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Interaction mechanism of molecular oxygen with excited states of luminophores in solution, in polymers, and at a surface

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EXTERNAL HEAVY ATOM EFFECT ON THE INTERSYSTEM CROSSING FROM THE
LOWER AND HIGHER EXCITED STATES OF RHODAMINE DYES ON A SILICA SURFACE

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UDC 535.373.2

In recent years there has been a growing interest in photophysical processes involving higher excited singlet and triplet states [1-3]. Intersystem crossing transitions between states of different multiplicity as well as external heavy atom (EHA) and molecular oxygen effects play an important role in these processes. The photophysical processes in heterogeneous systems involving solid-liquid and solid-gas interfaces have not been extensively studied.

In the present work the EHA and molecular oxygen effects on deactivation of lower and higher electronically excited states of adsorbed rhodamine dyes: rhodamine 6G (R6G), unsubstituted rhodamine (UR), and rhodamine 3B (R3B) have been studied. LiI, LiBr, and KI were selected as EHA. The dyes and EHA were absorbed on porous silica gel S-80 by sorption from aqueous solutions. Fast fluorescence (FL) of the dyes excited in the first absorption band (S_1) with the steady state monochromatic light selected by an MS-80 monochromator from a DKSh-1000 lamp and also in the second absorption band (S_2) with a nitrogen laser ($\lambda = 337.1$ nm) were studied. Also delayed fluorescence (DF) from the adsorbed dyes excited by a second harmonic of a YAG:Nd³⁺ laser ($\lambda = 530$ nm) was studied. The parameters of the laser setup were as follows: $W = 50$ MJ, $\tau_{0.5} = 20$ nsec, and temporal resolution 50 nsec.

In the first series of experiments the steady-state FL from homogeneous liquid solutions of R6G with EHA (LiBr and LiI) was studied with two types of excitation: by monochromatic light ($\lambda = 520$ nm) and by the nitrogen laser ($\lambda = 337$ nm). The concentration of LiI and LiBr salts in solution was increased from 5×10^{-5} to 10^{-3} and from 10^{-5} to 10^{-2} mole/liter, respectively. The quenching of the dye FL as a function of EHA concentration followed the Stern-Volmer dependence for both types of excitation. It should be noted that the discrepancy in FL quenching of aqueous solutions of R6G and other rhodamine dyes by LiI and LiBr salts constituted 15-20% being in agreement with the results on two-photon excitation to the second singlet state of R6G [4].

The second series of experiments involved studying heterogeneous systems and FL quenching of R6G adsorbed on S-80 silica gel ($C = 7.5 \times 10^{-3}$ molecules/nm²) by iodine and bromine ions dissolved in water in contact with silica gel surface. The Stern-Volmer quenching constants were the same within the experimental error as those obtained in homogeneous dye solutions excited into the first and second singlet states.

When the dyes adsorbed on S-80 were dried at 80°C in a vacuum, there was a difference in FL quenching by EHA for the two types of excitation. It should be noted that no effect of LiBr and KI salts on FL quenching of the dyes was observed. In the case of KI, the results were not reproducible, especially for nitrogen laser excitation. Moreover, the photostability of the adsorbed dyes was studied at $\lambda = 337.1$ nm excitation, however there was no appreciable photobleaching observed.

Figure 1 presents Stern-Volmer plots of adsorbed R6G FL quenched by EHA LiI. It is clear that, in the absence of oxygen, FL quenching of adsorbed R6G is more efficient for shortwavelength excitation than when excited in the first singlet state. The rate constants for quenching of S_2 and S_1 states by EHA LiI under steady state excitation were calculated. The quenching rate constants of R6G ($C = 7.5 \times 10^{-3}$ molecule/nm²) S_1 state, $K_{Q1}^{S_1}$, were calculated assuming that the quenching is governed by $S_1 \sim T_1$ intersystem crossing to the lowest triplet state. The rate constant $K_{Q2}^{S_2}$ was calculated from a formula which assumed that EHA did not enhance the rate of internal conversion $S_2 \sim S_1$:

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TABLE 1. EHA Quenching Rate Constants of the Second ($K_Q^{S_2}$) and the Lower ($K_Q^{S_1}$) Singlet as well as the Lowest Triplet, (K_Q^T) State of Rhodamine Dyes

