

Quenching of the Tb³⁺ Fluorescence by Other Rare-Earth Ions in Aqueous Chloride Solutions

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In the spectrum of molten $2\text{SnCl}_2 \cdot \text{KCl}$ it was not even possible to distinguish distinct bands in the Sn-Cl stretching region, but only a very broad feature extending from about 210 to 270 cm^{-1} (see Table II). Such a broad range of Sn-Cl stretching frequencies would be expected if the initial addition of KCl resulted not in straightforward separation of SnCl_3^- from $(\text{SnCl}_2)_n$ but in the intermediate formation of such polymeric species as $(\text{SnCl}_2 \cdot \text{SnCl}_3)^-$, $(2\text{SnCl}_2 \cdot \text{SnCl}_3)^-$, etc. Stable compounds of the type $2\text{SnCl}_2 \cdot \text{MCl}$ and $3\text{SnCl}_2 \cdot \text{MCl}$ ($\text{M} = \text{K}$ or Rb) have been crystallized from the molten state,⁵ and similar complexes have been invoked to explain the results of emf studies⁴ on molten mixtures of stannous chloride and alkali-metal chlorides. It is interesting to note, however, that in agreement with the present work, these studies gave no indication of the formation of higher complexes than SnCl_3^- , nor have stable compounds containing less than 50 mole % of stannous chloride been crystallized from these systems.

The dominating factor in determining the structures of molten stannous chloride and its molten mixtures with potassium chloride appears to be the well-established

preference of Sn(II) for 3 coordination. In the case of pure molten stannous chloride this condition is achieved by the formation of $(\text{SnCl}_2)_n$ chains, while the addition of potassium chloride results in depolymerization with the ultimate formation of pyramidal SnCl_3^- ions. These results contrast somewhat with those obtained in the case of lead chloride¹⁹; Raman spectral investigations failed to detect complex ions in pure molten lead chloride even though the pyramidal PbCl_3^- ion was characterized in mixtures of lead chloride and potassium chloride.

ACKNOWLEDGMENTS

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¹⁹ K. Balasubrahmanyam and L. Nanis, *J. Chem. Phys.* **40**, 2657 (1964).

Quenching of the Tb^{3+} Fluorescence by Other Rare-Earth Ions in Aqueous Chloride Solutions*

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The quenching of the Tb^{3+} fluorescence by Nd^{3+} , Ho^{3+} , or Er^{3+} ions has been studied by measurement of the fluorescence lifetime in aqueous chloride solutions. The probability for a quenching interaction P_{int} is found to be proportional to r^{-6} , where r is an average distance between the fluorescent ion and the quenching ion. The overlap of the Tb^{3+} emission spectrum and the absorption spectra of several quenching ions has been measured. P_{int} , determined by the lifetime measurements for these ions, is approximately proportional to the value of the overlap integral. These results can be interpreted on the basis of a "resonance" (i.e., nonradiative) transfer of energy from the fluorescent terbium level to excited levels of the quenching ion through a dipole-dipole interaction.

INTRODUCTION

The interaction between a fluorescent Tb^{3+} ion and other rare-earth ions may cause a quenching of the observed terbium fluorescence. The fluorescence quenching may take the form of a shortening of the observed emission lifetime through nonradiative decay processes originating from the ion interactions.¹ The results of experiments are described here in which the observation of the fluorescence lifetime has been used to study such

interaction in aqueous chloride solutions. Similar results have been reported for the fluorescence of organic solutions.²

The most probable mechanism for an interaction between rare-earth ions which affects the fluorescence lifetime has been described by Dexter using the theory of "resonance" transfer of energy.³⁻⁵ This theory, in which the energy is transferred by a virtual photon, has at least two implications which can be verified experi-

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¹ G. E. Peterson and P. M. Bridenbaugh, *J. Opt. Soc. Am.* **53**, 301, 494 (1963).

² T. Foerster, *Fluoreszenz Organischer Verbindungen* (Vandenhoeck and Ruprecht, Göttingen, Germany, 1951).

³ D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953); D. L. Dexter and J. H. Schulman, *ibid.* **22**, 1063 (1954).

⁴ C. C. Klick and J. H. Schulman, *Solid State Phys.* **5**, 131 (1957).

