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The application of luminescence-kinetic methods in the study of the formation of lanthanide ion complexes in solution

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Contents

I. Introduction 905
II. The rate constants for nonradiative transitions in lanthanide ions as an indicator of the structure of their environment 905
III. The application of nonradiative energy transfer between lanthanide ions in the study of complex formation 913
IV. A luminescence-spectroscopic method for the determination of the rates of rapid ligand exchange in lanthanide ion complexes in liquid solutions 917

Abstract. The mechanisms of the nonradiative transitions in lanthanide ions in solutions are discussed. The results of the use of this phenomenon in the study of the structures and stability constants of complexes of lanthanide ions in solutions are described. The possible uses of the nonradiative energy transfer between lanthanide ions in the determination of the stability constants of their complexes and for the detection of unstable dinuclear bridged complexes are considered. The luminescence-spectroscopic methods for the determination of the rates of rapid ligand exchange in lanthanide complexes in solutions are discussed. The bibliography includes 62 references.

I. Introduction

The luminescence-kinetic methods for the study of lanthanide complexes in solution have been increasingly widely used by investigators in recent years. This is due both to the ready accessibility of luminescence-kinetic apparatus to investigators (pulse type fluorimeters, pulse type tunable laser sources) and to the employment of Ln^{3+} as luminescence labels in biology and medicine.[1] The progress in the understanding of the mechanism of the quenching of the luminescence of Ln^{3+} ions has also played an important role.

This review deals with the following questions: the methods for the determination of the composition of the environment of the luminescent Ln^{3+} ion based on the measurement of its luminescence decay time; a version of the method involving the use of the phenomenon of the nonradiative energy transfer between ions; the study by the same method of unstable dinuclear bridged complexes; the luminescence-spectroscopic kinetic methods for the determination of the rates of rapid ligand exchange in lanthanide complexes.

The chemical properties of Ln^{3+} ions are known to be similar although not identical. On the other hand, their luminescence-spectroscopic properties differ greatly. This enables experimenters to select experimentally suitable ions and to carry out investigations involving them in a manner depending on the problem formulated. The greatest number of luminescence studies have been performed on Tb^{3+} and Eu^{3+} ions.[1,2] On the one hand, these ions have an appreciable luminescence quantum yield in most of the solvents used. On the other hand, the long-wavelength bands in the absorption spectra of these ions are located in the region where effective tunable dye-based lasers emit radiation, which is convenient for the experimenter. Yet another positive feature of the employment of these ions is the marked influence of the deuteriation of the surrounding molecules on the quantum yields and decay times of their luminescence, which makes it possible in many instances to obtain important information about the structure of the environment of the Ln^{3+} ion.

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II. The rate constants for nonradiative transitions in lanthanide ions as an indicator of the structure of their environment

1. Modern ideas about the mechanism of nonradiative transitions in lanthanide ions in solutions

Ln^{3+} ions luminesce not only in crystals and glasses but also in aqueous solutions.[3] However, only Gd^{3+}, Tb^{3+}, and Eu^{3+} luminesce with an appreciable yield in water. The luminescence yields of the remaining lanthanide ions in water are low. The luminescence yields of Ln^{3+} ions in various media obey the general rule governing nonradiative transitions. The probability of the latter is lower the greater the electronic energy of the quantum converted into the energy of the vibrational or translational motion and the lower the maximum energy of the vibrational quanta in the molecular groups surrounding the ion.[4]

The most important step towards the understanding of the mechanism of the nonradiative transitions in Ln^{3+} ions was taken by Krop and Windsor.[5] They observed an appreciable increase (by a factor of several tens) in the decay time (τ) in the quantum yield (q) of the luminescence of Eu^{3+} ions from the $^5D_0$ level and of the Tb^{3+} ions from the $^5D_4$ level on passing from an aqueous to a deuteriated solution. This effect was explained by the smaller number of high-frequency quanta of the stretching vibrations of the H_2O molecules ($\nu_3^H \approx 3400$ cm^{-1}) compared with D_2O ($\nu_3^D \approx 2250$ cm^{-1}) required for the law of conservation of energy to hold in the nonradiative transitions. It was also established that the rate constant for the nonradiative transition (k_{nr}) in the Eu^{3+} and Tb^{3+} ions varies linearly with the mole fraction of H_2O in the H_2O-D_2O mixture as the solvent. The linear dependence of k_{nr} for the ions on the fraction of OH groups in the mixture was confirmed by Gallagher[6] and Heller[7] and by the latter also for Dy^{3+} and Sm^{3+}. These facts indicate that the

Table 1. The luminescence decay times for lanthanide ions in ordinary and deuteriated water and in hydrated crystals.

Ion (emitting level)	Base	T/K	τ/μs	Ref.
Tb^{3+}	H_2O	293	475	11
($^5D_4$)	D_2O	293	4000	11
	$TbCl_3 \cdot 6H_2O$	298	485	8
	$TbCl_3 \cdot 6D_2O$	298	2390	8
	$Y(C_2H_5SO_4)_3 \cdot 9H_2O$ (10% Tb^{3+})	300	429	9
	$YCl_3 \cdot 6H_2O$ (10% Tb^{3+})	300	482	9
Eu^{3+}	H_2O	293	125	11
($^5D_0$)	D_2O	293	4000	11
	$EuCl_3 \cdot 6H_2O$	298	130	8
	$EuCl_3 \cdot 6D_2O$	298	1650	8
	$Eu(C_2H_5SO_4) \cdot 9H_2O$	300	116	9
	$Eu(C_2H_5SO_4) \cdot 9D_2O$	300	750	9
Dy^{3+}	H_2O	293	3	10
($^4F_{9/2}$)	D_2O	293	60	10
	$GdCl_3 \cdot 6H_2O$ (1% Dy^{3+})	293	4	10
	$GdCl_3 \cdot 6D_2O$	293	67	10

quenching effects of each O–H oscillator around the Ln^{3+} ion are independent of one another. These results permit a choice to be made betwen two models of the exchange of the electronic excitation energy quantum; exchange with excitation of an individual high vibrational state of the molecular group surrounding the lanthanide ion; exchange for a set of vibrations of several molecular groups.

A similar effect of deuteriation in hydrated crystals of lanthanide ion salts has been observed by other workers.[8–10] Their data are presented in Table 1, which shows that τ for the Ln^{3+} ions in the hydrated crystals is close to τ for aqueous solutions and that the change in τ on passing from protonated to deuteriated crystals is similar to its change on deuteriation of aqueous solutions. These findings agree well with the fact that the inner (first) sphere surrounding the Ln^{3+} ion consists of water molecules both in water and in crystals.

2. The inductive-resonance theory of nonradiative transitions in lanthanide ions

Ideas concerning the nonradiative transitions in lanthanide ions have been developed[11] on the basis of inductive resonance energy transfer from the excited Ln^{3+} ion to the surrounding molecular groups, with their excitation to higher vibrational states. Questions concerning the energy transfer from the Ln^{3+} ion to water molecules have been discussed in the studies mentioned above,[5,9] but the mechanism of the interaction, initiating the energy transfer step and permitting semiempirical calculations of the constant k_{nr}, was not specified in them. In other investigations,[11–13] it was postulated that the nonradiative transitions are caused by electromagnetic interactions between the oscillator corresponding to the radiative downward electronic or vibronic transition from the deactivating level and the oscillator of the vibrational transition in the groups surrounding the ion and involved in energy resonance with the electronic (vibronic) oscillator.[11–13] The energy level scheme explaining this model is presented in Fig. 1.

Thus the model mentioned above is close to the energy transfer model in Förster's theory[14] with the difference that the energy acceptor is a purely vibrational oscillator. As in Förster's model, it is postulated that the energy transfer step is followed by the rapid (compared with the rate of transfer) deactivation of the vibrational oscillator excited in the transfer process. This hypothesis has been

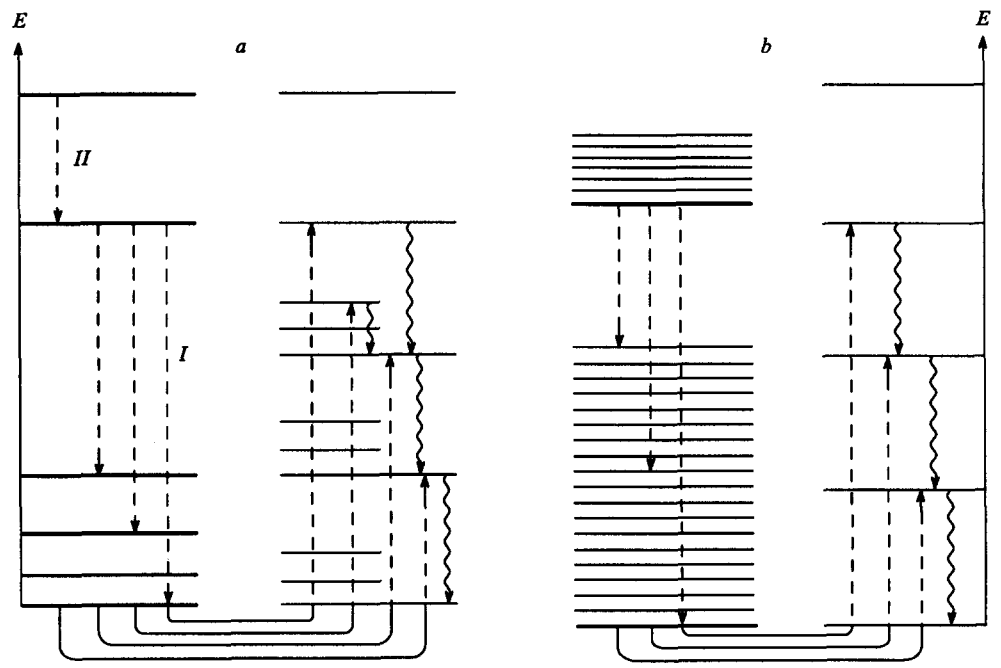


Figure 1. The energy level scheme explaining the inductive-resonance theory of nonradiative transitions: (*a*) weak vibronic linkage (Ln^{3+} ions) [(*I*) multiphonon nonradiative transition; (*II*) single-phonon nonradiative transition]; (*b*) strong (moderately strong) vibronic linkage (transition metal ions). The electronic (bold lines) and vibronic (thin lines) levels of the ions are shown on the left-hand sides of Figs *a* and *b*; the promoting-accepting vibrational levels of the molecules surrounding the ions are shown on the right; the vertical dashed lines designate the energy transfer inducing the nonradiative transition between the electronic levels of the ions and the excitation of the vibrational levels of the surrounding molecules.

confirmed experimentally in studies undertaken to estimate the rates of vibrational relaxation in solutions.[15] A further approximation, permitting specific calculations of the rate constants for nonradiative transitions, involves the selection of a multipolar interaction. In most cases, the treatment may be restricted to the approximation involving the interaction of electrical dipoles, as has been done in the derivation of Förster's familiar formula for the nonradiative electronic energy transfer between organic molecules.[14] Experimental confirmation of the possibility of using this approximation will be given below.

In the dipole–dipole approximation, the rate constant for the nonradiative transitions in the Ln^{3+} ions from the given excited level may be calculated provided the following features are known: the true luminescence spectrum (purely electronic or vibronic) associated with the transition from the given level to all the lower electronic levels of the given ion and the overall rate constant for emission from this level; the quantitative vibrational absorption spectra of the molecular groups, ligands, and solvent molecules surrounding the ion in the region of overlap with the luminescence spectrum of the ion; the distances from the ion to each molecular group responsible for the given vibrational absorption.

The expression for k_{nr} assumes the following form in this case:

$$k_{nr} = \sum \frac{8.8 \times 10^{-25} k_e \varkappa^2}{n^4 R_i^6} \int_0^\infty I^n(\nu)\, \varepsilon_i^{vibr}(\nu)\, \nu^{-4}\, d\nu , \qquad (1)$$

where k_e is the rate constant for the electrical dipole radiative transition from the given level to all the lower levels (s^{-1}), $\varkappa^2$ a coefficient which depends on the mutual orientation of the interacting dipoles (the average quantity $\overline{\varkappa^2} = 2/3$ is normally employed), n the refractive index of the medium, R_i the distance from the Ln^{3+} ion to the corresponding molecular groups (cm), $I^n(\nu)$ the luminescence spectrum, normalised for a unit area, emitted from the same level and expressed in terms of quantum intensities on the wave number ν scale (cm^{-1}), and $\varepsilon_i^{vibr}(\nu)$ the molar decadic vibrational absorption coefficient in the main and overtone regions for the molecular groups responsible for the absorption bands overlapping with the luminescence spectrum.

Naturally it is almost impossible to take into account all the molecular groups surrounding the Ln^{3+} ion in solution and even their position relative to the ion is usually not known exactly. However, one should bear in mind that the strongest interactions inducing the nonradiative transition involve groups adjoining directly the Ln^{3+} ions, i.e. located in the inner coordination sphere. Such molecular groups usually make the greatest contribution to k_{nr}. Only in the absence from the inner coordination layer of vibrating molecular groups capable of initiating the nonradiative transition, for example owing to the smallness of the vibrational quantum, is it necessary to take into account the influence of the second and more remote layers of molecular groups surrounding the ion as the main contribution to k_{nr}.

In many cases, it is useful to take into account only the first (inner) ordered sphere comprising molecules surrounding the ion [Eqn (1)], while the more remote molecules can be regarded as a continuous medium. The influence of remote molecules is taken into account by using the formula derived by Galanin and Frank[16] for the decay of a dipole in the absorping medium

$$k'_{nr} = \frac{k_e}{16\pi^4 n^4 a^3} \int_0^\infty I^n(\nu)\, \alpha(\nu)\, \nu^{-4}\, d\nu , \qquad (2)$$

where a is the radius of the sphere around the ion in which there are no oscillators absorbing the emission from the Ln^{3+} ion and $\alpha(\nu)$ is the linear absorption coefficient of the solvent (cm^{-1}). When account is taken of the effect of the molecules (groups) in the inner sphere of the ion in accordance with Eqn (1), a is the size of the inner sphere and the contribution of the remaining molecules outside the inner sphere is calculated by Eqn (2) in terms of the continuous medium approximation.

