes.

II) The intensity of the phosphorescence of erythrosin decreased in the presence of 2×10^{-4} M $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, and a sharp emission with its maximum at 13.3 kK was observed; this was the same value as that of the phosphorescence of the chromium(III) complex observed under direct excitation. As is shown in Fig. 4, the phosphorescence of the donor at 14.3 kK decreases, and that of the acceptor at 13.3 kK increases, with the concentration of the complex. Because the light absorbed by the complex was less than two hundredths that by erythrosin, even at the highest concentration of the complex, the phosphorescence at 13.3 kK must be the sensitized one.

Oxygen did not quench the phosphorescence of a pure solution of the complex, but it did quench the phosphorescence of both the complex and

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[8] Y. Shimura, "Jikken Kagaku Koza," Vol. 11, Maruzen, Tokyo (1956), pp. 58—60.

[9] R. Cooperstein, "Inorganic Syntheses," Vol. 5, p. 130 (1957).

Table 1. A relation between the energies of phosphorescent levels and the bimolecular decay rates

Compound	Energy of triplet or ^2E kK	Energy of triplet of ligand kK	k_3+k_4 $l\ mol^{-1}\ sec^{-1}$
Erythrosin	16.4[a]		
Benzil	18.8[b]		
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	13.3[c]		6.2×10^6
$K_3[Cr^{III}(NCS)_6]$	12.9[c]		1.6×10^6
$Cr^{III}(acac)_3$	12.8[c]	25.4[d]	1.2×10^7
$Cr^{III}(oxin^*)_3$	~13.1	16[e]	4.8×10^7
$NH_4[Cr^{III}(NCS)_4(aniline)_2]$	~13.1		1.2×10^7

a) J. Pothuma and W. Berends, *Bioche. Biophys. Acta*, **112**, 422 (1966).
b) Reference 6.
c) G. B. Porter and H. L. Schläfer, *Z. physik. Chem. (Frankfurt)*, **40**, 280 (1964).
d) I. Hanazaki, F. Hanazaki and S. Nagakura, *J. Chem. Phys.*, **50**, 276 (1969).
e) Ref. 14.
* "oxin" is abbreviated from "8-oxyquinolinate ion".

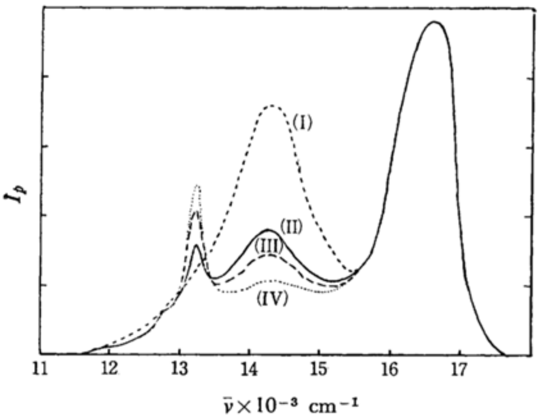

Fig. 4. Change of emission spectrum of erythrosin with $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, (I) erythrosin 6×10^{-4} M, (II) erythrosin 6×10^{-4} M, the complex 2×10^{-4} M, (III) erythrosin 6×10^{-4} M, the complex 4×10^{-4} M, (IV) erythrosin 6×10^{-4} M, the complex 7×10^{-4} M.

erythrosin in the binary system. At −196°C, where the solution was frozen, the sensitized phosphorescence vanished and the donor phosphorescence emerged very strongly. These facts support the theory that the sensitized phosphorescence is due to collisional energy transfer from the triplet state of the erythrosin to the complex. Such a collisional energy transfer has been reported in the system of benzil-$[Cr^{III}(en)_3{}^{*4}]^{3+}$, $Cr^{III}(acac)_3$, and $[Cr^{III}(CN)_6]^{3-}$ by Forster and his co-workers.[7]