⁵ D. Curie, *Luminescence in Crystals* (John Wiley & Sons, Inc., New York, 1963).

mentally. The first implication is that the radial dependence of the probability for a quenching interaction P_{int} takes the form $P_{\text{int}} \propto r^{-n}$, where n is an integer determined by the multipole orders of the interaction between the two ions and r is an average distance between the interaction ions. The second implication is that the strength of P_{int} is determined by the overlap of the Tb^{3+} emission spectrum and the absorption spectrum of the quenching ions.

The probability for a quenching interaction P_{int} may be studied by observation of the fluorescence lifetime. If a lifetime τ_{int} is associated with the nonradiative decay processes responsible for the quenching, then

$$P_{\text{int}} \propto 1/\tau_{\text{int}}. \quad (1)$$

In addition,

$$1/\tau_{\text{int}} + 1/\tau_{\text{fl}} = 1/\tau_{\text{obs}}, \quad (2)$$

where τ_{fl} is the fluorescence lifetime without quenching interactions, and τ_{obs} is the observed lifetime. The value of τ_{obs} was obtained by measuring the time for the fluorescence intensity to decay to $1/e$ of the initial value on an oscillogram. These values were checked by increasing the gain of the oscilloscope by a factor of at least 4 and repeating the above measurement. The τ_{fl} of the Tb^{3+} ion has been measured to be 340 μsec for normal water solutions and 1200 μsec for heavy-water solutions. The value of τ_{fl} has been estimated from the cases where interactions are small, i.e., $\tau_{\text{int}} \rightarrow 0$ implies that $\tau_{\text{obs}} \approx \tau_{\text{fl}}$.

Experimentally, the procedure has been to excite the fluorescence of the terbium ion in the solution with a light pulse from a General Radio Strobotac (type 1531-A). Solutions were used in these experiments to reduce the structure of the Tb^{3+} fluorescence and for convenience of sample preparation and handling. The value of τ_{obs} was obtained by monitoring the fluores-

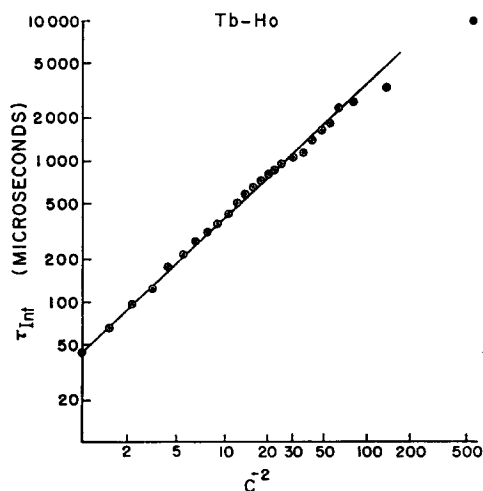


FIG. 1. The interaction lifetime τ_{int} in aqueous solutions of $\text{Tb}_{0.5}\text{Ho}_{0.5}\text{Cl}_3$ vs c^{-2} , where c is proportional to the concentration of Tb and Ho ions. τ_{int} is related to the observed lifetime τ_{obs} and the unquenched terbium lifetime τ_{fl} by $1/\tau_{\text{int}} = 1/\tau_{\text{obs}} - 1/\tau_{\text{fl}}$.

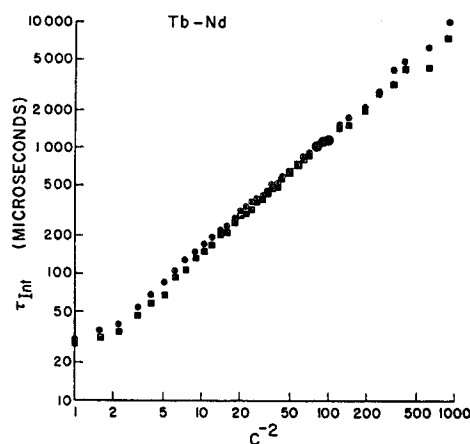


FIG. 2. The interaction lifetime τ_{int} in solutions of $\text{Tb}_{0.5}\text{Nd}_{0.5}\text{Cl}_3$ vs c^{-2} , where c is proportional to the concentration of Tb and Nd ions. τ_{int} is related to the observed lifetime τ_{obs} and the unquenched terbium lifetime τ_{fl} by $1/\tau_{\text{int}} = 1/\tau_{\text{obs}} - 1/\tau_{\text{fl}}$. The circles indicate dilution with water, and the squares indicate dilution with a 60% sucrose - 40% water solution.

cence decay with the output of an S-20 photomultiplier tube. The light of the excitation source and the fluorescence were isolated by appropriate filters. From the measurements of τ_{obs} and Eqs. (1) and (2), values could be obtained for τ_{int} and P_{int} .