Calculations by Eqns (1) and (2) make it possible to take into account the influence on the nonradiative transitions by a factor such as the vibronic interaction in terms of the vibronic component of the luminescence spectrum. The vibronic spectra of Ln^{3+} ions usually have a low intensity and in most cases hardly affect k_{nr}. They can improve the resonance conditions if the narrow absorption bands of C–H group type do not overlap with the narrow band due to the electronic transition in the Ln^{3+} ion. However, in the calculation of k_{nr} for transition metal ions, characterised by extensive vibronic spectra, the overlap of the vibrational absorption spectra with the latter is in most cases decisive. As shown in a theoretical study,[17] it is then important to divide the vibrations into two types: vibrations contributing to the vibronic luminescence spectrum (accepting vibrations) and vibrations the absorption spectrum of which in the region of the main frequencies or overtones overlaps with the luminescence spectrum (promoting-accepting vibrations), since they initiate the nonradiative transition and accept part of the energy. Another component of the exchanging electronic energy quantum is accepted by the vibrations active in the vibronic spectrum. The vibronic levels illustrating this approach are presented schematically in Fig. 1.

Within the framework of this approach, the anharmonicity of the vibrations is taken into account: automatically, since for a multiphoton nonradiative transition the luminescence spectrum $I^n(\nu)$, included in Eqns (1) and (2), largely overlaps with the vibrational spectrum in the region of the overtones and compound frequencies, the latter spectrum being determined by the anharmonicity of the promoting-accepting vibrations of the molecular groups surrounding the ion.

We shall now consider how the inductive-resonance theory of nonradiative transitions agrees with the experimental decay times and luminescence quantum yields for Ln^{3+} ions in solutions and other media obtained by the present authors and available in the literature. The decay time of the luminescence of Ln^{3+} ions with an energy gap $20\,000 \geqslant \Delta E \geqslant 4000-5000$ cm^{-1} depends greatly on the replacement of protium atoms by deuterium atoms in the molecular groups located in the vicinity of the ion. The effect of deuteriation is undoubtedly associated with the change in the rate of the nonradiative transitions because the luminescence yield varies in parallel with τ and there are no physical grounds for such a sharp increase in the emission rate constant on deuteriation. From the standpoint of the inductive-resonance theory of nonradiative transitions, the influence of deuteriation is determined by the sharp change in the vibrational absorption owing to the decrease in the stretching vibration frequencies when H is replaced by D. Fig. 2 (see next page) presents the luminescence spectrum of Dy^{3+} in D_2O and the vibrational absorption spectra of H_2O and D_2O and of H_2O in a $GdCl_3.6H_2O$ crystal. Comparison of the luminescence (Fig. 2a) and absorption (Figs 2*b* and 2*c*) spectra of H_2O and D_2O shows that in the case of D_2O the overlap integral in Eqns (1) and (2) is many times smaller than in the case of H_2O.

Comparison of the overlap integrals of the spectra in Eqns (1) and (2) for the usual and deuteriated compounds makes it possible to calculate, provided that the luminescence and vibrational absorption spectra are known, the influence of deuteriation on the nonradiative transition rate constant for the given ion and its environment. Table 2 shows that, for the majority of Ln^{3+} ions, the effect of the deuteriation of the molecules surrounding the ion can be calculated by Eqns (1) and (2) with satisfactory accuracy. Table 2 also presents the experimental luminescence decay times

$$\tau = (k_e + k_{nr})^{-1} ,$$

where k_e is the rate constant for the emission from the given level of the ion and k_{nr} is the rate constant for the nonradiative transition from the same level. Since k_e does not change on deuteriation of the molecules surrounding the ion and only k_{nr} is altered, the dependence of τ on deuteriation for different energy gaps is as follows: for large gaps, $\Delta E \approx 30\,000$ cm^{-1} (for example, for

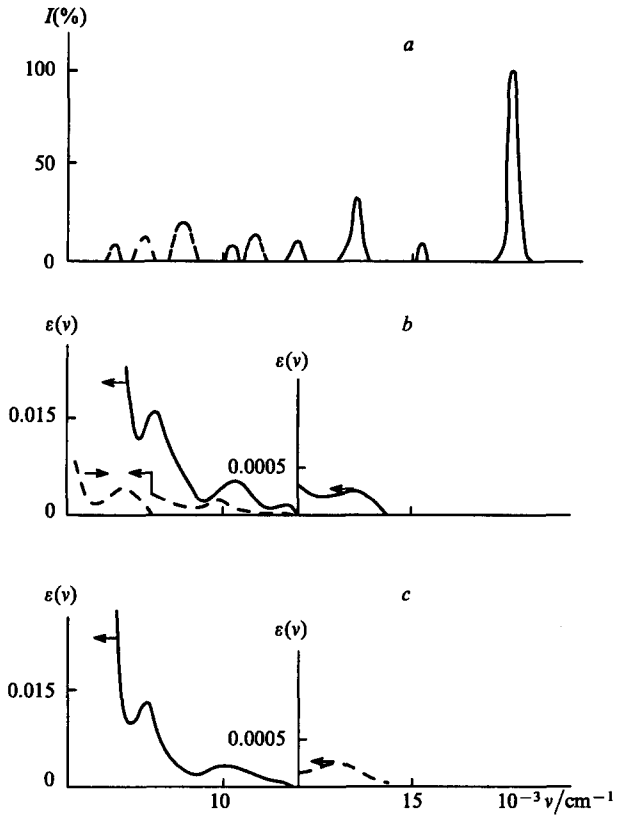


Figure 2. Luminescence spectra of the Dy^{3+} ion in D_2O (*a*) (the luminescence bands, the scale of which has been increased by a factor of 10, are shown by a dashed line), the absorption spectra of H_2O (continuous line) and D_2O (dashed line) in solution (*b*), and the spectra of H_2O in the $GdCl_3.6H_2O$ crystal (*c*) at 293 K.

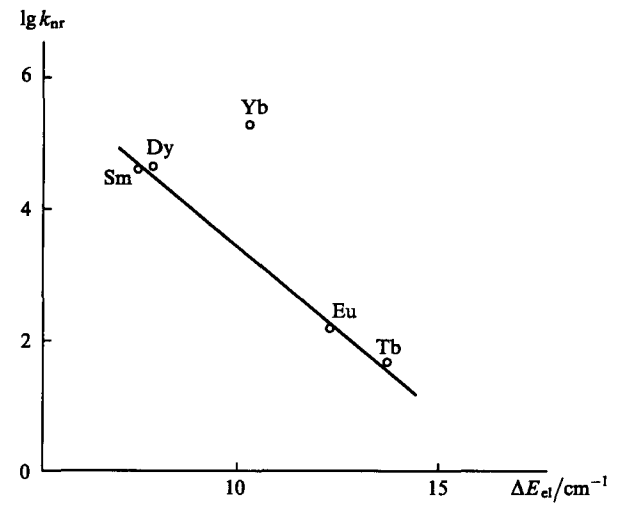


Figure 3. Dependence of the rate constant for the nonradiative transitions from the resonance levels of the Ln^{3+} ions in methanol-d_1 (293 K) on the difference between the energies of the emitting level and the lower level closest to it.

Gd^{3+}), the constant k_{nr} varies by many orders of magnitude, but τ is almost independent of deuteriation because in this region $k_e \geqslant k_{nr}$, so that $\tau \approx k_e^{-1}$. For gaps of medium size, $\Delta E = 20\,000-4000$ cm^{-1}, the constant k_{nr} depends less on deuteriation, but in this region $k_{nr} \geqslant k_e$ and τ increases markedly on deuteriation of the molecules surrounding the ion [$Eu^{3+}(^5D_0)$, $Yb^{3+}(^2F_{5/2})$, $Dy^{3+}(^4F_{9/2})$, $Nd^{3+}(^4F_{3/2})$]. In the region $\Delta E \leqslant 4000$ cm^{-1}, where $k_{nr} \gg k_e$ (for surrounding groups with H and D atoms), the dependence of k_{nr} and τ on such groups is determined by the overlap of the structural luminescence spectrum of the Ln^{3+} ion with the vibrational absorption spectrum, and may vary from a very large value for Er^{3+} ($^4I_{11/2}$) in water to low values for $Er^{3+}(^4I_{11/2})$ and $Pr^{3+}(^3P_0)$ in dimethyl sulfoxide, and even to an absence of the influence of deuteriation in $Eu^{3+}(^5D_1)$.

In this region, there is also the possibility of the opposite effect of deuteriation — a decrease in τ in deuterium-containing molecules.

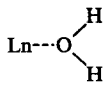
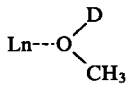
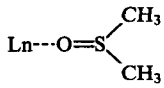
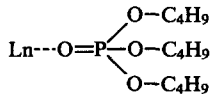
For Ln^{3+} ions surrounded by particular groups in the case where the nonradiative transition is of the multiphonon type, i.e. $\Delta E_{el} \geqslant 2h\nu_{vibr}^{max}$, a nearly inverse exponential dependence of k_{nr} on the energy gap ΔE_{el} between the emitting level and the nearest lower level is observed. Such an exponential dependence of k_{nr} on ΔE_{el} can be explained by the fact that the intensity of the overtones of the vibrational transitions diminishes approximately in a geometrical progression with increase in the number of the overtone.[18]

From the standpoint of the inductive-resonance theory of nonradiative transitions, the inverse exponential dependence of k_{nr} on ΔE for multiphonon transitions is a special case of a more general relation — the proportionality of k_{nr} to the overlap integral between the luminescence spectrum of Ln^{3+} ions and the vibrational absorption spectrum of the molecules surrounding the ion for an approximately constant k_e and a constant distribution of the quantum intensity in the luminescence spectrum. Fig. 3 illustrates such a relation. The appreciable deviation of the k_{nr} for ytterbium is due to the fact that an intense luminescence is observed for this ion in the region of the long wavelength band, whereas for the remaining ions (Sm^{3+}, Dy^{3+}, Eu^{3+}, and Tb^{3+}) the long wavelength bands constitute a small proportion of the overall luminescence intensity (see, for example, Fig. 2).

Table 2. The experimental constants k_{nr} (I) and their values calculated by Eqns (1) and (2) (II) for lanthanide ions in ordinary and deuteriated solvents.

Ln^{3+}	Transition	ΔE^{min}/cm^{-1}	Solvent	k_{nr}^H/k_{nr}^D		τ^D/τ^H	
				I	II	I	II
Eu^{3+}	$^5D_0-{}^7F_i$	12150	H_2O; D_2O	48	38	33	–
Yb^{3+}	$^2F_{5/2}-{}^2F_{7/2}$	10300	H_2O; D_2O	25	55	25	55
Dy^{3+}	$^4F_{9/2}-{}^6F_i$, ^6H_j	7000	H_2O; D_2O	20	18	20	18
Nd^{3+}	$^4F_{3/2}-{}^4I_i$	5000	H_2O; D_2O	5.0	9.0	5.0	9.0
Er^{3+}	$^4I_{11/2}-{}^4I_{13/2}$	3600	H_2O; D_2O	100	80	100	80
	$^4I_{11/2}-{}^4I_{13/2}$	3600	$(CH_3)_2SO$; $(CD_3)_2SO$	4.5	3.0	3.0	4.5
Pr^{3+}	$^3P_0-{}^1D_2$	3500	$(CH_3)_2SO$; $(CD_3)_2SO$	3.0	5.0	3.0	5.0
Eu^{3+}	$^5D_1-{}^5D_0$	1750	$(CH_3)_2SO$; $(CD_3)_2SO$	1.0	–	1.0	–

Table 3. Dependence of k_{nr} on the distance from the Ln^{3+} ion to the promoting-accepting vibrational oscillators.

Structural fragment of complex (Ln–O distance/Å)	$Dy^{3+}(^4F_{9/2})$			$Yb^{3+}(^2F_{5/2})$		
	$10^4 k_{nr}/s^{-1}$	$k_{nr}a^3$	$k_{nr}a^5$	$10^4 k_{nr}/s^{-1}$	$k_{nr}a^3$	$k_{nr}a^5$
 (2.2; 2.5)[a]	33	[b]	[b]	590	[b]	[b]
 (3.6; 3.9)[a]	5.0	3.0[c]	4.5[c]	22	10.0[c]	1.3[c]
 (5.0; 5.3)[a]	2.5	3.7	10.5	5.5	6.9	1.7
 (6.0; 6.3)[a]	1.5	3.8	15	4.5	9.7	3.5

[a] Here and henceforth the larger distance refers to Dy^{3+} and the smaller distance to Yb^{3+}.
[b] Aqueous solutions have not been included in the comparison column because the vibration frequency of the OH group differs appreciably from that of the CH group.
[c] Relative units.

According to the inductive-resonance theory of nonradiative transitions, for the interaction of the electrical dipoles in the Ln^{3+} ion and the ligands surrounding it [electrical dipoles comprising the Ln^{3+} ion and the ligand surrounding it?], the contribution to k_{nr} is inversely proportional to the sixth power of the distance between them. The electromagnetic interactions inducing the nonradiative transitions are universal and should be independent of the presence or absence of chemical bonds between them and the molecular group involved in the exchange.

Having postulated the occurrence of the dipole–dipole interaction, we compared the experimental and theoretical dependences of k_{nr} on the distances between the Ln^{3+} ion and the OH and CH groups most active in the exchange process. Eqn (2) was used for this purpose; the absorbing medium was assumed to be continuous and the dependence on the distance was expressed in terms of a sphere with a radius a. It was assumed that in the sphere there are no molecular groups with high frequency vibrations inducing the exchange of the electronic energy of the ion. Table 3 presents the values of k_{nr} for Dy^{3+} and Yb^{3+} in various solvents for increasing distances between the CH groups and the ion and the products $k_{nr}a^3$, which should remain constant if the electrical dipoles interact and hence Eqn (2) is valid. The products $k_{nr}a^5$, which would have remained constant if the interaction responsible for the nonradiative transition had been determined by the interaction between an electrical quadrupole and a dipole, i.e. if the formula for k_{nr} assumed the form

$$k_{nr}^{q} = \frac{9k_e}{32\pi^6 n^6 a^5} \int I^n(\nu)\,\alpha(\nu)\,\nu^{-6}\,d\nu,$$

are also presented.

