

Temperature-induced luminescence rise in aqueous solutions of rhodamine 6G

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A rise has been observed in the luminescence of the dye rhodamine 6G as the solution temperature was raised. The effect is interpreted on the basis of a model which has nonluminescing clusters which form in an aqueous solution undergoing a reversible temperature-induced dissociation into monomers having a high luminescence quantum yield.

An increase in the temperature usually has a negative effect on the luminescence yield of solutions.^{1,2} As the temperature is raised, the frequency and energy of collisions of molecules in the solution increase, as does the amplitude of intramolecular vibrations and the activity of quenchers.¹ The effect is to increase the rate constant of the radiationless relaxation from excited levels and thus to quench the luminescence.

In this letter we report experiments which have yielded the first observation of an increase in the luminescence intensity with increasing temperature (a temperature-induced luminescence rise) in an aqueous solution of rhodamine 6G. We also offer an interpretation of these results.

The experiments were carried out with the help of a 1-W LGN-404A multimode argon laser with output in five lines (the most important of which were 0.488 and 0.514 μm). The rhodamine 6G was dissolved in distilled water at room temperature. The concentration of the saturated solution at room temperature was 0.403 g/liter. Dissolved gases were removed from the solutions beforehand by boiling and by processing in an ultrasonic bath.

Figure 1a shows the experimental arrangement in the case of a thin layer (~ 0.2 mm) of solution between two glass substrates 5.0 mm thick. A laser beam ~ 5 mm in diameter is directed to the layer. The image of the center of the light spot coincided with the entrance window of a photodiode. The position of this entrance window with respect to the center of the image did not affect the behavior of the signal at the photodiode. Figure 2a shows the time evolution of the luminescence in a first experiment (Fig. 1a). Here $t = 0$ is the time at which the beam from the argon laser was turned on. The first (and sharp) decay in Fig. 2a is attributed to a decrease in the luminescence due to the filling of triplet levels of the dye molecules, which are metastable levels with $\tau \sim 10^{-3}$ s under ordinary conditions.² This interpretation is confirmed by a repetition of the experiment with a pulse YAG laser, which generated nanosecond pulses at a wavelength of 1.06 μm . The frequency of the light was then doubled, and the light was directed onto a layer of solution, as in Fig. 1a. A CO_2 laser beam was used to raise the temperature in the zone of the light spot.

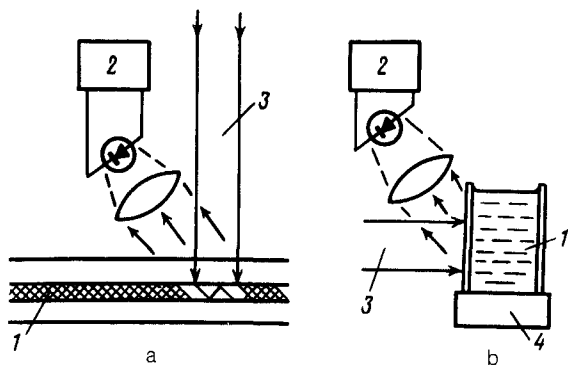


FIG. 1. Experimental arrangements. a: In the case of a thin layer between transparent substrates. b: In the case of a bulk sample. 1—Dye solution; 2—chart recorder; 3—beam from argon laser; 4) heater.

The time dependence of the luminescence intensity, averaged over $t = 2$ s, in an experiment with this formulation consists of exclusively a rise (of up to 200% of the level at 20°C , depending on the dye concentration) after the heating with the CO_2 laser is begun. This experiment also made it possible to exclude from consideration such a process as the formation by an excited monomer of a dimer with an unexcited component, since this process is controlled by diffusion and cannot continue if the illumination is brief.² The rise of the curve in Fig. 2a, starting at the beginning of the heating, occurs over a time on the order of the time required for the relaxation to a steady-state temperature distribution in the layer,³ $\tau \sim l^2/\chi \sim 10$ s. The next feature is a slow decay, which can evidently be attributed to a photochemical decomposition of the dye.⁴ The maximum rise consisted of up to half of the initial luminescence level. In order to rule out the possibility of thermodiffraction and photochemical decomposition, we carried out a third experiment (Fig. 1b), in which a diverging lens expanded the laser beam to a diameter ~ 3 cm. In this case the beam was directed to the cell (with a volume of 100 ml) holding the solution for only a short time. The temperature of the solution could be varied from 20°C to 100°C . The heating from below and the resulting convection caused a continuous mixing of the solution. The points in Fig. 2b

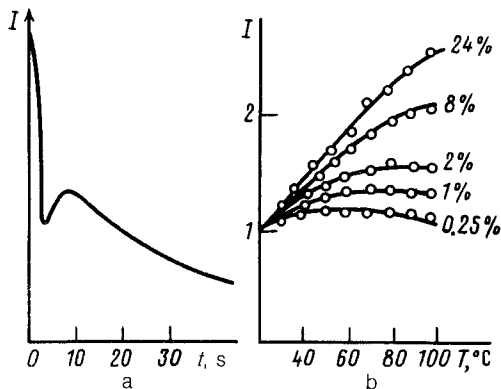


FIG. 2. a—Time evolution of the signal from the photodiode in the arrangement of Fig. 1a; b—luminescence intensity versus the solution temperature for various dye concentrations (expressed as a percentage of the concentration of the saturated solution at 20°C) as calculated for the following values of the constants in Eq. (3): $w_p = 10^{-5}$, $k_{a0}^- = 1$, $k_{d0} = 10^4$, $k_{n0} = 8 \times 10^4$, $k_f = 1$, $E_a = 500^\circ$, $E_d = 4300^\circ$, $E_n = 5000^\circ$. The luminescence intensity at 20°C has been adopted as the initial level ($I = 1$) for each curve. The points are experimental.