RADIAL DEPENDENCE OF THE QUENCHING INTERACTION

The radial dependence of the quenching interaction was obtained by determining τ_{int} as a function of concentration. Since concentration is proportional to r^{-3} , this procedure establishes the radial dependence. The experimental method for varying the concentration (and hence the distance between rare-earth ions) was to dilute saturated aqueous solutions of $\text{Tb}_{0.5}\text{Nd}_{0.5}\text{Cl}_3$, $\text{Tb}_{0.5}\text{Ho}_{0.5}\text{Cl}_3$ and $\text{Tb}_{0.5}\text{Er}_{0.5}\text{Cl}_3$ with water. The quantity τ_{obs} was measured as a function of the dilution, and the concentration dependence of τ_{int} was determined from Eq. (2).

The results of plotting τ_{int} as a function of r^6 (c^{-2}) on log-log paper are shown in Figs. 1-3. For these data, the starting concentration, i.e., $c=1$, is the solution obtained from a room-temperature equilibrium solution containing crystals of the hydrated rare-earth chloride salts. The approximate rare-earth cation concentration of the saturated aqueous solutions was determined to be 3.1 M. At low concentrations, the accuracy is poor because errors in measurement or in the value of τ_{fl} become important as $\tau_{\text{obs}} \rightarrow \tau_{\text{fl}}$. In addition, in Fig. 2 the result of dilution with aqueous sugar solution is included to demonstrate that there are no large extraneous effects depending on viscosity. The difference between the two curves is attributed to difficulty of handling the viscous sugar solutions. Also in Fig. 2 the departure from linearity at high concentrations is attributed to the finite lifetime ($\tau \approx 28 \mu\text{sec}$) of the excitation flash.

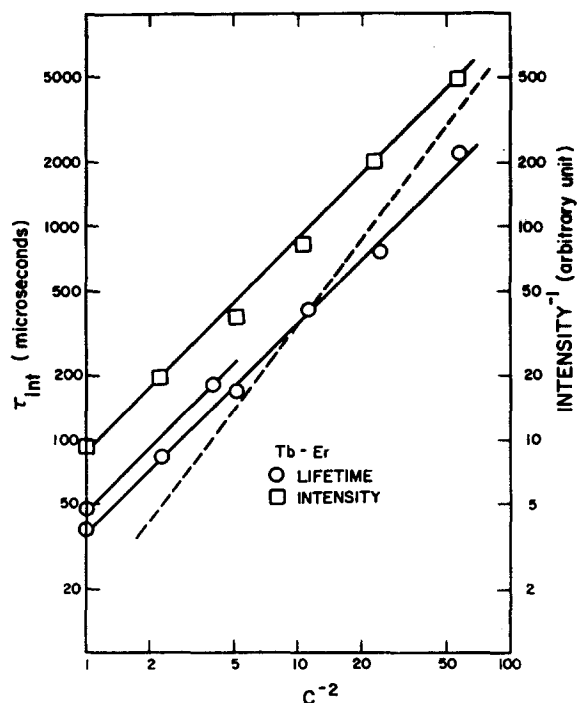


FIG. 3. Comparison of the interaction lifetime τ_{int} and the inverse fluorescence intensity in solutions of $Tb_{0.5}Er_{0.5}Cl_3$ vs c^{-2} , where c is proportional to the concentration of Tb and Er ions. τ_{int} is related to the observed τ_{obs} and the unquenched terbium lifetime τ_f by $1/\tau_{int} = 1/\tau_{obs} - 1/\tau_f$. The two points connected by the short line are results of lifetime measurements on heavy-water solutions. The dotted line indicates the result of plotting on interaction with an r^6 radial dependence (i.e., dipole-quadrupole interaction) on this graph.