The long-range and nonchemical nature of the interactions responsible for the nonradiative transitions in Ln^{3+} ions is confirmed by the influence on $\tau(k_{nr})$ by the solvent ion in the outer sphere of a bulky complex such as $Ln(NO_3)_3(TBP\text{-}d_{27})_3$ (here TBP-d_{27} is fully deuteriated tri-n-butyl phosphate).

Table 4 presents the values of τ and k_{nr} for lanthanide ion complexes with nitrate anions and the usual and fully deuteriated tri-n-butyl phosphate dissolved in CCl_4 and toluene-h_8. Toluene-h_8 is at a distance greater than 6 Å from the Nd^{3+} and Sm^{3+} ions and is not linked to them by any chemical bonds. However, it does affect appreciably τ and hence k_{nr} for the given ions.

The results of the study of the luminescence of the Dy^{3+} ion in the usual and fully deuteriated acetonitrile may be regarded as yet another confirmation of the inductive-resonance theory of nonradiative transitions. The point is that the frequency of the stretching vibration of the C≡N, group adjoining directly the Dy^{3+} ion (2254 cm^{-1}) is close to the stretching vibration frequency of the C–D bond (2257 cm^{-1}). It may be expected that τ for the Dy^{3+} ion in fully deuteriated acetonitrile is appreciably smaller than in the fully deuteriated dimethyl sulfoxide and acetone because the stretching vibration frequencies of the S=O and C=O groups are appreciably lower. However, measurements have shown that τ = 320 μs for Dy^{3+} in CD_3CN.[20] The value τ = 13.3 μs for Dy^{3+} in CD_3CN quoted by Haas et al.[19] is undoubtedly erroneous owing to the presence of the water impurity in this solution, the amount of which was not

Table 4. The influence of the outer-sphere solvent on τ and k_{nr} for the complexes $Ln(NO_3)_3(TBP)_3$ at 293 K.

Complex	τ/μs		k_{nr}/s^{-1}	
	toluene-h_8	CCl_4	toluene-h_8	CCl_4
$Nd(NO_3)_3(TBP\text{-}h_{27})_3$	2.1	3.0	4.8×10^5	3.3×10^5
$Sm(NO_3)_3(TBP\text{-}d_{27})_3$	350	1100	2.5×10^3	6×10^2
$Sm(NO_3)_3(TBP\text{-}h_{27})_3$	–	130	–	7.7×10^3
$Eu(NO_3)_3(TBP\text{-}d_{27})_3$	–	1600	–	0
$Eu(NO_3)_3(TBP\text{-}h_{27})_3$	1600	1600	0	0

Table 5. The energy and kinetic parameters and the decay times of the luminescence of lanthanide ions (μs) in solutions of the nitrate salts of the ions at 293 K.[1,10–13,20]

Parameter, solvent	Tb^{3+}	Eu^{3+}	Dy^{3+}	Sm^{3+}	Yb^{3+}	Eu^{3+}
	$^5D_4-\sum_i^6{}^7F_i$	$^5D_0-\sum_i^6{}^7F_i$	$^4F_{9/2}-\sum_{i,j}{}^6F_i,H_j$	$^4G_{5/2}-\sum_{i,j}{}^6F_i,H_j$	$^5F_{5/2}-{}^2F_{7/2}$	$^4I_{11/2}-{}^4I_{13/2}$
Parameters						
$\Delta E_{el}^{min}/cm^{-1}$	14800	12150	7850	7400	10300	3650
k_e/s^{-1}	100–550	70–600	750–2500	710–2000	2500	–
Decay times in						
H_2O	475	125	3	3	0.17	0.00012
D_2O	4000	4000	60	75	4.25	0.012
CH_3OH	1240	390	9	10.5	0.9	–
CD_3OH	1330	415	12	16	–	0.00077
CH_3OD	2600	2200	20	22	4.5	–
CD_3OD	3000	3300	150	175	12.5	0.033
$(CH_3)_2SO$	2600	1400	40	18	18	0.04
$(CD_3)_2SO$	–	–	235	255	149	0.18
$(CH_3)_2CO$	1200	1350	74	–	–	–
$(CD_3)_2CO$	–	–	235	–	–	–
CH_3CN	1900	1350	80	–	–	–
CD_3CN	–	–	320	–	–	–
$(C_3H_7O)_3PO$	1800	1600[a]	100[a]	130[a]	22	–
$(C_3D_7O)_3PO$	1800	1600[a]	500[a]	1100[a]	–	–
$POCl_3+SnCl_4$	–	3900	1300	2700	–	–

[a] Solution of the $Ln(NO_3)_3(TBP)_3$ complexes in CCl_4.

determined. The value of τ which we measured is greater by a factor of $\sim$1.5 than τ for the Dy^{3+} ion in dimethyl sulfoxide-d_6 (235 μs) and acetone-d_6 (235 μs) and is twice as great as τ in fully deuteriated methanol (150 μs). This finding has been explained in a study[20] where it was shown, by comparing the IR spectra of the usual and deuteriated acetonitrile, that the anharmonicity of the vibrations and the intensity of its overtones are small for the C≡N bond, which has an intense absorption band at 2254 cm^{-1}. On the other hand, the C–D vibrations, for which the intensity in the region of the main frequency is smaller compared with the C≡N vibration, become the principal vibrations, determining the absorption spectrum, in the region of overtones owing to the greater anharmonicity. Consequently, they make the greatest contribution to the overlap integral with the Dy^{3+} luminescence spectrum and hence they make the main contribution to k_{nr} for the Dy^{3+} ion despite the greater distance from the latter. This is fully consistent with experimental data.

In conclusion, it is essential to discuss the errors in the calculations of k_{nr} in accordance with the inductive-resonance theory. Firstly, owing to the rapid liquid exchange with the surrounding groups, an average pattern is observed in the liquid solutions and $\bar{\tau}$ may be made up of the times τ for the rapidly varying different conformations of the environment of the ion. So long as the exchange time is shorter than τ, the decay is exponential. If the ligand exchange time becomes greater than or equal to τ, the decay of the luminescence is nonexponential because each form of the complex decays with its own τ. The ligand exchange time for Ln^{3+} ions in water is of the order of 10^{-7} s.[21] Thus, if different complexes coexist in solution, a nonexponential decay of the luminescence will be observed for times shorter than 100 ns.

The next source of error in the calculations of k_{nr} is the inaccurate knowledge of the mutual disposition of the ligands and the ion, especially in liquid solutions. Yet another source of error consists in the fact that in most cases the spectrum of the pure solvent and not of the molecules directly coordinated to the Ln^{3+} ion is adopted as the vibrational absorption spectrum. The spectra of the directly coordinated molecules, especially of the OH groups of water or alcohols where the oxygen atom is linked directly to the Ln^{3+} ion, differ in the frequencies and anharmonicity of the vibrations, which undoubtedly introduces a definite error into the calculation of k_{nr}. In a number of instances no account is taken of the mutual orientation of the dipole moment of the electronic transition of the ion and of the vibrational absorption in the surrounding groups because the average value $\varkappa^2 = 2/3$ is used in Eqn (1). The quantity k_e in Eqns (1) and (2) introduces an appreciable error into the calculations of k_{nr} especially when its experimental determination is difficult and it is necessary to employ the value calculated by the Judd–Offelt method. Nevertheless, comparison of the experimental and theoretical values of k_{nr} in water and hydrated crystals shows that, even for water, the variations in frequencies and anharmonicity do not play a decisive role in the calculations of k_{nr}.

Yet another doubt is associated with the size of the interacting dipoles and with the possibility of using an expansion in powers of the distance between the ion and the promoting-accepting groups. However, one should note that the size of the emitting dipole is less than 0.6 Å, i.e. is smaller than the size of the 4*f* shell of the Ln^{3+} ions; the size of the dynamic oscillator in the high frequency vibration is close to the amplitude of the displacement of a light atom, i.e. $b = (2\hbar/m\omega)^{1/2} \approx 0.1$ Å, while the distance between the interacting centres is greater than 2.4 Å.[22] Thus the conditions used in the derivation of Eqn (1) are satisfied.

Table 5 presents the luminescence decay times for the most frequently used Ln^{3+} ions in various solvents. The results of the interpretation of these data are presented in Table 6. They represent estimates of the contributions to k_{nr} by various molecular groups at different distances from the Ln^{3+} ion for six such ions. The estimates are naturally fairly approximate because in most cases we are dealing with the overall influence on k_{nr} of the inner and more remote spheres surrounding the ion. By replacing the molecules in the inner sphere, we as a rule alter simultaneously the absorption by the entire remaining mass of the solution and hence its contribution to k_{nr}. Furthermore, in order to estimate the contribution of an individual molecular group, it is necessary to know as exactly as possible the number of molecular groups in the inner coordination sphere of the ion, which is not always available.

Table 6. Approximate estimates of the contributions of the molecular groups located at different distances from the Ln^{3+} ions to k_{nr}/s^{-1} according to different data.[1,2,11-13,21-29]

Ln^{3+}	Level	O–H 2.2–2.5 Å	N–H 2.2–2.5 Å	CH_3 3.6–3.9 Å	CH_3 5.0–5.3 Å	C_3H_7 6.0–6.3 Å	C–D 2.2–2.5 Å
Tb^{3+}	$^5D_4$	100–200	70	12	–	–	–
Eu^{3+}	$^5D_0$	400–500	800–1000	40	–	–	10
Dy^{3+}	$^4F_{9/2}$	20 000	–	9000	1700	900	1000
Sm^{3+}	$^4G_{5/2}$	18 000	–	9000	4300	750	700
Yb^{3+}	$^4F_{5/2}$	3.5×10^5	–	36 000	6000	5000	1.3×10^4
Er^{3+}	$^4I_{11/2}$	$(3-5) \times 10^8$	–	–	3.3×10^6	–	5×10^6

This quantity is influenced also by the change in the emission rate constant when the groups surrounding the Ln^{3+} ions are altered. The estimates of the contributions to k_{nr} by the first and all the remaining spheres based on Eqn (2) in terms of the dipole–dipole approximation for water molecules yield ~7:1 if the distances to the first and second coordination spheres are assumed to be 2.36 and 4.50 Å respectively (according to X-ray diffraction data[22]).

3. Determination of the stability constants of lanthanide ion complexes in liquid solutions by the method of nonradiative transitions

In one of the first studies devoted to the influence of the deuteriation of the solvent on the intensity (I) and decay time of the luminescence of Ln^{3+} ions, Kropp and Windsor[5] turned their attention to the dependence of τ and I on the presence of the anions of various acids in water and on the pH of the medium. In another study,[27] they were the first to suggest that the number of molecular OH groups attached directly to the Ln^{3+} ions and exhibiting high frequency vibrations be estimated from the changes in τ and I on complex formation. Here use was made of the property involving the independent effect of each oscillator on the deactivation of the ion (linear dependence of k_{nr} on the concentration of OH groups in the solution).

Kropp and Windsor[27] measured the dependence of the decay times of the luminescence of the Eu^{3+} and Tb^{3+} ions dissolved in ordinary and deuteriated water on the $KOOCCH_3$ and $KOOCCD_3$ concentrations (0–5 M). For the same concentrations of acetate and lanthanide ions, it is possible to formulate the following expression for the difference between the reciprocals of the luminescence decay times in ordinary and deuteriated water:

$$(\tau^H)^{-1} - (\tau^D)^{-1} = m(k_{nr}^{H_2O} - k_{nr}^{D_2O}) + \{k_e^H([Ac^-]) - k_e^D([Ac^-])\},$$

where m is the number of water molecules in the inner sphere of the ion at the given acetate concentration and $k_{nr}^{H_2O}$ and $k_{nr}^{D_2O}$ are the rate constants for the nonradiative transitions in the Ln^{3+} ions induced by H_2O and D_2O molecules respectively. The second expression in brackets on the right-hand side of the equation is zero because the constants k_e for the Ln^{3+} ion are the same in H_2O and D_2O in the presence of identical acetate concentrations. The estimation of the contribution by one water molecule to the quenching constant yielded the following results (k_{nr}/s^{-1}):

$$k_{nr}^{H_2O} = 9400/m_s; \quad k_{nr}^{D_2O} = 370/m_s;$$

for Eu^{3+} and

$$k_{nr}^{H_2O} = 2200/m_s; \quad k_{nr}^{D_2O} = 275/m_s,$$

for Tb^{3+}, where m_s is the number of water molecules in the inner hydration shell of the ion when no other ligands are present in it. Kropp and Windsor suggested that $k_{nr}^{H_2O}$ and $k_{nr}^{D_2O}$ are independent of the acetate concentration. From our point of view, this is incorrect, since according to Eqn (1) $k_{nr}^{H_2O}$ and $k_{nr}^{D_2O}$ are proportional to k_e and the latter constants for Eu^{3+} and Tb^{3+} have been shown by Kropp and Windsor themselves to depend on the concentration of acetate ions.

Later Horrocks and coworkers[2,28,29] used this method to determine the number of water molecules involved in complexes of Ln^{3+} ions, in particular in complexes of interest to biologists. The number of coordinated water molecules was determined from the formula

$$m = \frac{(\tau^H)^{-1} - (\tau^D)^{-1}}{k_{nr}^{H_2O}(Ln)},$$

where $k_{nr}(Eu) = 952\ s^{-1}$ and $k_{nr}(Tb) = 238\ s^{-1}$. A linear dependence of $(\tau^H)^{-1} - (\tau^D)^{-1}$ on the number of water molecules in the first coordination spheres of various complexes, determined from X-ray diffraction data, was observed. However, in our view, in this case too it is necessary to introduce a correction for the change in k_e and for the intensity distribution in the Ln^{3+} luminescence spectra, especially for the longest-wavelength bands.

