

Excited state relaxation and energy transfer between $Tb^{3+} \rightarrow Nd^{3+}$ and $Tb^{3+} \rightarrow Ho^{3+}$ in $POCl_3:SnCl_4$

JANARDAN JOSHI* and J C JOSHI†

Department of Physics, Government Post Graduate College, Uttarkashi 249 193, India

†Department of Physics, D S B Constituent College, Kumaun University, Nainital 263 002, India

MS received 1 February 1985

Abstract. Excited state relaxation in Tb^{3+} in $POCl_3:SnCl_4$ aprotic solvent has been examined. It is found that at a concentration of 10^{-1} M Tb^{3+} , the fluorescence exclusively originates from the 5D_4 level. The appreciable increase in the decay times of Tb^{3+} in this solvent compared to its values in H_2O or D_2O , suggests that the decrease in non-radiative relaxations is due to the low energy vibrations characteristic of this solvent. Non-radiative transfer of energy from $Tb^{3+} \rightarrow Nd^{3+}$ and from $Tb^{3+} \rightarrow Ho^{3+}$ in this solvent has been established by examining the lifetime data. Calculated values of energy transfer probabilities (P_{da}) in the liquid air temperature are analysed to obtain a clue regarding the nature of excitation transfer mechanism. In both the systems, the energy transfer from Tb^{3+} donors to Nd^{3+} as well as Ho^{3+} acceptors, occurs predominantly via a dipole-dipole process. At high temperature the energy transfer is increased.

Keywords. Excited state relaxation; energy transfer; fluorescence; Tb^{3+} donors; Nd^{3+} and Ho^{3+} acceptors.

1. Introduction

The luminescence of rare earths (RE) in solutions have been studied in less detail than in solids because of their low emission yields and shorter lifetimes. The main pathways for radiationless relaxations in the solid phase are the dissipation of excitation by multiphonon emission, concentration quenching (via cross relaxation) and quenching via a charge transfer state. In solutions containing rare earth ions the quantum yields and decaytimes of fluorescence is generally very low. Experimental studies on RE fluorescence have shown that when heavy water is substituted for ordinary water as solvent, both the fluorescence yield and decaytimes increase (Kropp and Windsor 1963, 1965, 1966; Pant *et al* 1971). Active rare earth ions in aqueous solutions undergo radiationless relaxations and the quantum yield of fluorescence are often low relative to the yields of the same ions in hydrogen-free solvents. Heller and coworkers (Heller 1966a, b; Lempicki and Heller 1966) have pointed out that the low quantum yields are by no means inherent in the nature of the liquid state. These relaxations result in part from the high energy vibrations of the bonds involving light atoms particularly hydrogen. The energy of stretching vibration between two atoms is a function of the inverse of the product of their masses. When this vibrational energy is of the order of the magnitude of the energy gap between the lowest excited state and the highest

* To whom all correspondence should be addressed.

ground state of the rare earth ion, the excess energy may be lost by the excited ion. This loss of energy results in a radiationless relaxation. The higher the energy of the vibrational modes associated with the solvent, the lower is the fluorescence efficiency of the ion. The decrease in the RE fluorescence in water or organic (protic) solvents is attributed to the radiationless deexcitation via the overtones of $-O-H$, $\geq C-H$, $>N-H$ groups of solvent molecules both in the primary and secondary solvation sphere of the rare earth ion.

Earlier, spectroscopic studies of rare earth ions in liquid solutions at room temperature were mostly confined to the solvents containing hydrogen or deuterium atoms. Using the clue about the atomic masses playing a prominent role in reducing high frequency vibrations of the solvent, Heller (1968a, b) has solved the problem of creating efficient liquid laser by dissolving RE^{3+} in liquid systems which contain no atoms lighter than oxygen. Such liquids, free from hydrogen atoms, are called 'aprotic' solutions. Such systems have no vibrations of sufficient energy to carry away the energy difference corresponding to the gap between excited and ground multiplets levels of RE^{3+} . $POCl_3$ and $SeOCl_2$ mainly belong to this class which are used in combination with $SnCl_4$, $ZrCl_4$, $SbCl_5$, $AlCl_3$ etc. to improve acidification so as to increase the solubility of RE salts. Depending upon the combination and composition of these solutions, remarkable enhancement in both the fluorescence and decaytimes of RE^{3+} in these heavy inorganic solvents is likely to occur.

For the luminescence studies of Tb^{3+} we have employed the $POCl_3 : SnCl_4$ aprotic solvent, which was used firstly by Blumenthal *et al* (1968), for room temperature liquid laser and recently by Chrysochoos and Takousbalides (1975, 1976). The Eu^{3+} emission in $POCl_3 : SnCl_4$ (5:1) has also been studied by Bhatt *et al* (1973). In this system $POCl_3$ molecules form the solvation shell around the RE^{3+} ion. The lightest atom in the shell is oxygen which is sixteen times heavier than hydrogen, as a consequence of which, the vibrational energies are likely to be about four times lower than that of hydrogen containing solvents.

