DETERMINATION OF ENERGY-TRANSFER RATE CONSTANTS IN CHELATE COMPLEXES OF RARE-EARTH IONS

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DETERMINATION OF ENERGY-TRANSFER RATE CONSTANTS IN CHELATE COMPLEXES OF RARE-EARTH IONS

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At present much attention is being devoted to the study of the luminescence of complexes of trivalent rare-earth ions (REI) with β-diketones and other organic ligands, since the effect of generation of stimulated emission has been obtained in solutions of these compounds ([1]). For REI in which the $^3\Gamma$-level of the organic ligand is located above the lower resonant level of the rare-earth ion (RE), absorption of the exciting light takes place in the organic part, whereas the emission is characteristic of the RE. It is assumed ([2]) that transfer in REI occurs through the $^3\Gamma$-level of the ligand. However, the value of the rate constant k_p for nonradiative transfer of electronic energy ligand–RE was unknown. In the literature there were only indications of a lower limit of the transfer rate for Eu^{3+} dibenzoylmethanate, $k_p \geq 10^7$ s^{-1} ([3]).

We have proposed a method for determining k_p in REI and have obtained values of k_p for complexes of dibenzoylmethanate (DBM) with Sm^{3+} and Eu^{3+}, and of acetylacetonate (AA) with Sm^{3+}, Eu^{3+}, Tb^{3+}, and Dy^{3+}. We made use of the competition between the process of intramolecular ligand–RE transfer and intermolecular energy transfer over the triplet levels of organic compounds ligand–quencher (acceptor) ([4]). The scheme of levels of the REI and quenchers is given in Fig. 1. As quenchers we used naphthalene for AA and acridine, anthracene, 1,2-benzanthracene, and pyrene for DBM (see Fig. 1). Excitation of the REI luminescence was carried out outside the absorption band of the quencher: $\lambda_{exc} = 3340$ Å for AA and $\lambda_{exc} = 4050$ Å for DBM. The measurements were carried out in toluene at 293° K. Piperidine was added to the solutions for better reproducibility of the results.

It was shown that in the case when the $^3\Gamma$-level of the added organic compound lies below the $^3\Gamma$-level of the organic part of the REI, quenching of RE luminescence is observed. If, however, the $^3\Gamma$-level of the added compound lies above the $^3\Gamma$-level of the chelate, quenching is not observed; for example, naphthalene and phenanthrene do not affect the luminescence intensity of solutions of Sm^{3+} DBM and Eu^{3+} DBM. The quenching is not due to the formation of associates

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

of the REI with the quencher, since upon freezing of the solution the quenching disappears completely. Direct quenching of the excited RE ions likewise does not occur, since τ and the luminescence spectra of the REI remain unchanged, despite a substantial decrease in the yield of the REI in the presence of the quencher.

Figure 3 presents dependences of the magnitude of REI quenching q_0/q on the concentration of quenchers. The experimental points lie well on straight lines in accordance with the Stern–Volmer–Vavilov formula. As is known, the rate constant k_{T} of triplet-triplet energy transfer between organic molecules in liquid solutions is equal to the diffusion constant if the $^3\Gamma$-level of the donor is 1000 cm^{-1} or more above the $^3\Gamma$-level of the acceptor (quencher) ([5]). This makes it possible, from the slopes of the straight lines in Fig. 3, to determine the sought rate constants for ligand–RE energy transfer by the formula $k_{\text{p}} = k_{\text{T}}C_{\text{T}}(q_0/q - 1)^{-1} = 1.1 \cdot 10^{10}C_{\text{T}}(q_0/q - 1)^{-1}$.

For the RECs studied, the following values of k_p were obtained: $Sm^{3+}AA > 10^{11}$ sec^{-1}, $Eu^{3+}AA \sim 5 \cdot 10^{10}$ sec^{-1}, $Tb^{3+}AA$ $(5.6 \pm 1.7) \cdot 10^8$ sec^{-1}, $Dy^{3+}AA$ $(5.0 \pm 0.6) \cdot 10^8$ sec^{-1}, $Sm^{3+}DBM$ $(1.1 \pm 0.2) \cdot 10^8$ sec^{-1}, $Eu^{3+}DBM$ $(3.5 \pm 0.5) \cdot 10^7$ sec^{-1}.* The maximum values of k_p in RECs $(5\text{-}10 \cdot 10^{11}$ $\text{sec}^{-1})$ indicate that, apparently, radiationless–

Fig. 1. Scheme of electronic levels in the phenomenon of triplet-triplet quenching of REC luminescence by organic molecules. $^1\Gamma^*$ and $^3\Gamma$ are the lower excited singlet and triplet levels of the organic molecules: DBM–dibenzoylmethanate and AA–acetylacetonate in the complex with RE (according to absorption of REC and the studied $Gd^{3+}AA$ and $Gd^{3+}DBM$). Quenchers: AH–anthracene, AK–acridine, H–naphthalene. The scheme of the levels of trivalent RE ions is given according to Dieke and Crosswhite (5); the notation of the levels is the same. Thick horizontal lines are electronic levels, thin ones are electron-vibrational levels. Solid vertical lines are radiative transitions, dotted lines are transitions in energy transfer.