In view of the foregoing, we believe it is more correct to use the luminescence decay time as an indicator in the method of corresponding solutions (as has been done by Gruzdev and Ermolaev[30]) rather than employing it directly to estimate the number of water molecules or other ligands in the first coordination sphere (as suggested by Kropp and Windsor and also by Horrocks). It is known[21] that ligand exchange in solution is fairly rapid for the majority of Ln^{3+} ion complexes compared with the decay times of the luminescence of ions exhibiting appreciable yields. In this case, the decay of the luminescence is exponential and the rate constant for the decay of the excited state of the Ln^{3+} ion is defined by the following expression:

$$\bar{k} = \bar{\tau}^{-1} = \frac{\sum_{n=0}^{N} \tau_n^{-1} \beta_n^* [L]^n}{\sum_{n=0}^{N} \beta_n^* [L]^n}, \quad (3)$$

where τ_n is the decay time of the luminescence of the corresponding complex, β_n^* the overall stability constant of the complex with n ligands and with the ion in the excited state, and [L] the equilibrium concentration of the free ligand. The rate constant for the decay of the excited state of the ion is the sum of two components: the emission rate constant and the rate constant for the nonradiative transitions. Both constants depend on the composition of the complex, but in the majority of cases the change in k_{nrn} when the structure of the complex is altered is appreciably greater than the change in k_{en}. Taking into account the data in Tables 5 and 6 and knowing the structure of the substituting and substituted ligands, it is possible to estimate the change in k_{nrn} following substitution for different Ln^{3+} ions. If k_{nr} changes little after substitution of, for example, an acetone molecule by a dimethyl sulfoxide molecule at Ln^{3+}, the sensitivity of the method can be increased sharply by employing as one of the ligands the fully deuteriated molecule,

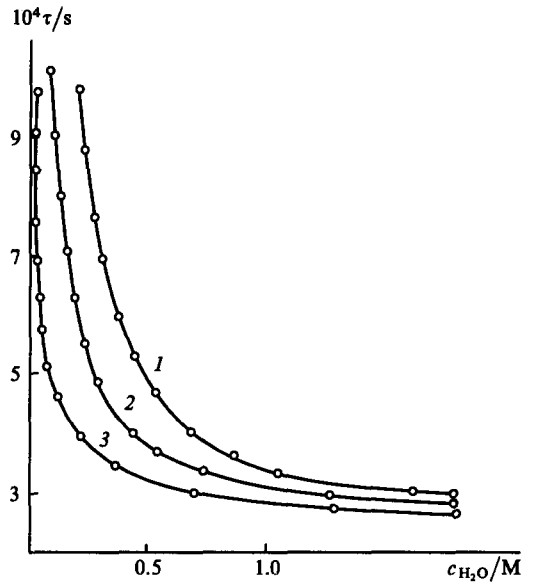


Figure 4. Dependence of the decay time of the luminescence of a europium nitrate solution in acetone on the overall concentration of water at 293 K; c_{Eu}/M: (*1*) 0.18; (*2*) 0.09; (*3*) 0.01.

i.e. $(CD_3)_2CO$ and $(CD_3)_2SO$ or conversely. One should then take into account the isotope exchange rate of hydrogen or deuterium.

As can be seen from Eqn. (3), the quantity $\bar{k}$ $(= \tau^{-1})$ is a function of the equilibrium free ligand concentration [L] only. Experiment showed that this function is unambiguous. In this case, it is possible to use the method of corresponding solutions for the determination of the stability constants.[31] The method has been used[30] to determine the stability constants of the Eu^{3+} complexes of water in acetone. Fig. 4 presents a series of curves reflecting the dependence of τ on the water concentration in dry acetone. Taking into account the material balance equation

$$c_L = \bar{n}c_{Eu} + \bar{n}^* c^*_{Eu^*} + [L], \qquad (4)$$

where c_L and [L] are the overall and equilibrium ligand concentrations respectively and $\bar{n}$ and $\bar{n}^*$ are the average numbers of ligands attached to the unexcited and excited ions, as well as the fact that in luminescence measurements the concentration of unexcited ions is always several orders of magnitude higher than that of excited ions, i.e. $c_{Eu} \gg c^*_{Eu^*}$, the second term on the right hand side of Eqn (4) may be neglected. The formation constant for the $Eu-H_2O$ system in acetone was determined with the aid of the curves presented in Fig. 4 and of Eqn (4). It is illustrated in Fig. 5. We emphasise that this expresses $\bar{n}$ as a function of [L] for unexcited Eu^{3+} ions, so that it may be compared with the results of traditional chemical methods.

Having a set of values $\bar{n}$ and [L], it is possible to calculate the stability constants of the complexes from the expression

$$\bar{n} = \frac{\sum n\beta_n[L]^n}{\sum \beta_n[L]^n}.$$

The calculation has been carried out by the least squares method (LSM) for three-ligand and four-ligand types of complexes. More accurate values were obtained for four-ligand types (*i*) of complexes.[30]

i	$\beta_i \times 10^{-(n+2)}/(\text{mol dm}^{-3})^i$	$K_i/(\text{mol dm}^{-3})^i$
1	1.27 ± 0.2	1.27 ± 0.2
2	5.6 ± 0.6	44.1 ± 8.6
3	4.4 ± 0.8	7.9 ± 1.6
4	5.9 ± 0.9	1.34 ± 0.4

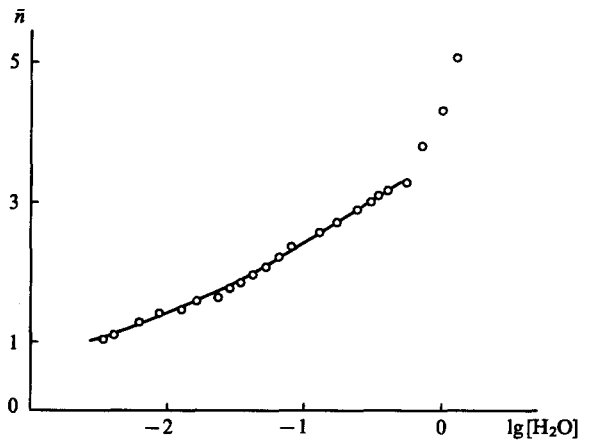


Figure 5. Dependence of the average number of water molecules in the first coordination sphere of the Eu^{3+} ion (europium nitrate solution in acetone) on the free ligand concentration [H_2O] at 293 K.

In the range $\bar{n} \geqslant 3$, the function $\bar{n} - \lg[H_2O]$ exhibits a sharp break (Fig. 5). It has been suggested that the displacement of the anion NO_3^- by water begins following an increase in the concentration of water in acetone and after the incorporation into the first coordination sphere of Eu^{3+} of more than three water molecules. The appearance in solution of free NO_3^- anions (a complex forming agent of the second type), which compete with Eu^{3+} for water molecules, is not taken into account in the method of corresponding solutions, so that the method yields unduly high values of $\bar{n}$ in this region.

This hypothesis that water displaces the NO_3^- anion for $\bar{n} \geqslant 2.5-3.0$ has been tested[30] by the energy transfer luminescence method. The dependence of the average rate of energy transfer from Eu^{3+} to Nd^{3+} in acetone on the average number of water molecules around Eu^{3+} is illustrated in Fig. 6. The concentration of Eu^{3+} (0.19 M) was 19 times greater than that of Nd^{3+} (0.01 M), which made it possible to use the values of $\bar{n}$ obtained above. For $\bar{n} = 2.5-3.0$, a sharp decrease in k'_t begins owing to the appearance of Coulombic repulsion between the complexes of the donor Eu^{3+} and the acceptor Nd^{3+} when their NO_3^- anions are substituted by water molecules. Therefore, only the values of $\bar{n} \leqslant 2.9$ were used in the calculation of the stability constants.

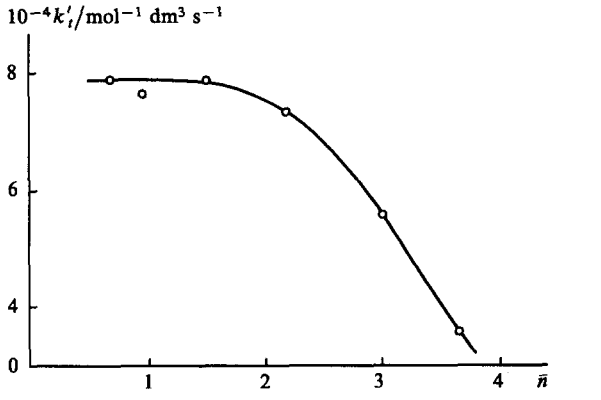


Figure 6. Dependence of the average rate constant for the energy transfer from europium to neodymium in acetone on the average number of water molecules in the first coordination sphere of Eu^{3+}. $c_{Eu} = 0.19$ M; $c_{Nd} = 0.01$ M.

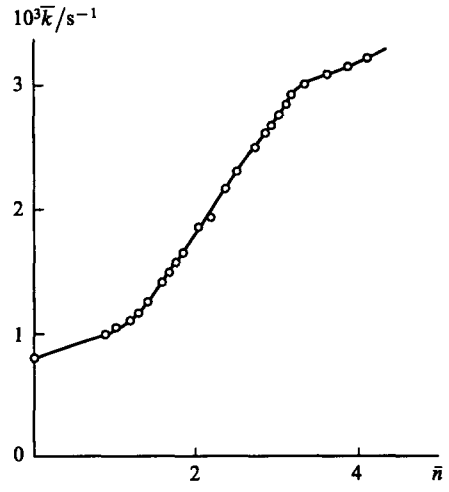


Figure 7. Dependence of the average rate constant for the deactivation of excited Eu^{3+} ions in acetone on the average number of water molecules in the first coordination sphere of the Eu^{3+} ion.

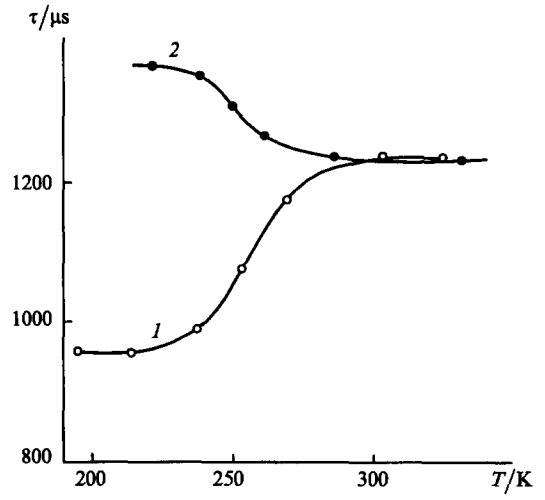


Figure 8. Temperature dependence of the decay time of the $Eu(NO_3)_3$ luminescence (c_{Eu} = 0.01 M) in partly dried acetone: (*1*) with added H_2O ($c_{H_2O} < c_{Eu}$); (*2*) with added D_2O ($c_{D_2O} < c_{Eu}$).

Fig. 7 presents the dependence of the average rate constant $\bar{k} = \bar{\tau}^{-1}$ for the deactivation of Eu^{3+} ions in acetone on the average number of water molecules $\bar{n}$ in the first coordination sphere of the ion. In the range of values of $\bar{n}$ from 1 to 3, the dependence of $\bar{k}$ on $\bar{n}$ is nearly linear. This shows that the emission constant k for complexes containing between one and three water molecules is invariant.

The luminescence-kinetic method also makes it possible to investigate the influence of the change in temperature on the structure of the environment of lanthanide ions in liquid solutions. It has been observed[32,33] that the decay times of the luminescence of Eu^{3+} and Tb^{3+} in weakly donating (according to Gutmann) solvents (acetonitrile, acetone, and ethyl acetate) increase with increase in temperature, in contrast to the usually observed temperature-induced quenching of the luminescence. On the other hand, in highly donating solvents (dimethyl sulfoxide, dimethylformamide, water), τ for the Eu^{3+} and Tb^{3+} ions is independent of temperature over a wide range of the latter.

It has been shown[32,33] that the increase in τ with temperature in weakly donating solvents is due to the removal of residual water molecules from the inner spheres of the ions and their replacement by solvent molecules which have lower deactivating capacities. Fig. 8 presents the curves describing the variation of τ for Eu^{3+} in partly dried acetone as a function of temperature. The activation energy for the splitting off of the last water molecule from the Eu^{3+} ion in acetone has been determined with the aid of these curves (36×10^3 J mol^{-1}).

Mention should be made of the method, proposed by Bünzli and Vuckovic, for the investigation of the inner coordination sphere of the Tb^{3+} ion in weakly donating solvents (acetonitrile) on the basis of the break in the Stern–Volmer linear plot for the quenching (or excitation) of the luminescence of the ion following the introduction of highly donating water molecules (quenching) or dimethyl sulfoxide molecules (excitation) into the solution.[34] The method is most effective when there is a large difference between the complex-forming capacities of the solvent and the added 'quenching agent' in relation to the Ln^{3+} ion. The complex nature of the quenching of the $Tb(NO_3)_3$ solution in acetonitrile by water[1,34] may be due to the fact that, after the displacement of three acetonitrile molecules from the outer sphere by water, the subsequent addition of water leads to the removal of NO_3^- anions.[30]

The possibility of using the inductive-resonance theory of nonradiative transitions for the study of complex formation involving the outer coordination sphere of lanthanide ions has been demonstrated.[35] Neutral neodymium complexes with three NO_3^- anions and three tributyl phosphate molecules were investigated. The quenching of the luminescence of the neodymium complex by water can be explained satisfactorily solely on the hypothesis that the water molecules hydrogen-bonded to a free tributyl phosphate molecule (asymmetric associated species) exert a quenching effect. On the other hand, the water molecules bound to two tributyl phosphate molecules (symmetrical associated species) have virtually no quenching effect on the luminescence of the neodymium complex. There are no free water molecules under these conditions. The high quenching constant can be explained by the protracted encounter between the neodymium complex and the asymmetric water associated species resulting from the formation of a hydrogen bond between the free hydroxy-group of water and a NO_3^- anion in the neodymium complex. The concentration of the asymmetric water associated species in solution was determined from the IR spectra.