The most probable scheme of the energy transfer may be as follows:

$$^3D^* \rightarrow {}^1D + h\nu \qquad k_1 \qquad \text{(P-I)}$$

$$^3D^* \rightarrow {}^1D \qquad k_2 \qquad \text{(P-II)}$$

$$^3D^* + {}^4A \rightarrow {}^1D + {}^2A^* \qquad k_3 \qquad \text{(P-III)}$$

$$^3D^* + {}^4A \rightarrow {}^1D + {}^4A \qquad k_4 \qquad \text{(P-IV)}$$

$$^2A^* \rightarrow {}^4A + h\nu \qquad k_5 \qquad \text{(P-V)}$$

$$^2A^* \rightarrow {}^4A \qquad k_6 \qquad \text{(P-VI)}$$

where D and A denote a donor and an acceptor respectively; the prefixes the multiplicity of the electronic state, and the asterisk, an excited state. An energy transfer to the first excited quartet state ($^4T_2$) of the complex from the donor triplet state is allowed according to the spin conservation rule. Therefore, P-III includes both the direct-energy transfer to the first excited doublet state (^2E) and that to $^4T_2$, followed by the intersystem crossing to ^2E. According to this scheme, some of the k's values are calculated from three different measurements: (i) The observed decay rates of the donor

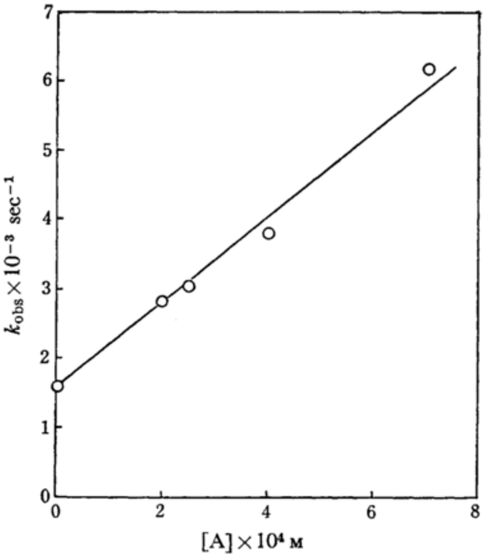

Fig. 5. A relation between the decay constant of erythrosin phosphorescence and the concentration of $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$.

[*4] en: ethylenediamine.

TABLE 2. DECAY RATE CONSTANTS OF FIRST ORDER AND SECOND ORDER PROCESSES

Method of measurement*	$k_1 + k_2$ sec^{-1}	$k_3 + k_4$ $\mathrm{mol}^{-1}\, l\, \mathrm{sec}^{-1}$
Decay rate	1.6×10^3	6.2×10^6
Intensity of donor phospho.		6.2×10^6
Intensity of acceptor phospho.		2.4×10^6

* See text.

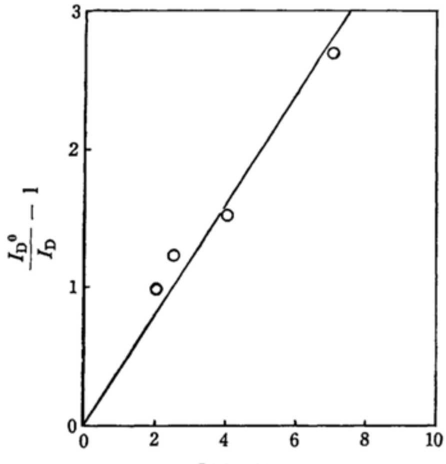

Fig. 6. A dependence of the phosphorescence of erythrosin on the concentration of $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$.

phosphorescence (k_{obs}) are expressed as:

$$k_{obs} = k_1 + k_2 + (k_3 + k_4)\ [A] \qquad \text{(I)}$$

The intercept and the slope of the straight line in Fig. 5 give the values of k_1+k_2 and k_3+k_4 respectively, which are listed in Table 2. (ii) The Stern-Volmer depencence on the acceptor concentration is shown in Fig. 6. $I_D{}^0$ and I_D show the intensities of the donor phosphorescence in the absence and in the presence of the acceptor respectively. The slope of the straight line in Fig. 6 is $(k_3+k_4)/(k_1+k_2)$, according to the reaction scheme. The value of k_3+k_4, which is calculated by using the value of k_1+k_2, agrees with that obtained by the first method. (iii) The reaction scheme produces Eq. (II);