The comparison of the concentration dependence of the lifetime of the Tb^{3+} ion with the concentration dependence of the Tb^{3+} -ion fluorescence intensity in aqueous solutions of $Tb_{0.5}Er_{0.5}Cl_3$ is shown in Fig. 3. Fluorescence intensity is frequently used to measure ionic interactions and in the present experiments yields the same result as the lifetime measurements. In addition, Fig. 3 contains two points showing the effect of a single dilution of a saturated (heavy water) solution of $Tb_{0.5}Er_{0.5}Cl_3$. Further dilutions were apparently contaminated with normal water.

Figures 1-3 reveal that $P_{int} \propto 1/\tau_{int} \propto 1/r^6$ over a wide range of concentrations. This result has also been observed in crystalline samples.⁶ The r^{-6} radial dependence for a quenching interaction is expected on the basis of "resonance" transfer of energy originating from a dipole-dipole interaction between rare-earth ions. In Fig. 3, an r^{-8} radial dependence (i.e., quadrupole-dipole interaction) curve is included to demonstrate that the present experiments rule out this type of interaction.

* W. W. Holloway, Jr., and M. Kestigian, J. Chem. Phys. **43**, 147 (1965).

OVERLAP OF THE Tb^{3+} EMISSION SPECTRUM AND THE ABSORPTION SPECTRUM OF THE QUENCHING ION

For the quenching of the Tb^{3+} fluorescence to take place through the "resonance" transfer of energy mechanism, it is necessary for there to be an overlap of the Tb^{3+} fluorescence spectrum and the absorption

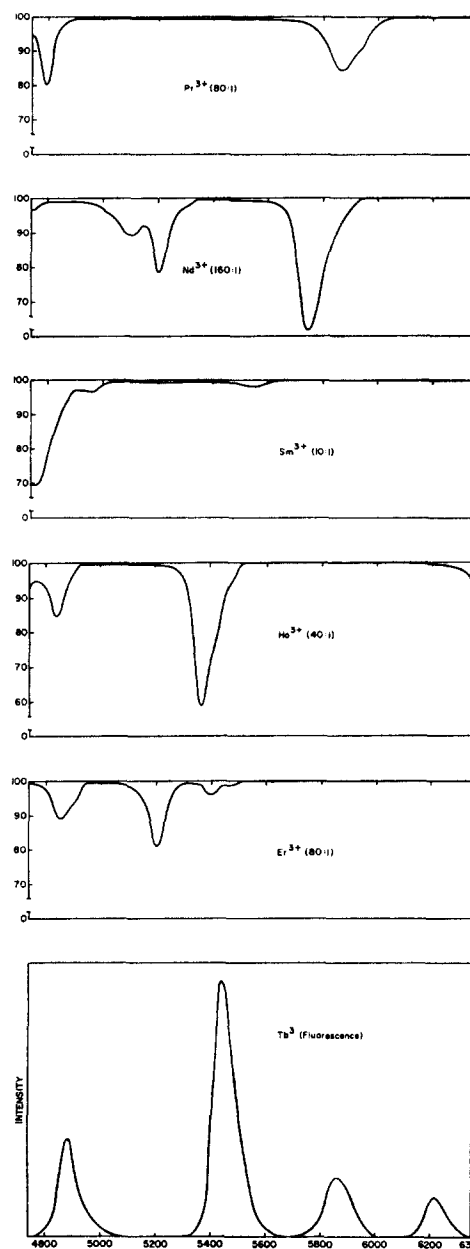


FIG. 4. Comparison of the Tb^{3+} ion fluorescence and the Sm^{3+} , Pr^{3+} , Er^{3+} , Ho^{3+} , and Nd^{3+} ion absorptions in aqueous chloride solutions. The numbers beside the ion designations indicate the dilution of the saturated solutions with water for a standard absorption length. The number provides a rough estimate of the strength of the ion absorption transitions.

spectrum of the quenching ion. Quenching of the Tb³⁺ fluorescence by the Sm³⁺, Pr³⁺, Er³⁺, Ho³⁺, and Nd³⁺ ions has been observed. In Fig. 4, the fluorescence spectrum of the terbium ion and absorption spectra for these five quenching ions are reproduced to indicate this overlap. The terbium emission spectrum of the aqueous chloride solution was recorded on a Perkin-Elmer Model 112-C spectrometer. The absorption spectra were taken on a Beckman DK-2 spectrophotometer using concentrations of solutions where the absorption strength is roughly linear with the amount of dilution.