III. The application of nonradiative energy transfer between lanthanide ions in the study of complex formation

The problem of the use of the phenomenon of nonradiative energy transfer between organic molecules and lanthanide ions for the investigation of the complex formation reaction between them in solutions has been examined in detail in a review.[36] Since the 17 years which have elapsed since then have not introduced appreciable corrections to the physical and chemical treatment of these phenomena, we shall not return to this problem and will concentrate attention on the application of the phenomenon of the nonradiative energy transfer between different lanthanide ions in liquid solutions to the study of complex formation.

In the first investigations of nonradiative energy transfer between different lanthanide ions in liquid solutions,[37–42] it was already noted that the bimolecular rate constants for the energy transfer (k_t'/dm^3 mol^{-1} s^{-1}) between Tb^{3+} and Eu^{3+} ions (energy donors), on the one hand, and Nd^{3+}, Ho^{3+}, Er^{3+}, etc. ions (energy acceptors), on the other, are five orders of magnitude lower than the rate constant for the process determined by diffusion in highly donating solvents, including water.[40,41] This is due to the low absorption coefficients of the energy acceptors and hence the low overlap integral (which enters into Förster's formula for the energy transfer rate constant) between the normalised luminescence spectra of the donors and the absorption spectra of the acceptors, the low emission rate constants for the energy donors, and the hindrance to the mutual approach of the energy donors and

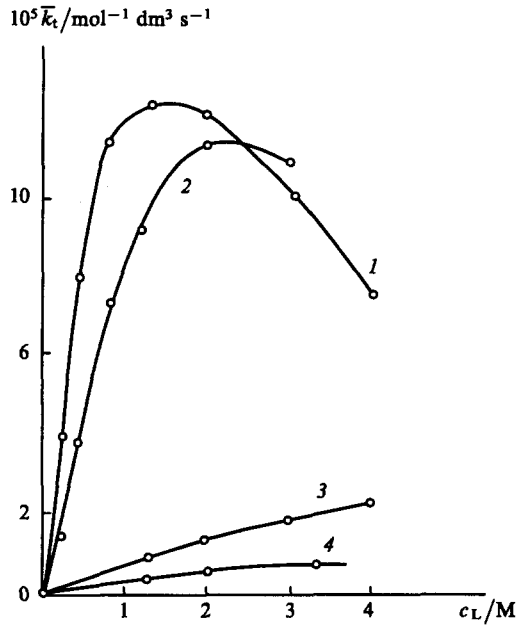


Figure 9. Dependence of the average rate constant for the nonradiative energy transfer from Tb^{3+} (0.03 M) to Nd^{3+} (0.015 M) in water at 293 K on the added carboxylic acid salts:[49] (*1*) CH_3COONa; (*2*) $CH_2ClCOOK$; (*3*) $CHCl_2COOK$; (*4*) CCl_3COOK.

acceptors owing to the Coulombic repulsion forces between the charged Ln^{3+} ion complexes surrounded by neutral solvent molecules.

It has been noted[41,42] that k'_t increases sharply after the addition to the aqueous solution of various alkali metal salts or acids whose anions form complexes with the lanthanide ions. Fig. 9 presents the dependence of the rate constant for energy transfer from Tb^{3+} ($^5D_4$) to Nd^{3+} in water on the concentration of various sodium and potassium salts and derivatives of acetic and other acids. The increase in the rate of transfer on formation of complexes between the lanthanides and the anions is caused both by the decrease in the Coulombic repulsion between the donor and acceptor owing to the neutralisation of the ionic charge on formation of complexes with the anions and by the formation of unstable bridged dinuclear donor Ln^{3+}–anion–acceptor Ln^{3+} complexes, which increase the duration of the encounter between the excited donor and acceptor.

The question of the influence of electrostatic repulsion and attraction of the charged donor and acceptor on the rate of energy transfer in solutions was first examined by Bodunov.[43,44] It was shown that this effect cannot explain quantitatively the experimental data.

The greatest increase in k'_t occurs in the inner-sphere complex formation reactions with anions which can give rise to bridged complexes. The outer-sphere complex formation also influences appreciably the energy transfer in certain cases.

The high sensitivity of k'_t to the inner-sphere complex formation made it possible to develop, using the phenomenon of energy transfer, a procedure for the determination of the stability constants of lanthanide ion complexes.[45] The method is a variant of Bjerrum's method of corresponding solutions,[31] extended to the case of the simultaneous presence in solution of two different central groups, and makes it possible to determine simultaneously the stability constants of complexes of two lanthanide ions—the energy donor and acceptor, where the indicator which depends unambiguously on the free ligand is k'_t. Using the experimental fact that the decay of the donor luminescence is exponential in the presence of the acceptor, it is possible to formulate the following expression for the rate of deactivation of the excited states of the donor in the presence of the acceptor:

$$-\frac{dc_{D^*}}{dt} = k_0^D c_{D^*} + k'_t c_{D^*} c_A ,$$

$$\bar{k}'_t = (k^D - k_0^D)c_A^{-1}; \quad k_0^D = \tau_{D0}^{-1}; \quad k^D = \tau_D^{-1} ,$$

$$\bar{k}'_t = \frac{\sum_{n=0}^{N}\sum_{m=0}^{M} k_t^{nm}\,\beta_n^{D^*}\,\beta_m^A\,[L]^{n+m}}{\left(\sum_{n=0}^{N}\beta_n^{D^*}\,[L]^n\right)\left(\sum_{m=0}^{M}\beta_m^A\,[L]^m\right)}, \qquad (5)$$

where c_{D^*} is the concentration of the excited energy donor (D^*), c_A the overall concentration of the unexcited energy acceptor (A), [L] the equilibrium concentration of the free ligand, and $\beta_n^{D^*}$ and β_m^A are respectively the overall stability constants of the complexes of the excited donor ions and unexcited acceptor ions

$$\beta_n^{D^*} = \frac{[D^*L_n]}{[D^*][L]^n}; \quad \beta_m^A = \frac{[AL_m]}{[A][L]^m}.$$

It follows from Eqn (5) that $\bar{k}'_t$ is an unambiguous function of the free ligand concentration [L] and can therefore be used as an indicator in the method of corresponding solutions. The quantity

$$\bar{\tau} = (\bar{k}_e^D + \bar{k}_{nr}^D)^{-1},$$

also depends on the free ligand concentration [L] and may be used to determine the stability constants. However, at the concentrations [L] employed it is small for aqueous solution (τ_0^D changes by not more than 2–3 units), while $\bar{k}'_t$ increases by 1–2 orders of magnitude following the addition of the ligand. Therefore $\bar{k}'_t$ was chosen as the parameter and the small changes in $\bar{\tau}_0^D$ were taken into account. For each acceptor concentration, $\bar{\tau}_0^D$ was measured at the donor concentration equal to the sum of the concentrations of the donor and acceptor at the point where the quenching was measured. This is legitimate bearing in mind the small variation of the stability constants in the series of lanthanides. When the donor gives rise to concentration-induced quenching, in the measurement of $\bar{\tau}_0^D$ it is necessary to add to the solution neutral [sic! (Ed. of Translation)] ions (La^{3+}, Gd^{3+}) at the concentration equal to that of the acceptor.

In order to determine the average numbers of ligands around the energy donor ($\bar{n}_D$) and acceptor ($\bar{m}_A$) and the equilibrium ligand concentration, two series of measurements are performed. In the first series, the dependence of $\bar{k}'_t$ on the energy donor concentrations c_D with c_A = const. is determined and plotted for several ligand concentrations c_L (Fig. 10*a*), while in the second series the dependences of $\bar{k}'_t$ on the acceptor concentration c_A with c_D = const. are plotted for the same ligand concentrations (Fig. 10*b*). The series of corresponding solutions for which $\bar{n}_D$, $\bar{m}_A$, and [L] are the same are found from the points of intersection of the experimental curves with the $\bar{k}'_t$ = const. straight lines. Under the conditions of the luminescence measurements, the concentrations of the excited donor and acceptor ions may be neglected compared with those of the unexcited ions, so that the material balance equation is written in the following form:

$$c_L = \bar{n}_D c_D + \bar{m}_A c_A + [L] .$$

The method described has been used[45] to investigate the formation of complexes between Tb^{3+} (energy donor) and Nd^{3+} (energy acceptor) ions and acetate ions CH_3COO^- in water at the ionic strength of the solution I = 2.0 and at a temperature of 293 K. A constant ionic strength was maintained by adding $NaClO_4$, so that the overall concentration of CH_3COONa and $NaClO_4$ was 2.0 M. The straight lines drawn through points corresponding to constant $\bar{k}'_t$ are presented in Fig. 11. The quantities $\bar{n}_D$ and $\bar{m}_A$ are determined from the slopes of the straight lines and [L] is determined from their intercepts on the ordinate axis, (c_L is the overall concentration of the ligand

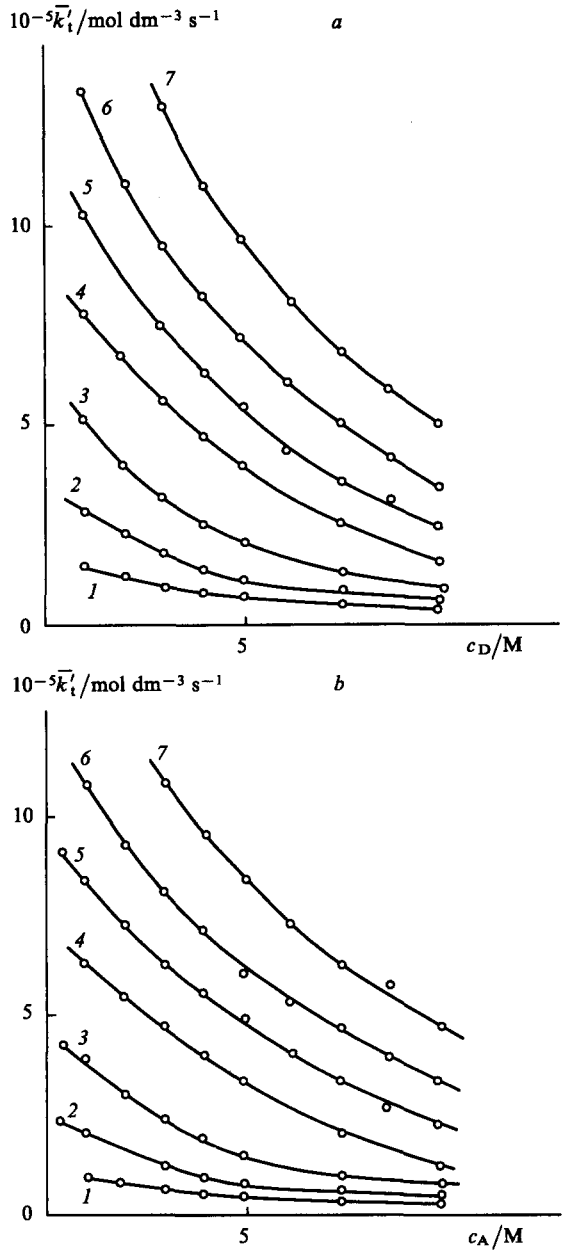


Figure 10. Dependence of the average rate constant for the energy transfer from $Tb^{3+}(^5D_4)$ to Nd^{3+} ions in water at 293 K and $I = 2.0$ on the concentration of the energy donor ions (*a*) at a constant concentration of the energy acceptor ions and on the concentration of the energy acceptor ions (*b*) at a constant concentration of the energy donor ions for different concentrations of sodium acetate (c_L/M): (*1*) 0.05; (*2*) 0.07; (*3*) 0.1; (*4*) 0.14; (*5*) 0.17; (*6*) 0.2; (*7*) 0.24.

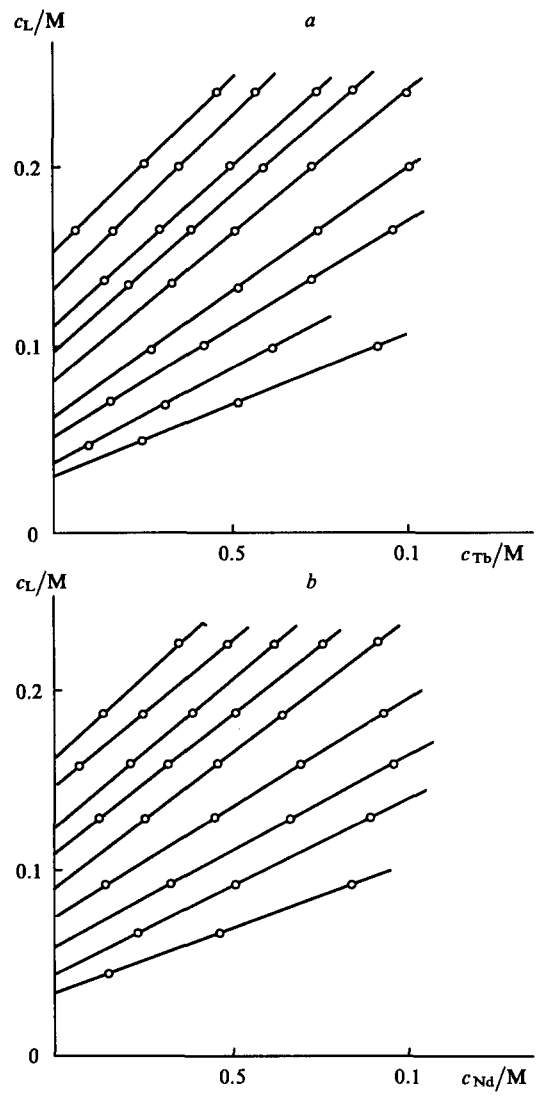


Figure 11. Dependence of the sodium acetate concentration on the concentrations of Tb^{3+} (*a*) and Nb^{3+} (*b*) for solutions with identical values of $\bar{k}'_t$ (corresponding solutions). The average numbers of the energy donors ($\bar{n}_{Tb}$) and the energy acceptors ($\bar{n}_{Nd}$) are determined from the slopes of the straight lines in Figs *a* and *b* respectively; the intercepts made by the straight lines on the ordinate axis yield the equilibrium ligand (acetate) concentrations.