$$\frac{1}{I_A} = \frac{k_5}{k_5 + k_6}\left(\frac{k_3 + k_4}{k_3} + \frac{k_1 + k_2}{k_3}\right)\frac{1}{[A]} \qquad \text{(II)}$$

where I_A denotes the intensity of the sensitized phosphorescence. Figure 7 shows that Eq. (II) holds. The ratio of the slope to the intercept is equal to $(k_3+k_4)/(k_1+k_2)$.

III) Four chromium(III) complexes—$Cr^{III}(acac)_3$, Cr^{III}(8-oxyquinolinate)$_3$, $NH_4[Cr^{III}(NCS)_4(aniline)_2]$, and $K_3[Cr^{III}(NCS)_6]$—were examined as acceptors. The rate constants (k_3+k_4) calculated in two different ways ((i) and (ii)) are shown in the last column of Table 1. Sensitized phosphorescences were found in the cases of $K_3[Cr^{III}(NCS)_6]$ and $NH_4[Cr^{III}(NCS)_4(aniline)_2]$, which were phosphorescent at −72°C on direct excitation. For $Cr^{III}(acac)_3$ and Cr^{III}-(8-oxyquinolinate)$_3$, k_6 must be larger than k_5, because these complexes emit no direct phosphorescence nor any sensitized phosphorescence at −72°C.

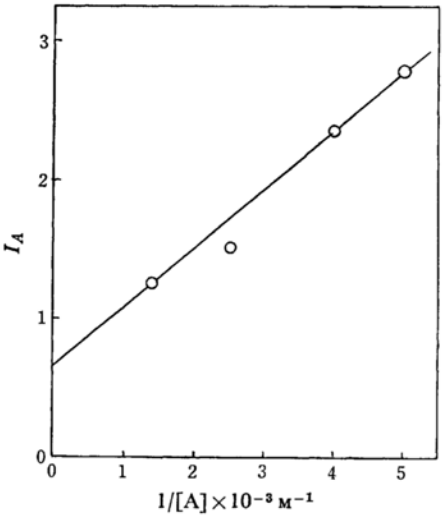

Fig. 7. Confirmation of Eq. (II).

When a mixture of erythrosin and one of the complexes besides $K_3[Cr^{III}(NCS)_6]$ was excited by a 534 mμ light at −196°C, only the phosphorescence of the former was observed. These facts support the idea of the occurence of a collisional energy transfer at −72°C.

For $K_3[Cr^{III}(NCS)_6]$, the phosphorescence was sensitized by erythrosin even at −196°C. Because collisional energy transfer can not occur in a rigid solution, the possible mechanisms to make a sensitized phosphorescence are: (i) a long-range energy transfer[10] (from the excited singlet state of erythrosin to the $^4T_2$ of the complex) and (ii) the complex formation of the donor with $K_3[Cr^{III}(NCS)_6]$. There is no reliable evidence on the basis of which to select one of them. However, the long-range energy transfer is unlikely to be operative because three complexes—$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, $NH_4[Cr^{III}(NCS)_4(aniline)_2]$, and $Cr^{III}(acac)_3$—all with absorption spectra similar to that of $K_3[Cr^{III}(NCS)_6]$, had no sensitized phosphorescence at −196°C. The long-range energy transfer at −72°C can be excluded because of the fact the value of k_3+k_4 obtained from the Stern-Volmer plot of the intensity of the donor phosphorescence was not larger than the value calculated from the decay constants of the donor phosphorescence. The alternative mechanism—static quenching—can be excluded at −72°C,

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[10] T. Förster, *Z. Electrochem.*, **56**, 716, (1952), "Fluoreszenz Organisher Verbindungen," Vandenhseck and Ruprecht, Göttingen (1951).

too, because oxygen quenches the phosphorescence of both the acceptor and the donor completely. These results are partly different from Forster's results in the system of benzil-$K_3[Cr^{III}(NCS)_6]$.