Fig. 2. Spectra of ligand phosphorescence and RE absorption. *a* and *b*–phosphorescence of $Gd^{3+}AA$ ($C = 4 \cdot 10^{-4}$ M) and $Gd^{3+}DBM$ ($C = 2 \cdot 10^{-4}$ M) in toluene + piperidine, 77 K; *c*, *d*, *e*, and *f*–absorption spectra of RE ions; *c*: 1–$Sm^{3+}AA$ in CCl_3H (8), 2–$Sm^{3+}(ClO_4)_3$ in H_2O (9); *d*: 1–Eu^{3+}–benzoylacetonate in an ethanol + methanol mixture (10), 2–$Eu^{3+}(ClO_4)_3$ in H_2O (9); *e*–$Tb^{3+}Cl_3$ in H_2O (11); for the Tb^{3+} band at 20500 cm^{-1} there are no data on the probability of the transition; *f*–$Dy^{3+}(NO_3)_3$ in H_2O (12). Along the abscissa axes are plotted wave numbers; along the ordinate axes, the distribution of the quantum intensity over the spectrum $\Phi(\nu)$ (spectra *a* and *b*) or the molar nat-

ural absorption coefficients $\varepsilon(\nu)$ (spectra c, d, e, and f). For the hatched curves the scale is increased by a factor of 10, and for the dotted curves by a factor of 100.

radiative energy transfer can occur not only from the lower triplet level of the ligand ($^3\Gamma$), but in some cases also from the fluorescent level ($^1\Gamma^*$). The lifetime of the $^1\Gamma^*$ level of the ligand in an REC, judging from the absence of REC fluorescence in the emission spectrum, can be estimated as $\tau_{^1\Gamma^*} \leq 10^{-11}$ sec. However, from high excited levels of the RE, energy transfer back to the ligand with excitation of the $^3\Gamma$-level is possible. If the lower resonance excited level of the RE is located below the $^3\Gamma$-level of the ligand, then the last stage will be transfer ligand ($^3\Gamma$)—RE with emission of line luminescence by the ion.

Since the electronic transitions induced upon transfer in RE are forbidden, it may be taken with confidence that energy transfer in RECs occurs by the exchange-resonance mechanism. The rate constant of transfer by the exchange-resonance mechanism is proportional—

* k_p were determined from quenching by the most effective acceptor—acridine (straight lines II AK and I AK in Fig. 3).

is proportional to the overlap of the electron shells of the interacting particles (in the present case, the overlap of the ligand π cloud with the f shell of the REE) and to the overlap integral of the donor emission spectrum (in our case, the ligand phosphorescence spectrum) with the REE absorption spectrum ([7,4]). Exchange-resonance transfer between the $^3\Gamma$ level of the ligand and the lower excited resonance levels in Sm^{3+}, Eu^{3+}, Tb^{3+}, and Dy^{3+} is allowed by the spin selection rules.

We estimated the relative magnitudes of the overlap integrals

$$\int \Phi(\nu)\varepsilon(\nu)\, d\nu$$

for transfer from the $^3\Gamma$ level of the ligand to various REE levels, where $\varepsilon(\nu)$ is the molar natural absorption coefficient of the REE, and $\Phi(\nu)$ is the quantum distribution of intensity in the phosphorescence spectra of Gd^{3+}AA and Gd^3DBM in solutions at 77° K. Since the first excited level of Gd^{3+} is located high—at $\nu 32\,000$ cm^{-1}—emission in these complexes takes place from the $^3\Gamma$ level of the ligand. The phosphorescence spectra of the ligand ($\Phi(\nu)$) and the absorption spectra of the REE ($\varepsilon(\nu)$), from which we estimated the overlap integrals, are given in Fig. 2. The sum of the overlap integrals for a given ligand and REE in most cases agrees only qualitatively with the experimental value of k_{p} for the corresponding REE complex. There is not even qualitative agreement for Dy^{3+}AA. Comparison of the overlap integrals with k_{p} is complicated by the fact that, for most of the REE complexes studied (Sm^{3+}DBM, Sm^{3+}AA, Eu^{3+}AA, Tb^{3+}AA, and Dy^{3+}AA), there is a series of REE levels lying close (± 300 cm^{-1}) to the $^3\Gamma$ level of the ligand. For these REE levels, back transfer from the REE