CH_3COONa and c_D and c_A are respectively the overall concentrations of the Tb^{3+} donor and the Nd^{3+} acceptor). Fig. 12 presents the dependence of the average number of ligands around the donors (curve *1*) and acceptors (curve *2*) on the free ligand concentration [L]. The stability constants of the Tb^{3+} and Nd^{3+} complexes of CH_3COO^-, calculated from these data by the least squares method on the assumption that the first three complexes are formed, are presented in Table 7 (see following page). The stability constants obtained by the Fronaeus graphical method[31] were adopted as the zeroth approximation. For comparison, Table 7 presents the stability constants of neodymium acetate complexes obtained under similar conditions by the potentiometric method.[46] The stability constants of the neodymium complexes obtained by the luminescence energy transfer and potentiometric methods agree satisfactorily.

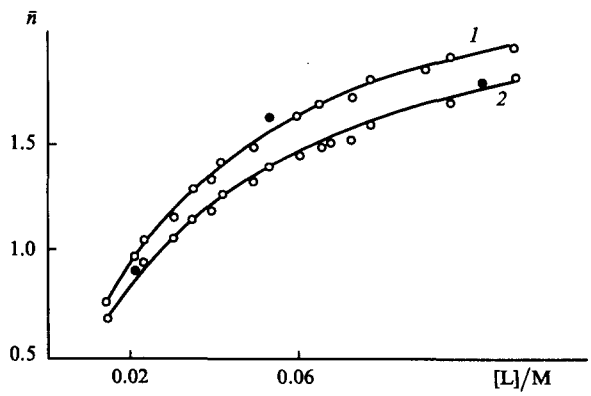


Figure 12. Dependence of the average number of acetate ions bound in the complexes with Tb^{3+} (curve *1*) and Nd^{3+} (curve *2*) on the equilibrium concentration of acetate ions [L]. The curves have been calculated from the stability constants obtained by the least squares method: (*1*) $\bar{n}_D = \bar{n}_{Tb}$; (*2*) $\bar{n}_A = \bar{n}_{Nd}$.

Table 7. The overall stability constants β_n, expressed in (M^{-n}), of the terbium and neodymium complexes of acetate ions in water at 293 K and $I = 2.0$.

Ln^{3+}	β_1	β_2	β_3	Treatment of data
Energy transfer method [45]				
Tb^{3+}	63 ± 6	1740 ± 60	5700 ± 630	LSM
Nd^{3+}	73 ± 8	1180 ± 60	3300 ± 550	"
Potentiometric method [46]				
Nd^{3+}	80 ± 3	1020 ± 100	2900 ± 500	Fronaeus graphical method

We shall not dwell on the application of the nonradiative energy transfer between lanthanide ions in the study of the structures of biological objects because this problem is dealt with elsewhere.[1,2]

1. Detection of unstable bridged lanthanide ion complexes by the nonradiative energy transfer method

The marked increase in k_t' [for energy transfer] between lanthanide ions in solutions in the presence of a series of acid anions cannot be explained solely by the decrease in the electrostatic repulsion. It has been suggested[47,48] that unstable bridged dinuclear lanthanide complexes exist in which the anion (for example, CH_3COO^-) is linked via one atom (in the case of acetate, it is an oxygen atom) to the energy donor ion (for example, to Tb^{3+}), whilst via another atom it is linked to the energy acceptor ion (for example, Nd^{3+}). The formation of this type of bridged complex leads to the arrest of the encounter between the excited ion and the energy acceptor and hence increases their residence time in close proximity, which in fact leads to a significant increase in k_t'.

Table 8 presents the measured average rate constants for energy transfer from terbium and europium ions to neodymium ions in water and alcohol in the presence of acetate anions at the concentration for which k_t' is a maximum.

The decay of the luminescence of the energy donor is exponential in all cases, which indicates a rapid ligand exchange. It is seen from the data in Table 8 that the maximum values of k_t' in the presence of CH_3COO^- anions increase in the sequence water < methanol < ethanol < n-propanol, k_t increasing by a factor of 20 on passing from water to n-propanol. This difference cannot be accounted for by electrostatic repulsion because the complexes are uncharged under these conditions. The formation of unstable bridged dinuclear complexes may be regarded as the only explanation.

Since the quenching of the luminescence of the donor by the acceptor in the presence of acetate is dynamic in all cases, i.e. $q_0/q = \tau_0/\tau$, two variants may be considered.

1. The rate of energy transfer in the bridged complex is high and exceeds the rate of its dissociation, but the equilibrium concentration of the complex is low because of the low value of its stability constant and we therefore do not see any difference between τ_0/τ and q_0/q.

2. The rate of dissociation in the bridged complex exceeds the rate of energy transfer in the latter and the acceleration of the bimolecular energy transfer reaction is associated with the prolongation of the encounter, i.e. with the increase in the average residence time of the acceptor in the vicinity of the excited donor. The quenching (transfer) step does not accompany each step involving the formation of the excited donor–ligand–unexcited acceptor complex.

The appreciable increase [by a factor of ~200 (Table 8)] in the average rate constant for energy transfer between lanthanide ions in the presence of acetate ions suggests that energy transfer in the bridged complexes makes the main contribution to the quenching and the reaction can be formulated thus:

$$[D^*L_j] + [AL_i] \underset{k_{diss}^{ji}}{\overset{k_{as}'^{(ji)}}{\rightleftharpoons}} [D^*L_jAL_i] \xrightarrow{k_t^{ji}} [DL_jA^*L_i] \xrightarrow{k_{diss}^{ji}} [DL_j] + [A^*L_i],$$

$$k_t'^{(ji)} = \frac{k_{as}'^{(ji)} k_t^{(ji)}}{k_{diss}^{ji} + k_t^{ji}},$$

where D and A are the energy donor and acceptor ions respectively, the asterisk designates the excited states, k_t^{ji} is the first-order intracomplex energy transfer rate constant, and $k_t'^{(ji)}$ is the second-order rate constant for energy transfer between donor complexes with j ligands and acceptor complexes with i ligands. The average energy transfer rate constant is then given by

$$\bar{k}_t' = \sum_j \sum_i k_t'^{(ji)} \alpha_j^{D^*} \alpha_i^A,$$

where $\alpha_j^{D^*}$ and α_i^A are respectively the relative concentrations of the complexes of the excited donor and the unexcited acceptor of each type.

For $k_t^{(ji)} \gg k_{diss}^{(ji)}$, the average energy transfer rate constant corresponds to the average rate constant for the formation of the bridged complexes and is almost independent of the acceptor ion. For $k_{diss}^{ji} \gg k_t^{ji}$, the average rate of transfer should depend greatly on the properties of the acceptor, namely on the overlap integral between the luminescence spectrum of the energy donor and the absorption spectrum of the energy acceptor.

Table 8. Rate constants for the nonradiative energy transfer from terbium and europium ions to neodymium ions at 293 K (according to Gruzdev's data[49]).

Solvent	c/M				$\bar{k}_t'$ / mol^{-1} dm^3 s^{-1}	
	CH_3COONa	Tb^{3+}	Eu^{3+}	Nd^{3+}	Tb^{3+} ($^5D_4$)	Eu^{3+} ($^5D_0$)
H_2O	0.0	0.03	0.03	0.1	7.5×10^3	3×10^3
	1.4	0.03	0.03	0.02	1.3×10^6	1.2×10^6
CH_3OH	0.0	0.02	0.02	0.03	2.4×10^4	1.0×10^4
	0.3	0.02	0.02	0.005	4.4×10^6	2.3×10^6
C_2H_5OH	0.0	0.02	0.02	0.03	3.8×10^4	2.2×10^4
	0.04	0.005	–	0.001	1.3×10^7	–
n-C_3H_7OH	0.0	0.02	0.02	0.03	5.5×10^4	4.0×10^4
	0.02	0.001	0.001	0.0001	2.8×10^7	1.8×10^7

Note. All the ions were introduced into the solution in the form of the nitrates; the CH_3COONa concentrations at which the maximum value of $\bar{k}_t$ is attained were employed.

Measurements have been made[49] of the maximum values of k_t' in the presence of CH_3COO^- ions at 293 K for three pairs of ions–energy donors and acceptors: $Dy^{3+}(^4F_{9/2})-Nd^{3+}$, $Tb^{3+}(^5D_4)-Nd^{3+}$, and $Tb^{3+}(^5D_4)-Eu^{3+}$. The following values have been obtained for these pairs (mol^{-1} dm^3 s^{-1}): 5×10^6; 1.3×10^6, and 9×10^4 respectively. They are correlated with the overlap integrals of the spectra for the above pairs, the ratios of which are $10:1.2:(\leqslant 0.1)$. This is unambiguous evidence in support of the second mechanism of the energy transfer in bridged complexes of the given type.

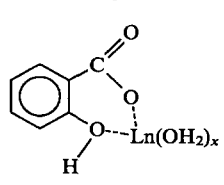
The important role of the bridged complexes in energy transfer between lanthanide ions has been confirmed.[49] A study was made of the energy transfer from salicylic (Sal^-), sulfosalicylic ($SSal^{2-}$), and anthranilic (Ant^-) acid complexes of samarium, terbium, and disprosium to the neodymium ion as the energy acceptor. At pH 5.9, the lifetimes of the Ln^{3+} complexes of Sal^- and $SSal^{2-}$ in water are more than 80 μs, which exceeds appreciably the lifetimes of the excited states of Dy^{3+} at the $^4F_{9/2}$ level and Sm^{3+} at the $^4G_{5/2}$ level [~ 3 μs (Table 5)]. The lifetime of the complex $[LnAnt]^{2+}$ in water exceeds 500 μs and is longer than the lifetime of Tb^{3+} at the $^5D_4$ level (475 μs). By creating in the solution a large excess of the Ln^{3+} ions (0.1 M) relative to the ligand concentration (10^{-4} M) and by exciting selectively only the Ln^{3+} ions bound in complexes via rapid ($\geqslant 10^8$ s^{-1}) intracomplex energy transfer from the ligands, this makes it possible to measure the rate constant for the reaction

$$[D^*L] + A \xrightarrow{k_t'} [DL] + A^*,$$

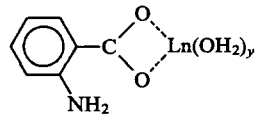
where $[D^*L]$ is the excited donor Ln^{3+} ion combined with the ligand and A the unexcited solvated energy acceptor Ln^{3+} ion. The following energy transfer reactions were investigated:

Reaction	$10^{-5}k_t'$/ mol^{-1} dm^3 s^{-1}
$(Dy^{3+})^* + Nd^{3+} \longrightarrow Dy^{3+} + (Nd^{3+})^*$	0.93
$[Dy^*Sal]^{2+} + Nd^{3+} \longrightarrow [DySal]^{2+} + (Nd^{3+})^*$	60
$[Dy^*SSal]^* + Nd^{3+} \longrightarrow [DySSal]^+ + (Nd^{3+})^*$	100
$[Dy^*Ant]^{2+} + Nd^{3+} \longrightarrow [DyAnt]^{2+} + (Nd^{3+})^*$	2.1
$(Tb^{3+})^* + Nd^{3+} \longrightarrow Tb^{3+} + (Nd^{3+})^*$	0.07
$[Tb^*Ant]^{2+} + Nd^{3+} \longrightarrow [TbAnt]^{2+} + (Nd^{3+})^*$	0.15
$(Sm^{3+})^* + Nd^{3+} \longrightarrow Sm^{3+} + (Nd^{3+})^*$	0.1
$[Sm^*Sal]^{2+} + Nd^{3+} \longrightarrow [SmSal]^{2+} + (Nd^{3+})^*$	3.4
$[Sm^*SSal]^+ + Nd^{3+} \longrightarrow [SmSSal]^+ + (Nd^{3+})^*$	4.6

Here the symbol for the lanthanide ion without brackets denotes a hydrate; the concentration of the Ln^{3+} ions was 0.1 M and that of the ligand 10^{-4} M. The rate constants for the nonradiative energy transfer between the lanthanide ion complexes in water at the ionic strength of the solution $I = 0.6$, 295 K, and pH 5.9 have been calculated[49] for the reactions listed above. The error in the determination of k_t' does not exceed 10%. The very marked acceleration of the energy transfer reaction for the complexes of lanthanide ions with salicylate and sulfosalicylate anions (by a factor of 35–100) and the very slight increase (by a factor of 2) in k_t' for the complex with the anthranilate anion are striking. The structure of the complex $[LnSal]^{2+}$ is



This complex is capable of giving rise to dinuclear bridged complexes via the free oxygen atom of the carboxy-group. On the other hand, the structure of the lanthanide complex with the anthranilate anion shows that it does not tend to form a dinuclear complex.



The slight increase in k_t' is in this case associated with the decrease in the electrostatic repulsion between the donor and the acceptor.

If it were possible to demonstrate unambiguously that the energy transfer in bridged complexes takes place via Förster's mechanism and to calculate the distance between the Ln^{3+} ions in the dinuclear complexes, one could estimate the rate constants for the intracomplex energy transfer in the bridged complex (k_t/s^{-1}). Then, having measured the rate constant for the energy transfer in solution k_t' (mol^{-1} dm^3 s^{-1}), it would be possible to calculate the equilibrium constant $K = k_t'/k_t$ for the bridged complex under the given conditions.

However, such calculations, which require reliable evidence for Förster's mechanism of energy transfer between lanthanide ions in solutions, the calculation of the overlap integral between the luminescence spectra of the energy donors and the absorption spectra of the acceptors, and a reasonable estimate of the relative disposition of the Ln^{3+} ions in the dinuclear bridged complex, have not so far been carried out.