Energy transfer processes between various rare earths in solutions have been studied to a limited extent. Holloway and Kestigian (1967) having studied the energy transfer from $Tb^{3+} \rightarrow Nd^{3+}$, Ho^{3+} , Er^{3+} in water, came to the conclusion that the energy transfer mechanism was induced resonance. Antipenko and Ermolaev (1969) investigated the radiationless transfer of energy from Tb^{3+} and Eu^{3+} to various rare earth ions (including Nd^{3+} and Ho^{3+}) in acetone and water. A comparison of the rate constants of the transfer and the overlap integrals of the energy donor and acceptor spectra has proved that the transfer in acetone is accomplished by the exchange resonance mechanism, whereas in water, evidently exchange-resonance and induced-resonance transfer co-exist. Recently, the fluorescence enhancement of Eu^{3+} by Tb^{3+} in dimethylsulphoxide (DMSO) has been manifested by Chrysochoos (1974) who observed that the energy transfer process does not appear to take place via clear cut dipole-dipole interactions but rather via complex multipole and/or exchange interactions. Energy transfer between some rare earths in $POCl_3 : SnCl_4$ was reported for the first time by Antipenko *et al* (1970), who suggested that the transfer is accomplished by an inductive-resonance mechanism. The study was, however, confined to Nd^{3+} , Pr^{3+} , Sm^{3+} , Eu^{3+} , Dy^{3+} donors and Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+} , Dy^{3+} , Ho^{3+} acceptors, and the attempts to obtain sensitized luminescence of the energy acceptors gave a negative result. To date, no information is available in the literature regarding the energy transfer from Tb^{3+} to Ho^{3+} , Nd^{3+} in $POCl_3 : SnCl_4$. Further, due to the

complexities of energy levels involved, the transfer mechanism in solutions is controversial. In the present investigation we wish to elucidate the transfer mechanism and character of multipolar transfer from Tb^{3+} donors to Nd^{3+} and Ho^{3+} acceptors in $POCl_3:SnCl_4$ aprotic solvent.

2. Experimental

The heavy inorganic solvent materials used in the study were $POCl_3$ (Analar grade, Albright and Wilson Ltd., England) and $SnCl_4$ (GR grade, E. Merck, AG, Darmstadt, Germany). Rare earth oxides Tb_2O_3 , Nd_2O_3 , Ho_2O_3 of 99.99 % purity were obtained from Indian Rare Earths Ltd., Kerala. These oxides were converted into chlorides by dissolving in Analar grade HCl and evaporating the solutions thus obtained in a low temperature oven.

The rare earth salts dissolve in $POCl_3$ to a limited extent, but they are fairly soluble when $SnCl_4$ is added, forming strong aprotic acid. For a solvent it is also necessary to have the transparency in the optical excitation and emission region of Tb^{3+} i.e. between 3000 Å and 8000 Å and this requirement is satisfactorily fulfilled by $POCl_3$. The fluorescence efficiency of RE^{3+} is considerably affected by the ratio of $POCl_3/SnCl_4$. At low concentrations of $SnCl_4$, rare earth salts are poorly soluble whereas at high concentrations of $SnCl_4$, the complex $2POCl_3 \cdot SnCl_4$ is precipitated. Therefore, the variation in $SnCl_4$ has to be confined to within these two limits. In our system $POCl_3$ and $SnCl_4$ were, therefore, mixed in a ratio 9:1 by volume. The anhydrous rare earth chlorides were dissolved in this mixture in appropriate amounts in pyrex glass tubes of uniform bore and the solutions were quickly sealed in vacuum to avoid moisture. The Tb^{3+} concentration was kept fixed at 10^{-1} M and the activator (Nd^{3+} and Ho^{3+}) ion concentrations were varied in the range 10^{-3} M to 10^{-1} M.

Fluorescence spectra and decay times were measured in the usual manner. The emission spectra obtained in this study were not corrected with respect to the sensitivity of the phototube, because in taking ratios, such a factor will eventually cancel out. Measurements were made at room temperature (300°K), liquid air temperature (80°K) and high temperature (350°K).