Figure 3

Figure 2: Figure 3

to the ligand is possible, and therefore a high probability of energy transfer to these levels does not lead to a simultaneous proportional reduction of the residence time of the REE complex in the $^3\Gamma$ state and, consequently, affects the experimentally determined value k_{p} in a more complicated way. Only in the case of Eu^{3+}DBM (see Fig. 1) are there no excited REE levels near the $^3\Gamma$ level. Calculation of the overlap in this case gives a ratio of the probabilities of transfer from DBM to the $^5D_1$ and $^5D_0$ levels of Eu^{3+} equal to $20:1$, which agrees with Baumic' s data ([3]) on the population in Eu^{3+}DBM of the $^5D_0$ level through $^5D_1$. A major difficulty in calculating the overlap integrals was the small amount of information on the absolute values of the REE absorption coefficients. We also had to assume, in accordance with ([13]), that the intercombination prohibition for the transitions considered in the REE is approximately the same. In further studies, the REE complexes should be chosen so that transfer can occur only to REE levels lying appreciably below the $^3\Gamma$ level of the ligand. Comparison of the overlap integrals with the experimental values of k_{p} should then make it possible to obtain information on the overlap of the electron shells of the ligand with the REE.

Fig. 3. Quenching of the luminescence of REE complexes by means of intermolecular triplet-triplet energy transfer in liquid solutions (toluene + piperidine, 293° K). Along the abscissa is plotted the concentration of quencher C_{T}; along the ordinate, the quenching value q_0/q, where q_0 is the luminescence yield of the REE-complex solution in the absence of quencher, and q is the same with quencher at concentration C_{T}. On the left, quenching of complexes with dibenzoylmethane (DBM); on the right, with acetylacetone (AA). Roman numerals at the straight lines indicate the REE component of the complex: I—Sm^{3+}, II—Eu^{3+}, III—Tb^{3+}, and IV—Dy^{3+}; quenchers: Acr—acridine, An—anthracene, P—pyrene, and H—naphthalene. The straight lines—IH, IIH, $IIIAK$, $IIIP$—are drawn only for clarity; in these cases the transfer constant (k_{t}) was determined from quenching at only one quencher concentration.

Thus, our experiments have shown that intermolecular triplet-triplet energy transfer between organic molecules in ···

their approach proceeds with a larger rate constant than k_p for the ligand—RE. The transition $^3\Gamma \leftarrow {}^1\Gamma$, induced during transfer in the organic molecule, is in most cases forbidden only intercombination-wise, whereas the transition induced in the RE is also symmetry-forbidden ([13]). In the exchange-resonance mechanism of transfer the intercombination prohibition is lifted, while the symmetry prohibition retains its significance. It is interesting that the efficiency of quenching of REK by different organic acceptors is not the same (left-hand part of Fig. 3); whether this is connected with differences in the overlap integral of the donor and acceptor spectra or whether quasi-chemical interactions play a

role in collisions is at present unclear.

From the results obtained above there follows a number of conclusions concerning the analysis of RE content from the luminescence of REK precipitates ([14]). There is no doubt that in fine-crystalline REK precipitates migration of the triplet exciton over the organic part takes place (the rate constant of triplet-triplet transfer between neighboring aromatic molecules in crystals is estimated as 10^{10}–10^{11} s^{-1} ([15,4])). Energy transfer to the RE proceeds either to traps, where the triplet energy is delayed (for example, on the surface of the crystal), or by capture of the exciton with a probability that depends on the overlap of the ligand phosphorescence spectra with the RE absorption spectrum. At the same time, the presence of organic impurities with a $^3\Gamma$ level lower than that of the ligand is also substantial, since they will reduce the yield of RE luminescence by capturing part of the excitation energy.

The synthesis of AA complexes was carried out by the method of A. G. Morachevsky, and the synthesis of DBM by the method of Crosby and Whan ([2]). We express our deep gratitude to Academician A. N. Terenin for his attention to this work, and to A. V. Karyakin, V. A. Arkhangel' skaya, and B. I. Maksakov for providing the RE.

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Note: Figure translations are in progress. See original paper for figures.