Luminophore	$K_Q^{S_1} \cdot 10^9 \text{ molecule}^{-1} \cdot \text{nm}^2 \cdot \text{sec}^{-1}$		$K_Q^{S_2} \cdot 10^{12} \text{ molecule}^{-1} \cdot \text{nm}^2 \cdot \text{sec}^{-1}$		$K_Q^T \cdot 10^6 \text{ molecule}^{-1} \cdot \text{nm}^2 \cdot \text{sec}^{-1}$	
	with O_2	without O_2	with O_2	without O_2	with O_2	without O_2
Unsubstituted rhodamine	3,4	2,8	5	5	—	—
Rhodamine 6G	22	10	18	1,5	—	1,5
Rhodamine 3B	3	1,8	63	9	—	—

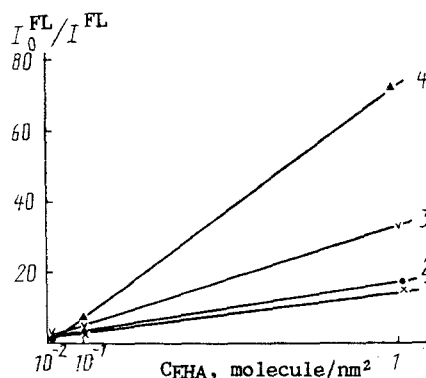


Fig. 1. FL quenching of adsorbed R6G ($C = 7.5 \times 10^{-3} \text{ molecule/nm}^2$) as a function of EHA concentration at surface for laser ($\lambda = 337.1 \text{ nm}$) (1, 4) and lamp ($\lambda = 530 \text{ nm}$) (2, 3) excitation at $p = 1.33 \times 10^{-2} \text{ Pa}$ (1, 2) and atmospheric pressure (3, 4).

$$\left(\frac{I_Q^{FL}}{I_0^{FL}} \right)_2 \left(\frac{I_Q^{FL}}{I_0^{FL}} \right)_1 - 1 = K_Q^{S_2} \tau_{S_2} [Q], \quad (1)$$

where $(I_Q^{FL}/I_0^{FL})_2$ and $(I_Q^{FL}/I_0^{FL})_1$ are the intensity ratios in the presence (index Q) and absence of EHA for the second and first singlet state, respectively; τ_{S_2} is the lifetime of the second singlet state; and $[Q]$ is the surface concentration of EHA. The value of $\tau_{S_2} = 3 \times 10^{-13} \text{ sec}$ for R6G was taken from [5]. The same value of τ_{S_2} was used for calculations of $K_Q^{S_2}$ for other rhodamine dyes. The quenching constants by EHA of the first and second singlet states of the adsorbed rhodamine dyes in the presence and absence of oxygen are presented in Table 1.

Analysis of the quenching constants by EHA LiI of the lower and higher singlet states of adsorbed rhodamine dyes reveals that in the absence of oxygen $K_Q^{S_2} > K_Q^{S_1}$ (they differ by 2-3 orders of magnitude). This effect of EHA on high singlet levels can be explained by the lowered ionization potential and increased ability to form charge transfer states (CTS) between EHA and dye molecules [6]. The complex with EHA leads to the formation of several CTS with different orbital symmetry corresponding to an electron transfer from different doubly occupied orbitals of an I^- ion. For example, the singlet, CTS $5p_x \rightarrow \pi^*$ and the triplet CTS $5p_y \rightarrow \pi^*$, where $5p_x$ and $5p_y$ are atomic orbitals of iodine and π^* is the molecular orbital of the dye, mix with S_2 and T_n states of different orbital symmetry through electrostatic intermolecular interactions. Due to this selectivity, spin-orbit interaction (SOI) between mixed states in the complex with EHA increases substantially at the expense of direct SOI from iodine atom [6]. The energy difference between CT and S_2 is considerably smaller than for S_1 and, therefore, they mix more efficiently, thus enhancing the EHA effect.