3. Results and discussion

The fluorescence intensity distributions of Tb^{3+} (10^{-1} M) and Tb-Nd, Tb-Ho coactivated $POCl_3:SnCl_4$ (9:1 v/v) systems for various concentrations of Nd and Ho, are presented in figures 1 and 2 at room temperature (300°K). In these relative fluorescence measurements the geometry of the system was kept constant for all samples. The emission spectrum of Tb^{3+} in $POCl_3:SnCl_4$ shows four bands at 490 nm, 545 nm, 590 nm and 620 nm, which are assigned to the transitions ${}^5D_4 \rightarrow {}^7F_6$, ${}^5D_4 \rightarrow {}^7F_5$, ${}^5D_4 \rightarrow {}^7F_4$ and ${}^5D_4 \rightarrow {}^7F_3$ respectively. The fluorescence of Tb^{3+} at this concentration (10^{-1} M) generally stems from the 5D_4 state similar to the emission of Tb^{3+} in aqueous, organic solvents as well as in DMSO whereas fluorescence of Tb^{3+} (10^{-2} M) in $POCl_3:SnCl_4$ arising from the 5D_3 state was observed for the first time by Takousbalides and Chrysochoos (1974), which has a strong dependence upon the concentration of Tb^{3+} , the temperature and the composition of the solvent. The

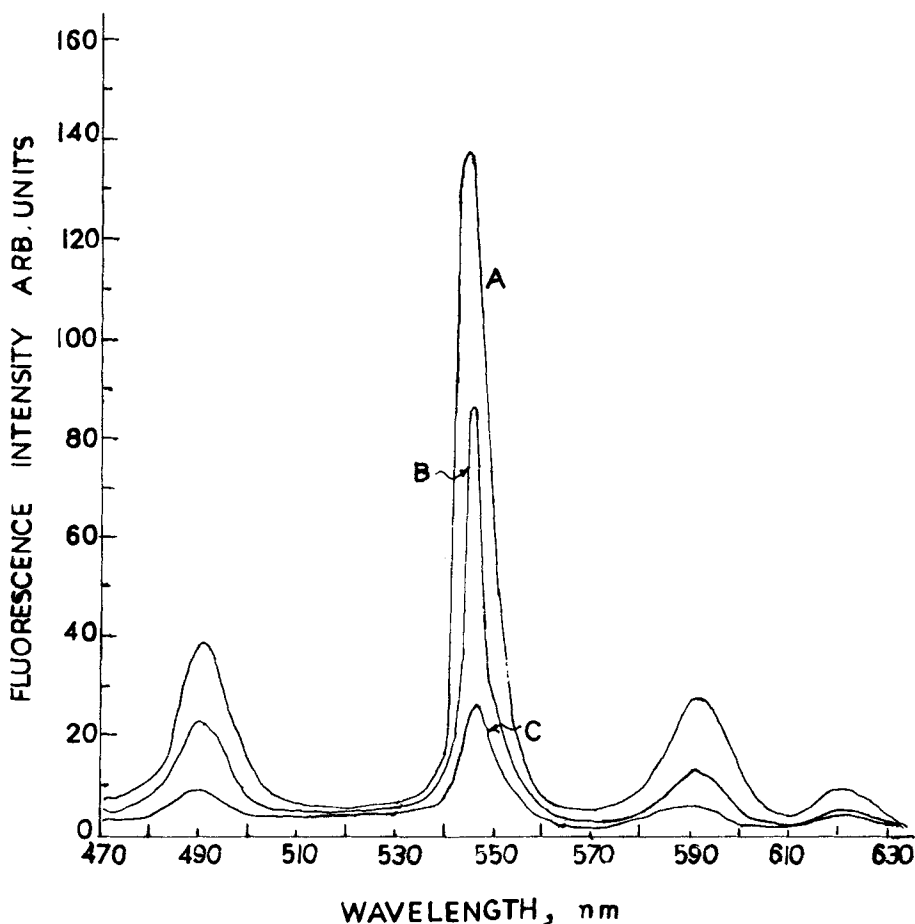
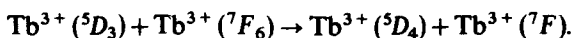


Figure 1. Fluorescence spectrum of Tb^{3+} (10^{-1} M) in $\text{POCl}_3:\text{SnCl}_4$ at 300°K with varying concentration of acceptor ions (Nd^{3+}): (A) Tb^{3+} (10^{-1} M) only; (B) Tb^{3+} (10^{-1} M) + Nd^{3+} (10^{-3} M); (C) Tb^{3+} (10^{-1} M) + Nd^{3+} (10^{-1} M).

emission from the 5D_3 state of Tb^{3+} , however, in our case could not be observed even at 80°K . The absence of this emission in our system is probably due to the fact that the Tb^{3+} concentration in our experiments is ten times higher than that of Takousbalides and Chrysochoos. At these concentrations the luminescence quenching due to ion-pair relaxation can take place via the reaction:



This results in a cross-relaxation of the Tb^{3+} ion from the 5D_3 to 5D_4 state. The objective in fixing a higher Tb concentration in our system is to avoid the participation of levels higher than 5D_4 , which make the transfer mechanism much complex. The Tb 5D_4 fluorescence intensity is also increased due to feeding from upper levels, which is an added advantage.

