OPTICS AND SPECTROSCOPY

ON THE CONCENTRATION DEPENDENCE OF THE SENSITIZED PHOSPHORESCENCE QUANTUM YIELD OF NAPHTHALENE IN TOLUENE AT 77 K

M. I. Deryabin and A. B. Tishchenko

A concentration dependence of the sensitized phosphorescence quantum yield of naphthalene (with benzophenone as a donor) in equimolar toluene solutions at 77 K is studied for concentrations of components ranging from 0.1 to 0.5 mole/litre. A nonmonotonic character of this dependence is established. With increasing solution concentration, intervals of increase (from 0.1 to 0.35) and decrease (from 0.35 to 0.5) of the sensitized phosphorescence quantum yield are observed. Reasons for this dependence are discussed.

INTRODUCTION

According to the existing notion of intermolecular triplet-triplet electronic excitation energy transfer in condensed media [1, 2], the sensitized phosphorescence (SP) quantum yield is considered to be independent of the solution concentration. Recall that by the SP quantum yield is meant the ratio of the number of quanta emitted by an acceptor in unit time to the number of triplet donor molecules quenched over the same time period as a result of energy transfer to the acceptor in the stationary mode [2]. Therefore, it can be independent of the concentration if the presence of the donor in the solution does not influence the rate constants of radiative and nonradiative triplet excitation energy deactivation in acceptor molecules. The fulfillment of the first condition follows from the quantum-mechanical Förster-Dexter theory of exchange-resonance energy transfer [1]. According to this theory, to prepare the initial and final quantum states, the corresponding unperturbed energy donor and acceptor wave functions are taken. Artyukhov and Mayer [3] demonstrated that this statement of the Förster theory is incorrect in the context of the modern theory of nonradiative transitions. They also demonstrated that the interaction between components in the donor-acceptor pair perturbs electronic states of isolated molecules still before the excitation of donor molecules. If this is the case, then we can expect a change in the rate constant of radiative triplet excitation energy deactivation for the acceptor as a result of interaction between excited acceptor and unexcited donor molecules. In its turn, this must lead to a change in the SP quantum yield. The second condition is fulfilled when the presence of donor molecules does not create additional channels of nonradiative triplet excitation energy deactivation in acceptor molecules compared to channels that already existed without donor molecules. However, as demonstrated in [4], heteroassociates efficiently quenching triplet acceptor molecules can be formed in solid solutions at high concentrations of donor-acceptor mixtures. This mechanism of quenching triplet acceptor molecules can also notably change the SP quantum yield.

From the foregoing it follows that a dependence of the SP quantum yield on the solution concentration can be expected for solid solutions of organic compounds.

This work is aimed at detecting and studying a dependence of the SP quantum yield on the solution concentration in vitreous toluene at 77 K.
EXPERIMENTAL PROCEDURE

We used benzophenone as an energy donor and naphthalene as an energy acceptor. Toluene vitrifying on fast cooling to 77 K served as a solvent in which both compounds dissolved well. The solution concentration was calculated at room temperature. In determining the average distance between impurity molecules, we took into account the thermal compression of toluene on cooling to 77 K.

The SP quantum yield for different solution concentrations was determined graphically [2] from the ratio of areas under SP spectra and from the difference between areas of the donor phosphorescence spectra recorded without and with acceptor molecules in the solution. This quantity was also calculated by the formula

\[ \Phi_{\text{cal}} = \frac{\kappa_{\text{rad}}}{\kappa_T}, \]  

where \( \kappa_{\text{rad}} \) is the rate constant of radiative triplet excitation energy deactivation for acceptor molecules, \( \kappa_T \) is the parameter equal to the sum of radiative and nonradiative deactivation constants for triplet acceptor molecules.

To determine \( \kappa_{\text{rad}} \) of the acceptor at different solution concentrations, we used the formula

\[ \frac{I}{I_0} = \frac{\kappa_{\text{rad}}}{\kappa_{\text{rad}}^0} \frac{q}{q_0}. \]  

RESULTS AND DISCUSSION

The SP quantum yield of naphthalene in vitreous toluene shown in Fig. 1 (curve 1) depends nonmonotonically on the solution concentration. Its value increases when the concentration of components in the equimolar solution increases to 0.35 mole/l. Further increase of concentration from 0.35 to 0.5 mole/l is accompanied by a decrease in the SP quantum yield.

To elucidate reasons for the observed dependence, we first studied the influence of the concentration on the rate constant of radiative triplet excitation energy deactivation \( \kappa_{\text{rad}} \) in acceptor molecules. Results of this study are shown in Fig. 2 in the form of the dependence of \( \kappa_{\text{rad}} \) on the average distance between components in the donor-acceptor pair. As can be seen from Fig. 2, the radiative deactivation rate constant for triplet naphthalene molecules exponentially increases as \( R \) decreases. The character of this dependence is satisfactorily described by the equation (solid curve)

\[ \kappa_{\text{rad}}(R) = \kappa_{0}^{\text{rad}} + A \exp(-\alpha R). \]