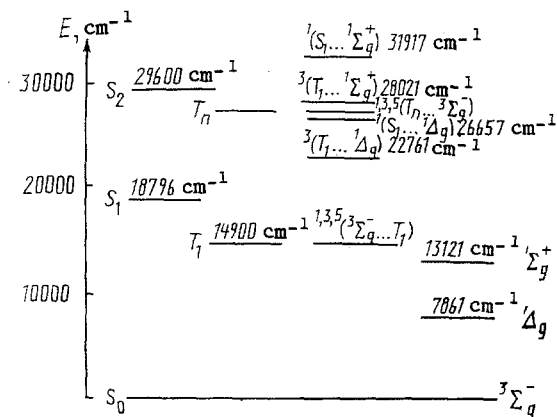


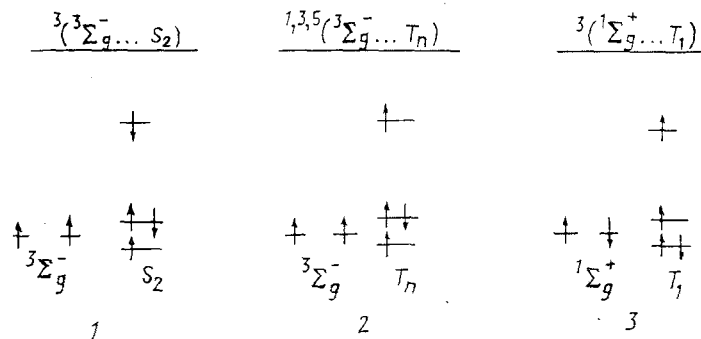
Fig. 2. Energy level diagram of R6G, oxygen, and its complex with the dye.

this selectivity, spin-orbit interaction (SOI) between mixed states in the complex with EHA increases substantially at the expense of direct SOI from iodine atom [6]. The energy difference between CT and S_2 is considerably smaller than for S_1 and, therefore, they mix more efficiently, thus enhancing the EHA effect.

It can be seen from Table 1 that for the dyes exhibiting different structure of chromophores ($-\text{N} \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} - \text{HP}$; $-\text{N} \begin{smallmatrix} \text{H} \\ \text{C}_2\text{H}_5 \end{smallmatrix} - \text{R6G}$; $-\text{N} \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} - \text{R3B}$) the EHA effect on FL quenching is practically identical, thus pointing to the involvement of their groups in complex formation with I^- .

The most interesting is the enhanced quenching of FL of rhodamine dyes by oxygen in the presence of EHA when excited into the second excited singlet state (Fig. 1, curves 3 and 4). The calculated values of quenching rate constants $K_Q^{S_1}$ and $K_Q^{S_2}$ exhibit differences of up to one order of magnitude (Table 1). It should be noted that in experiments with the combined effect of EHA and oxygen there was a general tendency of enhanced quenching when excited into the S_2 state; however, a strong scatter of data was observed even for small variations in sample preparation. The observed differences in quenching rates can be explained by qualitative quantum chemical considerations.

Energy levels of R6G, oxygen, and its complex with the dye are presented in Fig. 2. It appears from the diagram that the levels in the vicinity of S_2 and T_n states and the levels of the complex are energetically close, allowing thus transitions between them as a result of SOI in the presence of EHA. Orbital transitions and corresponding levels are as follows:



In the presence of O_2 new, nearly degenerate levels 2 and 3 of different multiplicity appear. In the presence of EHA, the increased SOI admixes to the levels 1 and 2, in addition to the allowed transition $^3(^3\Sigma_g^-\dots S_2) \rightarrow ^3(^3\Sigma_g^-\dots T_n)$ spin multiplets $^1(^3\Sigma_g^-\dots T_n)$ and $^3(^3\Sigma_g^-\dots S_2)$ of the complexes which increases the yield of T_n state and, therefore, diminishes the return to S_1 state. It is also interesting to consider depopulation of S_2 state via $^3(^3\Sigma_g^-\dots S_2) \rightarrow ^3(^1\Sigma_g^+\dots T_1)$ transition. Formally, levels 1 and 3 do not mix and do not interact as the interaction is

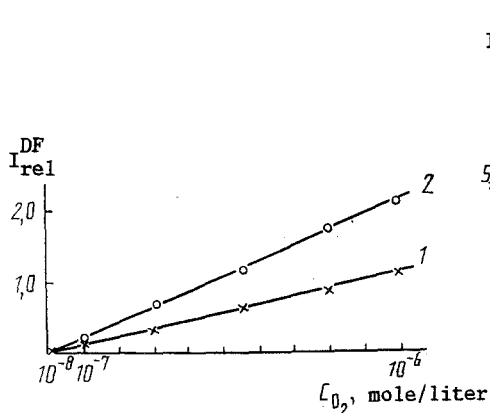


Fig. 3

Fig. 3. Effect of EHA (LiI salt) on DF intensity of R6G ($C_{R6G} = 7.5 \times 10^{-3}$ molecule/nm²) as a function of oxygen concentration. $C_{LiI} = 0$ (1) and 2.07×10^{-1} molecule/nm² (2).