Semilog plots of the typical decay curves of the transient fluorescence from 5D_4 level

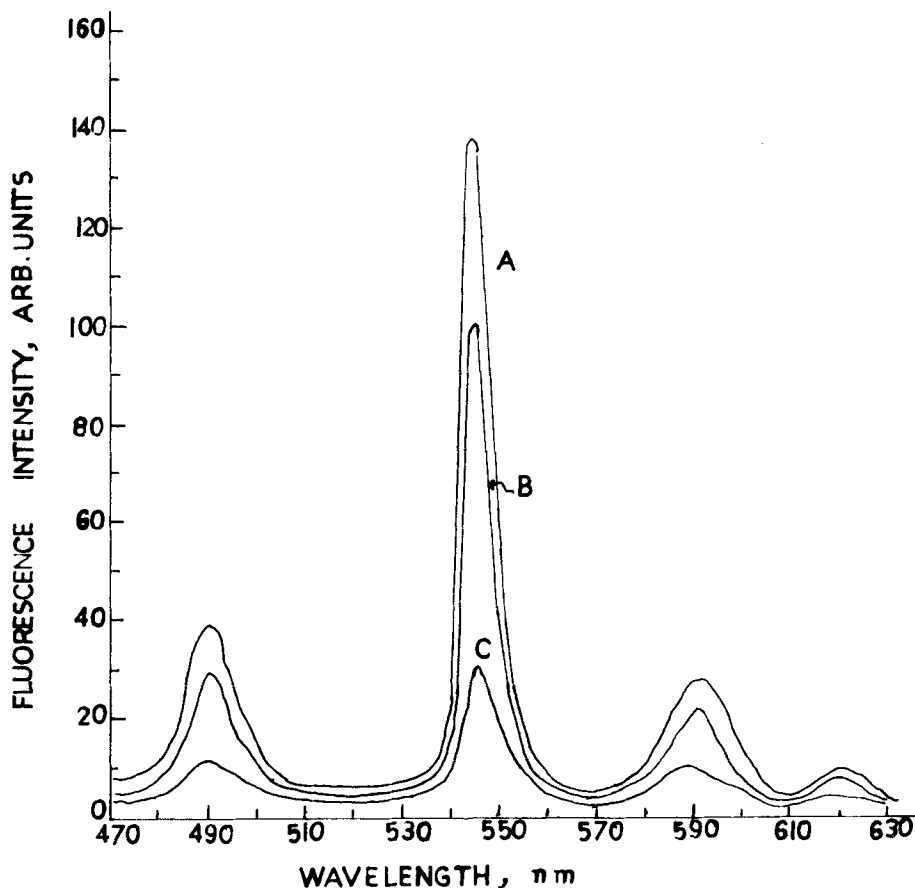


Figure 2. Fluorescence spectrum of Tb^{3+} (10^{-1} M) in $\text{POCl}_3:\text{SnCl}_4$ at 300°K with varying concentration of acceptor ions (Ho^{3+}); (A) Tb^{3+} (10^{-1} M) only; (B) Tb^{3+} (10^{-1} M) + Ho^{3+} (10^{-3} M); (C) Tb^{3+} (10^{-1} M) + Ho^{3+} (10^{-1} M).

of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ at room temperature (300°K) are illustrated in figures 3 and 4 at various concentrations of coactivators Nd^{3+} and Ho^{3+} respectively. The straight lines suggest that the fluorescence emitting state (5D_4) decays exponentially in pure Tb^{3+} as well as in the presence of Nd^{3+} and Ho^{3+} , contrary to the behaviour in glasses where the departure from exponentiality occurs in the early part of decay. This exponential behaviour is characteristic of the liquid state where due to Brownian motion the average distance between any two donors and acceptors remains constant whereas in glasses the distances between donor-acceptor pairs vary statistically. The pure exponential nature of the decay of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ in the Nd or Ho-free samples, as well as the homogeneously broadened emission bands are indicative of the fact that Tb^{3+} in this solvent has essentially one fluorescent site.