The overlap of the emission and absorption spectra as it determines the strength of quenching interactions may be computed from the integral^{4,5}

$$P_{\text{int}} \propto \int \frac{\epsilon(h\nu) \alpha(h\nu)}{(h\nu)^4} d(h\nu), \quad (3)$$

where ϵ is the emission spectrum and α is the absorption spectrum. To obtain a quantitative estimate of the amount of overlap between the fluorescence of the Tb³⁺ ion and the absorption levels of the other Ln³⁺ ions, a saturated aqueous solution of TbCl₃ was excited with ultraviolet radiation. The spectral lines of the fluorescence were recorded using a Perkin-Elmer Type 112-C spectrometer. The spectrometer employed an EMI 9558-B photomultiplier (S-20 response) to detect the fluorescence radiation, and to improve the resolution a Bausch & Lomb grating (1200 grooves/mm) was used instead of a prism. Filter jars, containing the aqueous solutions (also used in the lifetime measurements) of the Tb_{0.9}Ln_{0.1}Cl₃ (where Ln is one of the five lanthanide ions of Fig. 4) were interposed between the Tb³⁺ fluorescence source and the spectrometer. The comparison of the fluorescence spectra with and without the solution filter provided a direct measurement of the overlap. After appropriate corrections, such as detector sensitivity and absorption of fluorescence by the terbium in the filter were taken into account, these data were used in Eq. (3) to estimate the relative magnitude of P_{int} . The relative P_{int} was also determined at these concentrations for each of the quenching ions from measurements of the lifetimes. The comparison of the relative P_{int} obtained from lifetime measurements and the overlap measurements is given in Table I. The relationship between fluorescence lifetime and spectral overlap is clearly in evidence. The experimental error, estimated to be 25%, exists principally in the

TABLE I. Comparison of the probability for a quenching interaction, P_{int} , determined from fluorescence lifetime measurements and from the overlap of the fluorescence and absorption transitions for the Tb³⁺-ion fluorescence by other rare-earth ions in saturated aqueous chloride solutions.

	P_{int} (from lifetime measurements) (sec ⁻¹)	P_{int} (from overlap measurements) (arbitrary units)	$\frac{P_{\text{int}}(\text{overlap})}{P_{\text{int}}(\text{lifetime})}$
Tb _{0.9} Sm _{0.1} Cl ₃	33	60	1.8
Tb _{0.9} Pr _{0.1} Cl ₃	86	230	2.7
Tb _{0.9} Er _{0.1} Cl ₃	220	450	2.0
Tb _{0.9} Ho _{0.1} Cl ₃	398	943	2.4
Tb _{0.9} Nd _{0.1} Cl ₃	1465	2460	1.7

measurement of the overlap and arises both from the lack of resolution of the fluorescence lines and from the contributions to the overlap value from weaker and unmeasured fluorescence transitions.

DISCUSSION

In the aqueous chloride solutions which we have measured, the probability for a quenching interaction of the terbium fluorescence by other rare-earth ions has an r^{-6} radial dependence (where r is the average distance between active and quenching ions) and the strength of the interaction is proportional to the overlap of the emission spectrum and the quenching-ion absorption spectrum. These two features may both be explained on the "resonance" transfer of energy theory, where there is a dipole-dipole interaction between the ions which influence the fluorescence. Identical results have been obtained for the radial dependence of this interaction in solids,⁷ although in highly doped crystals other effects may be found.⁶

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We are pleased to acknowledge many enlightening suggestions of Dr. R. Newman. The assistance of G. F. Sullivan with these experiments is gratefully recorded.

⁷ L. G. Van Uitert, *Luminescence of Inorganic Solids*, P. Goldberg, Ed. (Academic Press Inc., New York, 1966), Chap. 9, pp. 465-534.