It is worth noticing that the values of k_3+k_4 are $10^7 M^{-1} sec^{-1}$ for the complexes containing aromatic ligands and $10^6 M^{-1} sec^{-1}$ for the complexes containing only inorganic ligands. The rate constant for $NH_4[Cr^{III}(NCS)_4(aniline)_2]$ is twice that for $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$. These results show that these aromatic ligands play an important role in the quenching and in the energy-transfer reaction. The effect of some aromatic ligands upon the quenching rates is more distinct in the reaction at room temperature.[4,6] It has been reported that the quenching of the triplet states of some aromatic compounds with Cr^{III}-(acac)$_3$ was diffusion-controlled and that the quenching rate was several hundred times as great as that for the naphthalene-$Cr^{III}Cl_3$ system.[*5,1] In the case of rare earth complexes, it is well known that the aromatic ligands with triplet levelslower than that of the donor triplet accept the excitation energy from the donor very efficiently as in the case of the energy transfer between aromatic molecules.[11] The proposed mechanism is a series of successive processes as follows:

$$^3D^* + M\text{-}^1L \rightarrow {}^1D + M\text{-}^3L^* \qquad \text{(P-VII)}$$

$$M\text{-}^3L^* \rightarrow M^*\text{-}^1L \qquad \text{(P-VIII)}$$

The $M\text{-}^3L^*$ symbol indicates that the triplet-excited energy is localized in part of the ligands. The energy transfer process (P-VII) is diffusion-controlled if the energetical requirement is satisfied.[12]

In the case of the 8-oxyquinolinate complex, the energy of the triplet state of the ligand (16.2 kK for Pb^{II}(8-oxyquinolinate)$_2$[13]) may be lower than that of the benzil molecule, therefore, the following reaction must be diffusion-controlled:

$$^3\text{Benzil}^* + Cr^{III}(\text{8-oxyquinolinate})_3 \rightarrow {}^1\text{Benzil} + Cr^{III}(\text{8-oxyquinolinate})_3^* \qquad \text{(P-IX)}$$

However, for the complexes of other lignads, a different type of energy transfer is required, because the triplet levels of the ligands higher than erythrosin make it impossible for the (P-VII) process to occur (see Table 1).

It is well known that 3d electrons in chromium (III) are likely to mix with the p_π electrons of aromatic ligands more than do 4f electrons in rare earth chelates. It is plausible that this mixing makes the interaction between 3d electrons and donor triplet electrons much larger at the frontier of the complexes, then, the excitation energy of the donor in triplet state can be directly transferred to the central chromium ion. It may be through this mechanism that Cr^{III}(acac)$_3$, the ligand triplet state of which is located at 25.4 kK, very efficiently quenches the triplet state of six aromatic molecules—triphenylene (23.8 kK), benzanthrone (16.8kK), anthracene (15.2 kK), *etc.* These quenching rate constants have been measured by Hammond and his co-worker.[6)]

A financial support from Fuji Photo Film Co., Ltd., is gratefully acknowledged.

[*5] Present results show that the rate constants of the quenching with Werner type complexes, such as $K_3[Cr^{III}(NCS)_6]$ and $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ are not much smaller than those with complexes containig aromatic ligands at −72°C. This fact is explained as follows. Since the solvent of high viscosity at low temperature makes the contact time longer the energy is effectively transfered from the donor to the acceptor.

11) M. L. Bhaumik and M. A. El-Sayed, *J. Chem. Phys.*, **42**, 787, (1965); V. L. Ermolaev, E. A. Saenko, G. A. Domrachev, Yu. K. Khudenskii and V. G. Aleshin, *Opt. Spectry.*, **22**, 466 (1967).

12) V. L. Ermolaev, V. G. Aleshin, and E. A. Saenko, *Soviet Physics. Doklady*, **10**, 1186, (1966).

13) D. C. Bhatnagar and L. S. Forster, *Spectrochim. Acta*, **21**, 1803, (1965).

14) K. DeArmond and L. S. Forster, *ibid.*, **19**, 1687 (1963).