The fluorescence decay time of the 5D_4 level at room temperature was found in our system as $2800 \mu\text{sec}$, which is quite comparable to its values in glasses. Holloway and Kestigian (1967) found that the decay-time of Tb^{3+} in water solution is about $340 \mu\text{sec}$

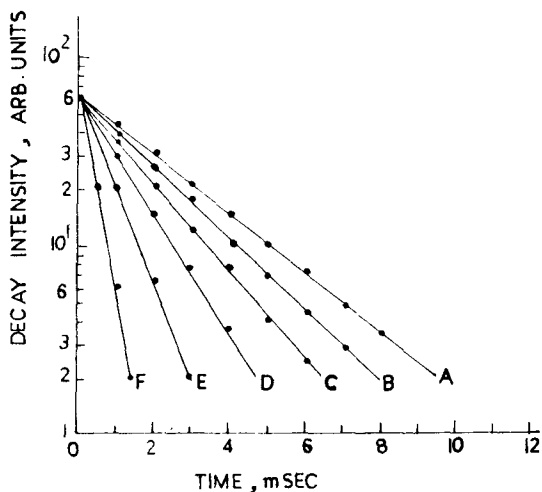


Figure 3. Semilogarithmic plot of the decay curve of Tb^{3+} (10^{-1} M) in $\text{POCl}_3:\text{SnCl}_4$ at various concentrations of Nd^{3+} (X), ($T = 300^\circ\text{K}$) where X is: (A) 0; (B) 10^{-3} M; (C) 5×10^{-3} M; (D) 10^{-2} M; (E) 5×10^{-2} M; and (F) 10^{-1} M.

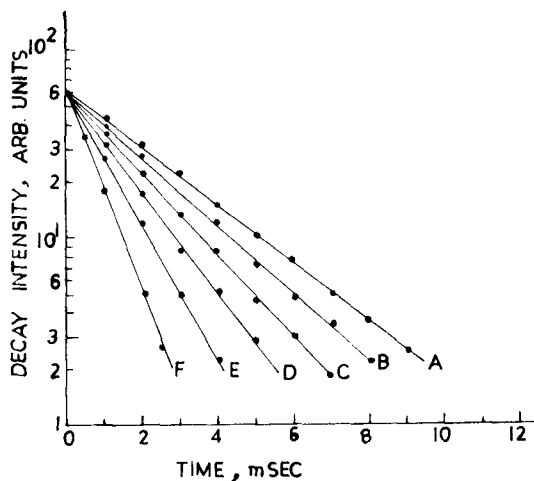


Figure 4. Semilogarithmic plot of Tb^{3+} (10^{-1} M) decay in $\text{POCl}_3:\text{SnCl}_4$ with various amounts (X) of co-activator (Ho^{3+}) ($T = 300^\circ\text{K}$) where X is: (A) 0; (B) 10^{-3} M; (C) 5×10^{-3} M; (D) 10^{-2} M, (E) 5×10^{-2} M, and (F) 10^{-1} M.

and that in D_2O is about $1200 \mu \text{ sec}$. Our values of decaytimes in $\text{POCl}_3:\text{SnCl}_4$ are very much higher than those in H_2O or D_2O . Similar increase in the decaytimes and fluorescence intensities for various rare earths in aprotic solvents has been reported by Heller. Tokousbalides and Chrysochoos (1972) have also observed that both the fluorescence efficiencies and lifetimes of Sm^{3+} in $\text{POCl}_3:\text{SnCl}_4$ are enhanced about 1000 times their values in aqueous solutions. In H_2O or D_2O solvents the non-radiative

relaxation processes result in the transformation of the excitation energy of the RE^{3+} ions into vibrational energy of the molecules of the solvent. The probability of such a process depends on the number of vibrational quanta that must be created in order to carry away the excitation energy of the ion. A process requiring the simultaneous creation of several quanta is highly unlikely. In cases where the available vibrational energy quantum is small compared to the excitation energy of the ion, a non-radiative energy relaxation will seldom take place e.g. in POCl_3 , where the highest energy vibrational quantum is 1300 cm^{-1} ; the stretching mode of >P=O group. On the other hand relaxation will take place more frequently when the available vibrational quantum is nearly equal to the excitation energy of the RE^{3+} ion. According to Siebrand and Williams (1968) the radiationless transition probability per unit time from Tb^{3+} to solvent vibrational modes is given by

$$W = (2\pi/\hbar) \cdot \beta^2 \cdot \rho \cdot F,$$

where β is the electronic transition matrix element (induced by vibronic interaction of solvent perturbations), F is the Franck-Condon factor and ρ is the effective density of the quasicontinuum formed by the solvent vibrations. Both ρ and F are greatly affected by the high frequency vibrations, making W appreciable, hence a low quantum yield will be observed in H_2O or D_2O . In $\text{POCl}_3:\text{SnCl}_4$ system, the absence of high frequency vibrations greatly reduce the density of the quasicontinuum formed by the solvent vibrations matched with the emitting state of Tb^{3+} . This reduces the non-radiative loss with the consequent enhancement in fluorescence yield.