IV. A luminescence-spectroscopic method for the determination of the rates of rapid ligand exchange in lanthanide ion complexes in liquid solutions

A new luminescence-spectroscopic method has been proposed[50] for the investigation of rapid ligand exchange reactions in lanthanide ion complexes. The main idea of the method is that one creates with the aid of a short light pulse a nonequilibrium distribution in the assembly of excited lanthanide ion complexes in solution. By following the kinetics of the variation of the luminescence spectra after the cessation of the exciting light pulse, it is possible to obtain information about the rate and, by altering the experimental conditions, also about the nature and mechanism of the relaxation processes. Such processes are the ligand exchange reactions (in particular, the dissociation and association reactions), electrophilic substitution reactions, conformational changes in the excited complexes, and the excitation energy migration process. Since the equilibrium constants for the excited and nonexcited lanthanide complexes differ only slightly, selective excitation of individual centres is essential in order to create a nonequilibrium distribution in the excited state.

The following conditions must be met for the successful application of the proposed method: 1. The rate of the transition of the complex from one form to another must exceed appreciably the rate of deactivation of the excited Ln^{3+} ions under the experimental conditions. 2. The two types of complexes, the kinetics of the transition reaction of which we have investigated, must have different spectral densities of the emission rate constant at the frequencies (wavelengths) at which the luminescence is recorded. 3. The duration of the selectively exciting light pulse must be appreciably shorter than the duration of the reaction investigated.

The simplest case of the coexistence in solution of only two types of complexes, $MLSolv_1$ and $MSolv_2$, has been examined.[50] Henceforth, for simplicity we shall omit the designations of the solvation shells of the complexes and the complexes will be designated by ML and M. The first type of complex (ML) can be converted into the second type (M) as a result of the ligand dissociation reaction and the second can be converted into the first as a result of the addition of the ligand during the lifetime of the

excited ions $\tau_1 = k_1^{-1}$ and $\tau_2 = k_1^{-1}$. It is then possible to formulate the following reaction scheme for the excited ions:

$$\begin{array}{ccc} M^*L & \underset{k_{as}[L]}{\overset{k_{diss}}{\rightleftharpoons}} & M^* + L \\ k_1 \downarrow & & \downarrow k_2 \\ ML & & M \end{array}$$

The system of differential equations describing the time variation of the concentrations of the excited complexes (c_1^*) and the solvates (c_2^*), taking into account the ligand exchange reactions, assumes the following form:

$$\frac{dc_1^*}{dt} = -(k_1 + k_{diss})\, c_1^* + k_{as}[L]\, c_2^*,$$

$$\frac{dc_2^*}{dt} = k_{diss}\, c_1^* - (k_2 + k_{as}[L])\, c_2^*, \qquad (6)$$

where [L] is the equilibrium ligand concentration. Eqns (6) are solved subject to the condition that k_{diss}, $k_{as}[L] \gg k_1$, k_2. The experimental luminescence intensity at a frequency ν is

$$I(t, \nu) = k_{e1}(\nu)\, c_1^* + k_{e2}(\nu)\, c_2^*,$$

where $k_{e1}(\nu)$ and $k_{e2}(\nu)$ are the spectral emission densities for the complex and the solvate at the frequency ν. After introducing the symbols N_1 and N_2 for the initial concentrations of the complex and the solvate at time $t = 0$, for which one can arbitrarily adopt the instant when the short exciting light pulse terminates, we obtain a solution in the following form:

$$I(t, \nu) \qquad (7)$$
$$= (N_1\alpha_2 - N_2\alpha_1)\{k_{e1}(\nu) - k_{e2}(\nu)\}\exp\{-(k_{diss}+k_{as}[L])t\}$$
$$+(N_1 + N_2)\{k_{e1}(\nu)\alpha_1 + k_{e2}(\nu)\alpha_2\}\exp\{-(k_1\alpha_1+k_2\alpha_2)t\},$$

where α_1 and α_2 are the fractions of the excited complex and solvate at equilibrium ($\alpha_1 + \alpha_2 = 1$).

The first term in Eqn (7) describes the relaxation of the system to equilibrium via excited states and the second describes the kinetics of the decay of the luminescence of the system in the state of equilibrium. In order to be able to determine the sum of the rates of the forward and reverse complex formation reactions $\{k_{diss} + k_{as}[L]\}$ from the luminescence decay curve, the first term in Eqn (7) must be nonzero. An essential condition for this is that the excitation of one of the forms should be selective ($N_1\alpha_1^{-1} \neq N_2\alpha_2^{-1}$), and also that the spectral densities of the emission rate constant for the complex and solvate at the frequency corresponding to the observation of the luminescence should differ [$k_{e1}(\nu) \neq k_{e2}(\nu)$]. When the total luminescence light is recorded, Eqn (7) includes the integral of the product of the distribution of the spectral emission density for each complex and of the spectral sensitivity of the photoreceiver as well as the spectral transmission coefficient for the light filter employed. In order to be able to observe the effect, the above quantities must be nonzero.

The kinetics of the decay of the luminescence of labile complexes in solutions have been investigated.[51] Account was taken of the stepwise nature of the complex formation reaction and it was assumed that the rate of ligand exchange is appreciably higher than the rate of deactivation of the excited ions. When account is taken of these postulates, the solution of the equations for the luminescence intensity after pulse excitation consists of two parts, similar to the solution of the equations for two complexes. One part represents the sum of $n - 1$ 'fast' exponential functions corresponding to the establishment of equilibrium between different types of excited complexes and the second represents a significantly 'slower' exponential relation corresponding to the decay of the luminescence from the equilibrium state of the system of excited complexes. As in the simplest case, the observation of luminescence requires a nonequilibrium excitation of the system and a difference between the spectral densities of the emission rate constants for the test complexes at the observation frequency. It has also been concluded that, when three or more types of complexes with comparable rates of interconversion are present in solution, it is difficult to obtain quantitative data for the rates of ligand exchange. However, if the first stage of the complex formation is appreciably slower than the other stages, the measurement of the rate constants becomes possible.

The possibilities of the method proposed have been demonstrated.[50, 52, 53] In order to achieve the selectivity of the optical excitation, two procedures were used. In the first, the aromatic ligand in lanthanide ion complexes with such ligands (1,10-phenanthroline, 2,2′-bipyridyl, and naphthoic, salicylic, and sulfosalicylic acids) was excited by a nitrogen laser (λ_{exc} = 337 nm, $\Delta t \approx 20$ ns). This was followed by rapid ($t \leqslant 10^{-9}$ s) nonradiative energy transfer from the triplet state of the ligand to the lanthanide ion.[12, 36] In the second procedure, the excitation was achieved with the aid of a tunable laser based on the dye rhodamine 6G in the region of the $^5D_0 \leftarrow {}^7F_0$ transition of the europium ion. The selectivity was ensured by excitation in the spectral absorption band of the Eu^{3+} ion corresponding to the complex which it was necessary to excite.

Fig. 13 presents Eu^{3+} luminescence decay curves at the $^5D_0$ level (in D_2O at 295 K after pulse excitation by a nitrogen laser). Heavy water was used as the solvent because the lifetime of the excited state of the europium ion in it is many times greater than in H_2O (Table 5), so that the necessary condition is fulfilled — the rate of deactivation of the excited ion is many times lower than the rate of the ligand exchange.

The overall luminescence decay curve consists of two exponential components: the 'fast' component corresponding to the relaxation of the solution to the equilibrium state and the 'slower' exponential section corresponding to the decay of the equilibrium luminescence (Fig. 13). Since the concentration of 1,10-phenanthroline was 10^{-3} M and that of Eu^{3+} was 10^{-2} M and the absorption coefficient (λ = 334 nm) is 10^4 times greater

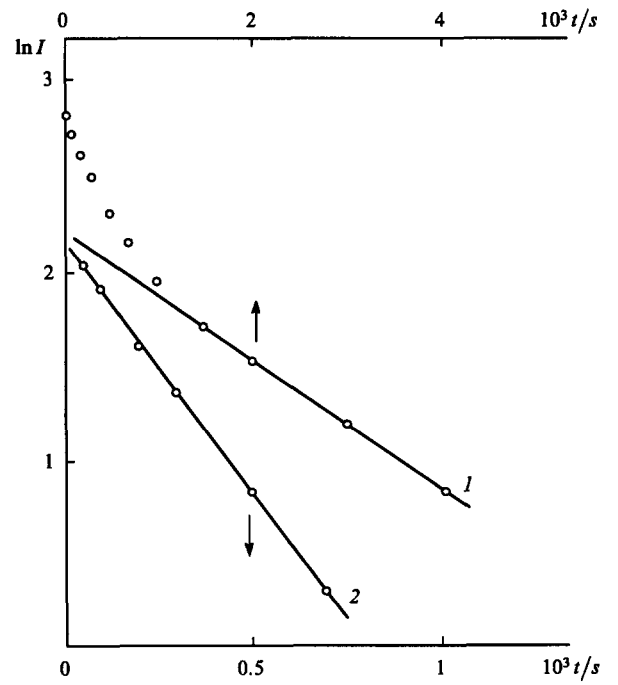


Figure 13. Time variation of the Eu^{3+} luminescence intensity corresponding to the λ = 613 nm emission band and sensitised by the intracomplex energy transfer from 1,10-phenanthroline (Phen). Solvent — D_2O, 295 K $c_{Eu(NO_3)_3 \cdot 6D_2O}$ = 0.01 M, c_{Phen} = 0.001 M, pulse excitation by a nitrogen laser (Δt = 20 ns, λ_{exc} = 337 nm); (*1*) equilibrium luminescence; (*2*) relaxation process.

Table 9. Rate constants for the dissociation of excited lanthanide ion complexes in solutions at 295 K.[49-53]

Ligand	Ion (level)	Solvent	k_{diss}/s^{-1} [a]	Reaction mechanism
Selective excitation by nonradiative energy transfer from the ligand to the lanthanide ion				
1,10-Phenanthroline	Eu^{3+} ($^5D_0$)	D_2O	2700 (44.4) [b]	dissociative opening of the chelate ring
2,2′-Bipyridyl	Eu^{3+} ($^5D_0$)	D_2O	22 000 (36) [b]	"
1-Naphthoate anion	Eu^{3+} ($^5D_0$)	CD_3OD	2.5×10^3	"
	Eu^{3+} ($^5D_0$)	$CD_3OD + D_2O$, 3:1	5.5×10^5	"
	Eu^{3+} ($^5D_0$)	$CH_3OH + H_2O$, 3:1	8.3×10^5	"
	Sm^{3+} ($^4G_{5/2}$)	$CD_3OD + D_2O$, 3:1	6.3×10^5	"
	Sm^{3+} ($^4G_{5/2}$)	$CD_3OD + D_2O$, 1:1	2.0×10^6	"
	Sm^{3+} ($^4G_{5/2}$)	D_2O	4.4×10^6	associative activation
	Sm^{3+} ($^4G_{5/2}$)	H_2O	5.5×10^6	associative activation
Salicylate anion	Tb^{3+} ($^5D_4$)	CH_3OH	4.0×10^3 [a]	"
	Tb^{3+} ($^5D_4$)	D_2O	7.6×10^9 [a]	acid catalysis
	Tb^{3+} ($^5D_4$)	H_2O	1.0×10^{10} [a]	acid catalysis
5-Sulfosalicylate dianion	Tb^{3+} ($^5D_4$)	CH_3OH	4.0×10^3	addition of H^+
	Tb^{3+} ($^5D_4$)	D_2O	7.9×10^9 [a]	"
	Tb^{3+} ($^5D_4$)	H_2O	1.05×10^{10} [a]	"
Selective laser excitation at the wavelength corresponding to the $^5D_0 \leftarrow {}^7F_0$ transition of the Eu^{3+} ion				
1,10-Phenanthroline	Eu^{3+} ($^5D_0$)	D_2O	2.7×10^3	dissociative opening of the chelate ring
Acetate anion	Eu^{3+} ($^5D_0$)	H_2O	7.0×10^6 [d]	associative activation
	Gd^{3+} ($^8S_{7/2}$)	H_2O	7.0×10^6 [d]	associative activation
	Sm^{3+} ($^6H_{5/2}$)	H_2O	3.7×10^7 [e]	"
Iminodiacetate	[EuDCTA]$^-$ ($^5D_0$) [f]	H_2O	2.6×10^3	"

[a] The errors in k_{diss} do not exceed 20% – 30%.
[b] The numbers in brackets represent the activation energies for the reactions in kJ mol^{-1}.
[c] Second-order rate constant k' in mol^{-1} dm^3 s^{-1}.
[d] Value for the unexcited ion based on the data of Silber et al.[54] obtained by the temperature jump method.
[e] Value for the unexcited ion based on the data of Garza and Purdie[55] obtained by the acoustic absorption method.
[f] DCTA = 1,2-diaminocyclohexanetetraacetate.

for phenanthroline than for Eu^{3+}, there was a high excitation selectivity and the observed fast exponential function may be set equal to the dissociation rate constant (k_{diss}) for the complex. The value of this constant and also the value of the rate constant for the dissociation of the europium complex of 2,2′-bipyridyl in D_2O at 295 K are presented in Table 9.

The study of the dependence of k_{diss} for the above complexes on the temperature and the pH of the solution suggested a dissociative mechanism of the reaction in which the rate-limiting stage is the transfer of one of the donor nitrogen atoms to the second sphere of the Ln^{3+} ion (opening of the chelate ring), which is followed by rapid dissociation of the complex.

The study of the kinetics of the dissociation of europium and samarium complexes of the 1-naphthoate ion demonstrated that the rate of dissociation of the complex is greatly influenced by the solvent. On passing from pure methanol to a mixture of methanol and water and then to pure water, the rate of dissociation increases by three orders of magnitude (Table 9). One should bear in mind that, on excitation as a result of nonradiative energy transfer from the aromatic ligands, the $^5D_0$ level of the Eu^{3+} ion is populated via the $^5D_1$ level of europium. On the other hand, the rate of the nonradiative transition from the $^5D_1$ level to the $^5D_0$ level of europium is 10^6 s^{-1},[56] which limits the possibilities for the study of rapid dissociation reactions. Therefore the data for Sm^{3+}, where the rate of relaxation to the emitting $^4G_{5/2}$ level is appreciably higher, is quoted in Table 9 as the rate of dissociation of naphthoic acid [the naphthoic acid complex?] in water.