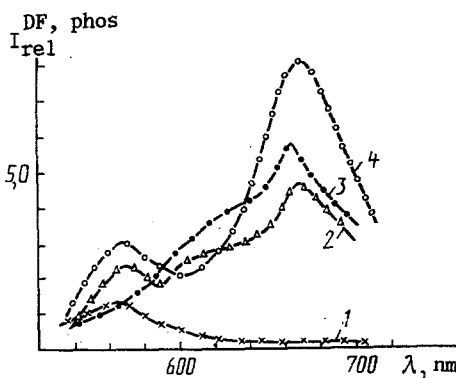


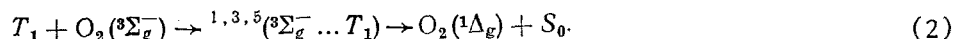
Fig. 4

Fig. 4. EHA effect on DF and phosphorescence of R6G ($C_{R6G} = 7.5 \times 10^{-3}$ molecule/nm²). EHA concentrations: 0 (1), 2.07×10^{-1} (2), 2.073 (3), and 20.7 molecules/nm² (4).

orbitally forbidden. However, weak intermolecular exchange interactions lead to some minor mixing since the transition between them is cooperative. If however, one takes into account efficient mixing via SOI between $^3\Sigma_g^-$ and $^1\Sigma_g^+$ states in oxygen molecule [7] and enhanced SOI between S_2 and T_1 states due to EHA, the deactivation route $1 \sim 3$ can be considered efficient. For more detailed discussion of the EHA role in these processes, additional quantum chemical calculations are needed.

The combined effect of EHA and oxygen was also discovered during studies on deactivation from lower triplet and singlet levels. The process was studied by monitoring delayed fluorescence from adsorbed R6G in the presence of EHA LiI.

Figure 3 presents the intensity of DF of R6G in the presence (curve 1) and absence of LiI (curve 2) as a function of oxygen concentration at the surface. The measurements were conducted at a constant concentration of triplet molecules monitored via dye phosphorescence at $\lambda = 670$ nm. It can be seen from Fig. 3 that in the presence of EHA the DF intensity rises significantly with oxygen concentration relative to pure adsorbed dye molecules. The proposed scheme of the EHA effect is based on the previously described effect of SOI on the mixing of spin multiplets (singlets and triplets) within the encounter complex:



The increase of I^{DF} of the adsorbed dye occurs as a result of singlet-triplet annihilation (STA) [8]:



The two-stage STA process (3) is accompanied by the rise of DF of the dye which can be recorded on an oscilloscope in the microsecond time domain [8].

Therefore, the combined effects of EHA and oxygen on the excited state of the adsorbed rhodamine dyes result in mixing of spin multiplets as a result of external SOI in the encounter complexes between oxygen and excited dye molecule.

The effect of EHA on deactivation of the lowest triplet state of R6G was also studied in the present work. Figure 4 illustrates spectral changes in DF emission from adsorbed R6G in the presence of LiI salt in deoxygenated sample. It can be seen from Fig. 4 that I^{DF} ($\lambda = 560$ nm) and I^{phos} ($\lambda = 670$ nm) increase with EHA concentration. The calculated rate constants of quenching of adsorbed R6G triplet states by EHA are presented in Table 1. The comparison with the quenching constants of the S_1 state by EHA indicates that they differ by 3-4 orders of magnitude. A selective enhancement by EHA of radiative transitions

from the lowest triplet states of adsorbed rhodamine dyes as compared with their nonradiative deactivation was also discovered in this work.

Therefore, the combined sorption of rhodamine dyes and EHA of LiI salt on S-80 silica gel with fractal surface, leads to the formation of charge transfer complexes with the structure which is not observed in homogeneous solutions. Combined effects of EHA and oxygen on the intersystem crossing from the higher and lower excited singlet and triplet states are observed.

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