The decaytimes of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ at the temperature 80°K , 300°K and 350°K with various concentrations of activators are presented in table 1. It is observed that in pure Tb^{3+} , the decaytime at room temperature is $2800 \mu \text{ sec}$ which increases to $3200 \mu \text{ sec}$ at liquid air temperature and decreases to $1600 \mu \text{ sec}$ at 350°K . This strong temperature dependence of decaytime suggests that non-radiative processes largely decrease at liquid air temperature. A similar effect of temperature on intensity was also observed. It is inferred that with the increase in temperature there is a rapid increase in the temperature-dependent non-radiative rate constants, with the consequent decrease in decaytimes. Collisions of the second kind (Cario and Franck 1923) may also be effective in the quenching of Tb^{3+} fluorescence.

Table 1. Decaytimes of Tb^{3+} in $\text{POCl}_3:\text{SnCl}_4$ with varying acceptor concentrations and temperatures.

Acceptor concentration (mole)	Donor lifetime (m sec) in presence of acceptor (Nd^{3+})			Donor lifetime (m sec) in presence of acceptor (Ho^{3+})		
	80 K	300 K	350 K	80 K	300 K	350 K
0	3.2	2.8	1.4	3.2	2.8	1.4
10^{-3}	2.7	2.3	1.3	2.8	2.4	1.3
$5 \cdot 10^{-3}$	2.2	1.9	1.0	2.4	2.0	1.1
10^{-2}	1.7	1.4	0.7	2.0	1.6	0.8
$5 \cdot 10^{-2}$	1.1	0.9	0.5	1.4	1.2	0.6
10^{-1}	0.6	0.5	0.2	1.0	0.8	0.4

Donor (Tb^{3+}) concentration = 10^{-1} M (fixed)

In $\text{POCl}_3:\text{SnCl}_4$ absorption does not take place at the excitation wavelength (365 nm). Therefore, energy transfer from the solvent to the rare earths is ruled out. Further, the absorption spectra of this aprotic solvent appear (Chrysochoos and Tokousbalides 1973) at wavelengths shorter than 300 nm, hence the decrease in Tb^{3+} fluorescence due to absorption by solution is also prohibited. Thus the overall reduction in the fluorescence of Tb^{3+} ion with increasing activator (Nd^{3+} and Ho^{3+}) concentration (figures 1 and 2) suggests that the non-radiative transfer of energy takes place from Tb^{3+} to Nd^{3+} and from Tb^{3+} to Ho^{3+} in $\text{POCl}_3:\text{SnCl}_4$. Further, the decrease in the decaytime of Tb^{3+} on increasing Nd^{3+} and Ho^{3+} contents at all temperatures (figures 3 and 4, table 1) support the non-radiative transfer of optical excitation. The electronic energy level diagrams of Tb^{3+} , Nd^{3+} , Ho^{3+} (presented in figure 5) have been reproduced after Dieke and Crosswhite (1963), because the energy level diagrams of RE^{3+} in crystals are also applicable to those in solution with the only difference that the pertinent absorption bands will be broader in the latter case. The excitation of 365 nm will populate the ($^3\text{G}_6$, $^5\text{L}_{10}$) excited levels of Tb^{3+} . The excited ion quickly relaxes to the $^5\text{D}_4$ metastable state, where the radiative transition is obtained at several ground multiplets. Energy transfer may take place from the $^5\text{D}_4$ levels of Tb^{3+}

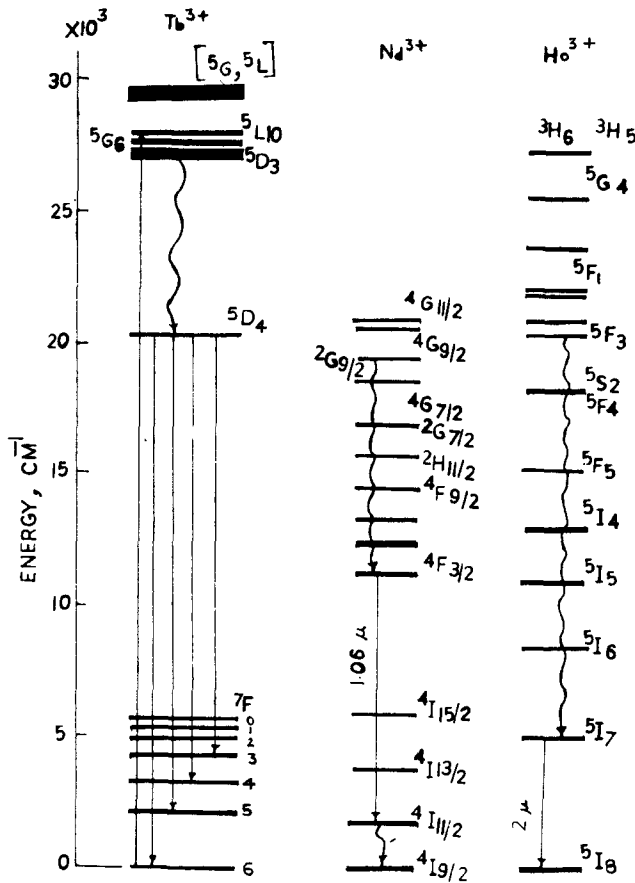


Figure 5. Energy level diagrams of Tb^{3+} , Nd^{3+} and Ho^{3+} .