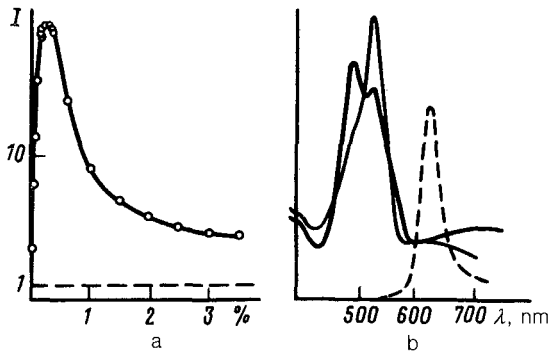


FIG. 3. a: Luminescence intensity in the arrangement of Fig. 1b versus the solution concentration (expressed as a percentage of the concentration of the saturated solution at 20 °C). The unit of intensity here is the intensity in the case of a saturated solution. b: Absorption spectra for dilute (light line) and concentrated (heavy line) solutions. Dot-dashed line—luminescence spectrum which is the same for the two solutions.

show the experimental temperature dependence of the luminescence for five dye concentrations (expressed as a percentage of the concentration of the saturated solution). In the saturated solution, the increase in the luminescence with the temperature was at a maximum, up to 350% at 100 °C of the level at 20 °C. Figure 3a shows the concentration dependence of the luminescence measured in the arrangement of Fig. 1b at 20 °C.

The experimental data were interpreted on the basis of the existing information^{2,5,6} on the tendency of rhodamine 6G molecules in an aqueous solution to form associated complexes or “clusters.” The absorption and luminescence spectra recorded for two dye concentrations (Fig. 3b) show that structural changes occur in the equilibrium configuration of the dissolved molecules as the concentration is increased. In particular, the appearance of the first maximum on the absorption band in the concentrated solution can be attributed to a combining of the rhodamine molecules into clusters which have a shifted absorption spectrum and which undergo essentially no luminescence, since the luminescence spectrum is the same in the two cases. There are some further arguments in favor of this suggestion: First, it follows from the dependence of the luminescence on the dye concentration (Fig. 3a) that as this concentration is increased, there is a decrease in the luminescence intensity. Second, the relative rise in the luminescence with increasing temperature increases with increasing solution concentration (Fig. 2b). As we mentioned above, we are ruling out the possibility that excited rhodamine molecules form clusters with an unexcited monomer; that process could lead to a similar behavior.

In an effort to interpret the experimental data, we consider a very simple model which incorporates the formation of dimers (clusters of two monomers) and the excitation and luminescence of the monomer component. We will not write out the equation for the excitation of the dimers, since it forms a closed system by itself and does not affect the relation between the amounts of different components of the dye. Our model is described by the system of kinetic equations⁷

$$\begin{aligned}
 \dot{N}_d &= k_A N_0^2 - k_d N_d \\
 \dot{N}^* &= W_p N_0 - k_f N^* - k_n N^* \\
 2N_d + N^* + N_0 &= N.
 \end{aligned} \tag{1}$$

We find the following expression for the luminescence intensity in the steady state:

$$I_L = k_f N^* = \frac{k_f}{k_f + k_n} W_p \left[\sqrt{\left(\frac{B}{2A}\right)^2 + \frac{N}{A}} - \frac{B}{2A} \right], \quad (2)$$

where $A = 2(k_A/k_d)$ and $B = 1 + [W_p/(k_f + k_n)]$. For the temperature dependence of the rate constants for the formation and decay of the dimers and the rate constant for the radiationless relaxation of the excited monomer we have the expressions^{2,7}

$$k_A = k_{A0} e^{- (E_A/T)}, \quad k_d = k_{d0} e^{- (E_d/T)}, \quad k_n = k_{n0} e^{- (E_n/T)}, \quad (3)$$

where E_A , E_d , and E_n are the activation energies for the corresponding processes. For the radiative transition we adopt a rate constant $k_f = \text{const}$.

Figure 2b shows the temperature dependence of the luminescence for various rhodamine concentrations according to calculations from Eqs. (1) and (2) with the help of (3) and rate constants chosen on the basis of the experimental points. The corresponding values of the constants are given in the figure caption.

In summary, it can be concluded from this study that the temperature-induced quenching may be accompanied in solutions by mechanisms which raise the total luminescence yield with increasing temperature. This point must be taken into consideration in, for example, the development of dye lasers.

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