The dissociation reactions of the salicylic and sulfosalicylic acid complexes of the Tb^{3+} ion (the $^5D_4$ level) in methanol and water have been investigated. It has been shown that the rate of dissociation in water depends greatly on the pH of the solution, k_{diss} being directly proportional to the concentration of H^+ (H_3O^+) ions in water. Bimolecular constants, close in magnitude to the diffusion rate constant in water, are therefore quoted in Table 9 for these complexes. It is most likely that the first stage of the dissociation of these complexes involves the addition of a proton to the free oxygen of the COO^- group with subsequent departure of the ligand from the lanthanide ion. The constants k_{diss} have been measured by a similar method[57] for Tb^{3+} with the same ligands in water at $I = 0.06$ and pH 7.0. The constants k_{diss} exceeded by an order of magnitude those quoted by Gruzdev and Ermolaev[52,53] (Table 9). It may be that this is associated with the unduly high ligand concentration, comparable to the concentration of the Ln^{3+} ion. Complexes of lanthanide ions with different numbers of ligands coexist under these conditions and it is difficult to determine the values of k_{diss}. Furthermore, the authors[57] postulate that the rate of equilibration with respect to the excited ions is equal to the difference between the rates of dissociation and association, whereas it is in fact equal to their sum [see Eqn (7)]. These discrepancies are not discussed in the study quoted above.[57]

However, the selective excitation of the complexes via the excitation of the ligand and the nonradiative energy transfer to the Ln^{3+} ion is limited by the employment of mainly aromatic ligands. Therefore, in order to study the nonaromatic ligand exchange reactions, the second method for the creation of a high nonequilibrium distribution of the excited ion complexes — the method involving the selective excitation of specific complexes by illuminating the solution with the monochromatic light of a pulse-type tunable laser — was employed. The Eu^{3+} ion and its absorption band, corresponding to the $^5D_0 \leftarrow {}^7F_0$ transition, the position and strength of the oscillator of which are extremely sensitive to changes in the structure of the inner coordination sphere of the ion, are most suitable for these purposes.[1] The widely used rhodamine 6G-based tunable laser is also very suitable.

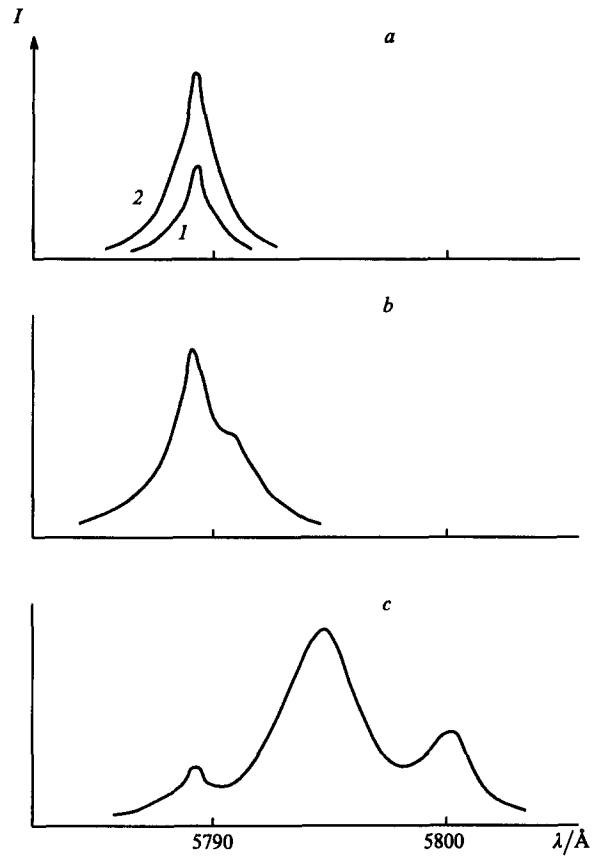


Figure 14. Luminescence excitation spectra in the $^5D_0 \leftarrow {}^7F_0$ transition in aqueous solutions containing Eu^{3+} ions (at the wavelength corresponding to the $^5D_0 \leftarrow {}^7F_0$ band) measured with the aid of a rhodamine 6G-based tunable laser: (*a*) $Eu(NO_3)_3$ (0.05 M) in H_2O (curve *1*) and $Eu(NO_3)_3$ (0.05 M) + NaAc (0.01 M) in H_2O (curve *2*); (*b*) $Eu(NO_3)_3$ (0.05 M) + Phen (0.01 M) in D_2O; (*c*) $Eu(NO_3)_3$ (0.05 M) + Na_2H_2EDTA (0.01 M) in D_2O, pD = 5.5; T = 295 K.

Fig. 14 presents the luminescence excitation spectra in the $^5D_0 \rightarrow {}^7F_1$ transition for various europium complexes in water by light corresponding to the $^5D_0 \leftarrow {}^7F_0$ band, measured with the aid of a rhodamine 6G-based tunable laser.[58] Such spectra correspond to the absorption spectra, the direct measurement of which is difficult owing to the extremely low oscillator strength of the transition. The rates of ligand exchange in the europium complexes of the acetate anion have been investigated by this method.[53,58] The selectivity of the excitation of the tunable laser was achieved because the molar absorption coefficient of the complex $(EuCH_3COO)^{2+}$ is approximately five times greater than that for the hydrate, although the positions of the $^5D_0 \leftarrow {}^7F_0$ absorption bands are identical. The luminescence decay curve for an aqueous solution of $Eu(NO_3)_3$ (5×10^{-2} M) + $NaCH_3COO$ (10^{-2} M) at 293 K, measured using the light corresponding to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ band, is presented in Fig. 15. The relaxation time corresponding to the initial nonexponential section of the decay curve in Fig. 15 is 120 ns. Since the equilibrium is greatly displaced towards the solvates, the dissociation of the complex $(EuCH_3COO)^{2+}$ makes the main contribution to this quantity [see Eqn (7)]. Assuming that the stability constant of the complex (87 mol^{-1} dm^3) does not change appreciably on excitation, we obtain a dissociation rate constant of $(7 \pm 2) \times 10^6$ s^{-1}, which is close to the dissociation rate constant of the europium complex of the naphthoate anion and to the value found for the gadolinium acetate complex by the temperature jump method, but differs greatly from data obtained for samarium by the acoustic absorption method (Table 9).

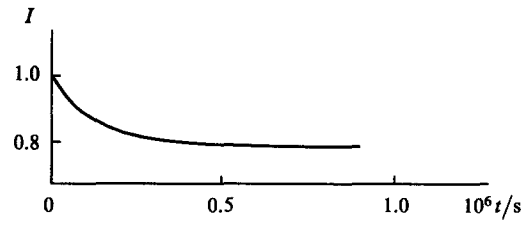


Figure 15. The luminescence decay curve for a solution of the europium complex of the acetate anion $(EuCH_3COO)^{2+}$ in water at the wavelength corresponding to the $^5D_0 \rightarrow {}^7F_2$ band (613 nm) on pulse excitation ($\Delta t \cong 20$ ns) by a rhodamine 6G-based tunable laser. The single-ligand complex $(EuCH_3COO)^{2+}$ is excited preferentially; $c_{Eu(NO_3)_3 \cdot 6H_2O}$ = 0.05 M; c_{CH_3COONa} = 0.01 M, T = 295 K.

Other processes may also lead to a nonexponential type of decay of the luminescence. Firstly, we have the reaction involving the substitution of the central atom in the excited state:
The contribution of this reaction may be determined from the

$$M^*L + M \longrightarrow M^* + ML\,.$$

dependence of the rate constant for the transition process on the concentration of the solvated ion.

Secondly, we have nonradiative electronic excitation energy transfer from the selectively excited complex to the unexcited solvate. As in the previous case, in order to distinguish the energy transfer from the dissociation of the complex, it is sufficient to investigate the dependence of the process on the concentration of solvated ions. It is more difficult to distinguish the energy transfer (migration) from the reaction involving the substitution of the central atom, since the rates of these processes increase with increasing concentration of the solvate. However, the energy transfer from the excited Ln^{3+} ions should not depend on the concentration of the lanthanum or lutetium added to the solution because the energy transfer to the latter is impossible for energetic reasons, whereas the central atom substitution reaction should accelerate in their presence.

It must be emphasised that the study of the transition process in connection with the kinetics of the decay of the luminescence after selective excitation makes it possible to obtain unique data concerning the migration (transfer) of energy between identical lanthanide ions in solutions. For example, the rate of migration of energy from the $^5D_0$ level of the Eu^{3+} ion in its complex with EDTA to the solvated Eu^{3+} ion in D_2O has been measured by this method.[59]

Thirdly, the nonexponential decay may be due to the presence of several types of complexes with different decay times which are not interconverted during the lifetime of the excited state of the ion. This process should be reflected in all the emission bands, whereas the dissociation reaction should be reflected only in the emission bands where the emission rate constant changes appreciably as a result of the dissociation. For example, under nonexponential conditions induced by several types of complexes, such conditions should be observed satisfactorily for europium on the basis of both the $^5D_0 \rightarrow {}^7F_1$ band and the $^5D_0 \rightarrow {}^7F_2$ band, whereas the dissociation of the complex can be observed only from the $^5D_0 \rightarrow {}^7F_2$ band.

The possibility of obtaining data on the kinetic parameters of the ligand exchange at excited lanthanide ions in solutions has also been considered.[1,2,60] Three variants were examined depending on the ratios of the rates of deactivation of the excited ions (complexes) and the rate of ligand exchange.

1. Slow exchange. The selective excitation of each complex in solution leads to luminescence involving exponential decay with τ characteristic of the given selectively excited complex, naturally provided that there is no energy transfer between the ions (complexes). In the case of incomplete (or in the total absence) of

selectivity of the excitation and also in the presence of energy transfer, a nonexponential decay of the luminescence is observed. Incidentally, this case can also be used to measure the rate of the slow ligand exchange, provided that the reaction leads to an appreciable shortening of τ. This method has been used[61] to investigate the rate constant for the incorporation of water in the inner sphere of chromium(III) hexathiocyanate. Later the same workers[62] used this method to determine the rates of the slow isotope exchange of hydrogen for deuterium in the complexes $Cr(en)_3^{3+}$ (where en = ethylenediamine) and $Cr(NH_3)_2(NCS)_4^-$ and their dependence on the pH(pD) of the solution.

2. Fast exchange. Having stated correctly that ligand exchange which is fast compared with the luminescence decay time leads to the exponential decay of the emission in later stages after the attainment of equilibrium with respect to the excited complexes. Horrocks and coworkers[2,60] for some reason neglected the transition process, which was later examined by Gruzdev and Ermolaev in 1977,[50] and did not point out the possibility of using it to measure the rates of rapid reactions.

3. The intermediate rate of exchange—corresponding to the case where the luminescence decay and exchange times are similar. In this case, differential equations have been formulated[60] for the concentrations of two types of complexes undergoing interconversion and deactivated at their own rates, similar to the equations quoted by Gruzdev and Ermolaev[50] [see Eqn (5)]. However, since the condition $\tau_1^{-1}, \tau_2^{-2} \ll k_{dis}, k_{as}[L]$ does not hold in this instance, a more complex solution is obtained than the solution based on the approximate formulae quoted by Gruzdev and Ermolaev[50] [Eqn (7)]. The intermediate case has been studied experimentally[60] in relation to the equilibrium between the europium complexes of 1,2-diaminocyclohexanetetraacetate ($DCTA^{4-}$) and iminodiacetate ($IMDA^{2-}$).

$$Eu(DCTA)^- + IMDA^{2-} \underset{k_{diss}}{\overset{k_{as}[IMDA^{2-}]}{\rightleftharpoons}} Eu(DCTA)(IMDA)^{3-}. \quad (8)$$

The experiment was performed at 293.5 K in aqueous solution at $EuCl_3$, H_4DCTA, and H_2IMDA concentrations of 0.4, 0.04, and 0.12 M respectively at pH 6–9 (NaOH) and I = 1.0 (KCl). Each complex was excited selectively by a dye-based laser at the wavelength corresponding to the $^5D_0 \leftarrow {}^7F_0$ band and each complex was detected selectively at the wavelengths of the $^5D_0 \rightarrow {}^7F_0$ bands of the Eu^{3+} ion. The decay of the luminescence was measured at three pH values for each pair of the combinations of the excitation wavelength (exciting mainly one of the complexes) and the observation wavelength characteristic of each complex—altogether four combinations. Using the solutions of the differential equations obtained and the expressions for the overall emission from the two complexes and including the fraction of the emission by each complex as a parameter, Horrocks et al.[60] found the constants k_{dis} and k'_{as}. The following values were obtained at pH 6.99:

$$k_{diss}\{Eu(DCTA)(IMDA)^{3-}\} = 2.56 \times 10^3\ s^{-1};$$

$$k_{as} = k'_{as}[IMDA^{2-}] = 13.4 \times 10^3\ s^{-1};$$

$$\tau\{Eu(DCTA)^-\} = 0.32\ ms;$$

$$\tau\{Eu(DCTA)(IMDA)^{3-}\} = 0.805\ ms.$$

It has been suggested that, instead of Eu^{3+}, the Sm^{3+} and Dy^{3+} ions be used in the study of faster ligand exchange reactions, as their luminescence in hydrogen-containing solvents decays faster by two orders of magnitude than that of Eu^{3+}.[2,60] However, in this case it is simpler and more accurate to employ Eu^{3+} complexes by carrying out measurements for the transition process on the basis of the decay of the Eu^{3+} luminescence using the method proposed by Gruzdev and Ermolaev.[50]

* * *

Luminescence research methods have been used recently in a wide variety of fields of science and engineering. This applies particularly to chemistry, photochemistry, and biology. Kinetic luminescence methods, in particular those involving laser excitation, have become more accessible to investigators. In the present review, we have attempted to draw the attention of chemists, with interests in the field of the chemistry of solutions of the lanthanide elements, to the possibilities of the study of these systems provided by the luminescence-kinetic methods.

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