Table 2. Calculated values of energy transfer probabilities and efficiencies in $\text{POCl}_3\text{:SnCl}_4$.

Acceptor concentration (mole)	Energy transfer from $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$				Energy transfer from $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$							
	Transfer probability $P_{tr} \cdot 10^3 \text{ sec}^{-1}$		Transfer efficiency η_T		Transfer probability $P_{tr} \cdot 10^3 \text{ sec}^{-1}$		Transfer efficiency η_T					
	80 K	300 K	350 K	80 K	300 K	350 K	80 K	300 K	350 K			
10^{-3}	0.05	0.07	0.14	0.15	0.17	0.18	0.04	0.06	0.14	0.12	0.14	0.18
$5 \cdot 10^{-3}$	0.14	0.17	0.37	0.31	0.32	0.37	0.10	0.14	0.28	0.25	0.28	0.31
10^{-2}	0.27	0.35	0.80	0.47	0.50	0.56	0.18	0.26	0.62	0.37	0.42	0.50
$5 \cdot 10^{-2}$	0.59	0.75	1.37	0.65	0.67	0.68	0.40	0.47	1.04	0.56	0.57	0.62
10^{-1}	1.35	1.64	4.37	0.81	0.82	0.87	0.68	0.89	1.87	0.68	0.71	0.75

to several excited levels of Nd^{3+} as well as Ho^{3+} which are in resonance with Tb^{3+} transitions. Direct transfer from 5D_4 of Tb^{3+} may occur to ${}^4G_{9/2}$, ${}^4G_{5/2}$, ${}^2G_{7/2}$, ${}^2H_{11/2}$ levels of Nd^{3+} , which relaxes to the metastable ${}^4F_{3/2}$ level. Similarly in Tb^{3+} to Ho^{3+} energy transfer the various recipient levels of Ho^{3+} in resonance with the Tb^{3+} fluorescence are 5F_3 , 5S_2 , 5F_4 , which on direct transfer and rapid relaxation through a sequence of intermediate levels may populate the 5I_7 metastable level of Ho^{3+} . The transitions from the ${}^4F_{3/2}$ level of Nd^{3+} and 5I_7 level of Ho^{3+} to their respective ground levels lying in the infrared region of the spectrum could not be detected as our measuring system was not sensitive in this region.

The energy transfer probabilities (P_{da}) and transfer efficiencies (η_T) were calculated using Reinfeld's formulae, frequently used in our earlier computations. The calculated values are presented in table 2.

As suggested earlier it is quite likely that at 350°K or 300°K , the collisions of solvent molecules may help in the energy transfer and a diffusion controlled process may be very effective, which in turn may make the transfer mechanism very complex (including exchange resonance mechanisms etc.). To avoid the undue interference of collisions the P_{da} data at 80°K (where diffusion-controlled processes are minimised) were analysed for the elucidation of precise transfer mechanisms. A plot of the calculated values of $\log P_{da}$ versus the log of acceptor concentration (figure 6) yields a straight line for both the systems $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$ and $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$. The gradient of the curve is found

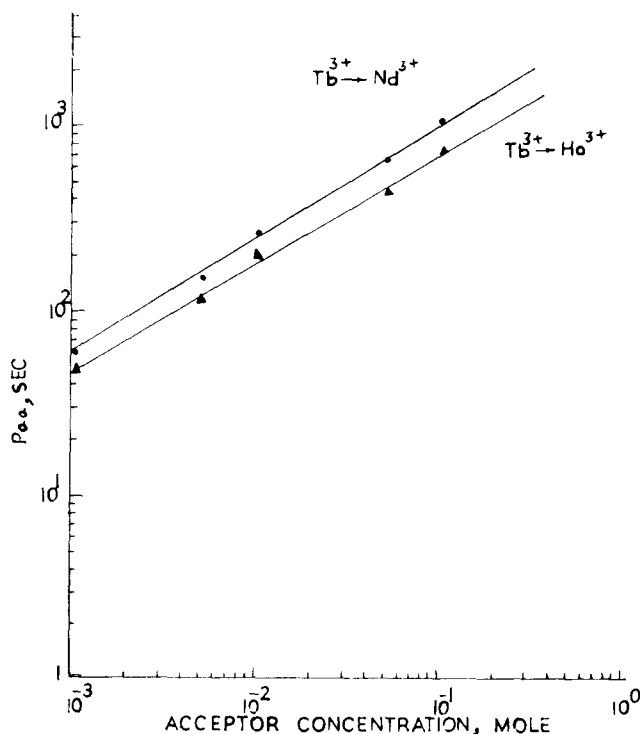


Figure 6. Log-log plot of energy transfer probability (P_{da}) vs acceptor concentration: the upper curve shows $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$ energy transfer whereas the lower one shows $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$ energy transfer.

nearly equal to 2, which is the $\theta/3$ value from Van Uiter's formula, suggestive of a dipole-dipole mechanism of energy transfer from Tb^{3+} donors to Nd^{3+} and Ho^{3+} acceptors. The higher values of P_{da} for $\text{Tb}^{3+} \rightarrow \text{Nd}^{3+}$ transfer than for $\text{Tb}^{3+} \rightarrow \text{Ho}^{3+}$ transfer, suggest that in the former system the transfer is more efficient than in the latter. This is further corroborated by a greater value of transfer efficiency (η_T) in the former compared to the latter, in accordance with the fact that the spectral overlap of Tb^{3+} emission with Nd^{3+} absorption is better than that with Ho^{3+} absorption.

Table 2 shows that transfer efficiencies as well as transfer probabilities increase with increase in temperature. In solid media such a phenomenon is attributed to the increased overlap of donor and acceptor levels due to thermal broadening, facilitating the broad path for energy transfer. However, in solution such a process may occur primarily due to collisional transfer. In $\text{POCl}_3:\text{SnCl}_4$ solvent the species POCl_2^+ and SnCl_4^- are presumed to be generated which form a solvation sphere around the Tb^{3+} ion dissolving terbium chloride (Tokousbalides and Chrysochoos 1976). If a rigid solvation sphere around Tb^{3+} is established the quenching effect may be attained with the solvent molecules primarily located in such a sphere. Higher temperatures may partially destroy such a solvation sphere allowing penetration by solvent molecules from the secondary solvation sphere of the ion. As a consequence collisions will be increased and energy transfer will be enhanced. Such a process seems predominant at elevated temperatures.

Acknowledgement

Partial financial support from the UGC, New Delhi, is gratefully acknowledged by JJ.

References

- Antipenko B M, Bataev I M, Ermolaev V L, Lyubimov E I and Privalova T A 1970 *Opt. Spectrosc. (USSR)* **29** 177
- Antipenko B M and Ermolaev V L 1969 *Opt. Spectrosc. (USSR)* **26** 415
- Bhatt B C, Joshi G C and Pant D D 1973 *Indian J. Pure Appl. Phys.* **11** 226
- Blumenthal N, Ellis C B and Grafstein D 1968 *J. Chem. Phys.* **48** 5726
- Cario G and Franck J 1923 *Z. Phys.* **17** 202
- Chrysochoos J 1974 *J. Lumin.* **9** 79
- Chrysochoos J and Takousbalides P 1973 *Spectrosc. Lett.* **6** 435
- Chrysochoos J and Takousbalides P 1975 *J. Lumin.* **11** 119
- Chrysochoos J and Takousbalides P 1976 *J. Lumin.* **14** 325
- Dieke G H and Crosswhite H M 1963 *Appl. Opt.* **7** 675
- Heller A 1966a *Appl. Phys. Lett.* **9** 106
- Heller A 1966b *J. Am. Chem. Soc.* **88** 2058
- Heller A 1968a *J. Mol. Spectrosc.* **28** 101
- Heller A 1968b *J. Mol. Spectrosc.* **28** 208
- Holloway W W Jr and Kestigian M 1967 *J. Chem. Phys.* **47** 1826
- Kropp J L and Windsor M W 1963 *J. Chem. Phys.* **39** 2769
- Kropp J L and Windsor M W 1965 *J. Chem. Phys.* **42** 1599
- Kropp J L and Windsor M W 1966 *J. Chem. Phys.* **45** 761
- Lempicki A and Heller A 1966 *Appl. Phys. Lett.* **9** 108
- Pant D D, Bhatt B C and Sanwal D N 1971 *Indian J. Pure Appl. Phys.* **9** 324
- Siebrand W and Williams E 1968 *J. Chem. Phys.* **49** 1860
- Tokousbalides P and Chrysochoos J 1972 *J. Phys. Chem.* **76** 3397
- Tokousbalides P and Chrysochoos J 1974 *Chem. Phys. Lett.* **29** 226
- Tokousbalides P and Chrysochoos J 1976 *J. Chem. Phys.* **64** 1863