Intermolecular orientational "upward" relaxation in viscous solutions of organic compounds

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A short-wave time shift of the fluorescence spectra and a decrease of the afterglow in the long-wave region of the fluorescence spectrum has been observed as a result of anti-Stokes-line excitation in viscous solutions of 3-amino-N-methyl phthalimide and 4-amino-N-methyl phthalimide.

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It is known that complex molecules in a solution after optical excitation expend a part of their energy due to an energy exchange with the solvent. This process is accompanied by a reduction in time of the frequency of the emitted light quantum, i.e., a shift of the fluorescence spectrum toward the long-wave region during the emission. This spectral shift can be observed experimentally in the dipole dye molecules in viscous polar solutions as a result of Stokes-line excitation.[1-3] The mechanism of the effect is connected with the intermolecular orientational relaxation of the dye-molecule solvate to the equilibrium state from an energetically higher, nonequilibrium Franck-Condon state, in which it is found as a result of variation of the dipole moment of the molecule in the transition to the excited electronic level.

In this paper we describe a new effect, which is also connected with the intermolecular orientational relaxation of the solvate, but in contrast to the aforementioned case, the energy of the emitted quanta increases rather than decreases in time beginning with the moment of excitation. This effect, called "upward" relaxation, was observed in polar dye solutions during anti-Stokes line excitation.

A nanosecond laser fluorometer, analogous to the one described in Ref. 4, was used in the experiments. The fluorometer made it possible to photograph the fluorescence pulses in different parts of the luminescence spectrum (the width of the spectral gap is 12 Å).

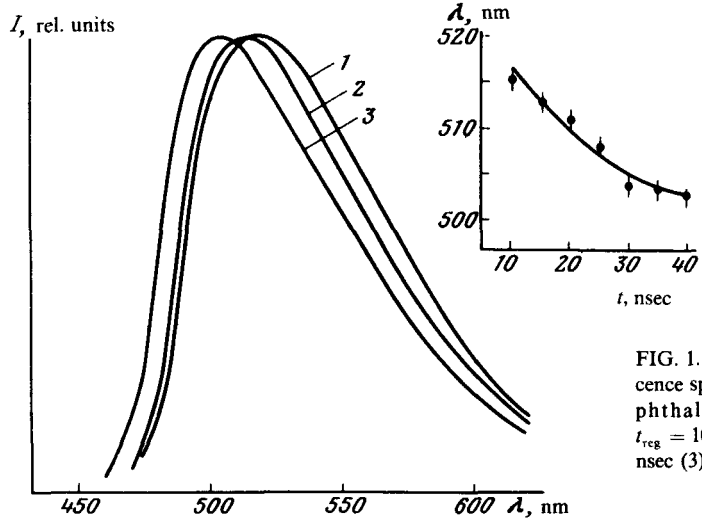

FIG. 1. Time variation of the fluorescence spectrum of 3-amino-N-methyl phthalimide ($C = 10^{-3}$ mole/l); $t_{reg} = 10$ nsec (1), 20 nsec (2), and 30 nsec (3).

A short pulse ($\tau_{0.5} = 2$ nsec) from a tunable dye laser with a narrow ($\Delta\lambda = 0.5$ A) line excited the fluorescence. The afterglow time was calculated from the measured fluorescence pulses on an analog computer using a similar melthod to that described in Ref. 5.

We investigated phthalimide derivatives of 3-amino-N-methyl phthalimide and of 4-amino-N-methyl phthalimide in n-propanol, which are characterized by a strong effect of universal intermolecular interactiong (UIMI) on the fluorescence parameters.

The conducted investigations showed that excitation of the fluorescence in the anti-Stokes region of the spectrum when the time of the orientational relaxation τ_r of the solvate is close to the lifetime of the excited state τ^* of the molecule produces a qualitatively different behavior of the fluorescence spectrum compared to that in Refs. 1–3, where the excitation occurred in the Stokes region of the spectrum. Figure 1 shows the instantaneous fluorescence spectra of 3-amino-N-methyl phthalimide in n-propanol ($T = -90$ °C) at an excitation frequency of 472 nm. This figure also shows the dependence of the location of the maxima of the instantaneous fluorescence spectra on the time after the start of the excitation. As seen in Fig. 1, after the excitation there is a significant shift of the spectrum in time toward the short-wave side relative to its initial position ($\lambda = 515$ nm), to the position corresponding to the emission of equilibrium centers at room temperature ($\lambda = 492$ nm). The very large shift of the maximum of the luminescence spectrum amounts to 13 nm; the relaxation time of the spectrum is ~ 30 nsec. The experiments showed that there is no shift of the luminescence spectrum in time in the frozen solutions.

Figure 2 shows the fluorescence pulses of 3-amino-N-methyl phthalimide, which were photographed in the different parts of the spectrum. The upper right-hand side of Fig. 2 shows the dependence of the afterglow time on the recorded wavelength. It can be seen that fluorescence damping occurs much faster at the long-wave end of the spectrum than at the short-wave end; moreover, the luminescence time at the wave-

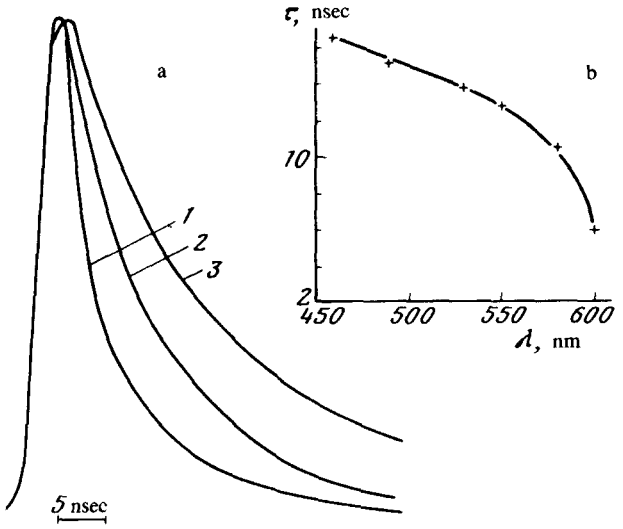

FIG. 2. Time dependence (A) of the fluorescence of 3-amino-N-methyl phthalimide ($C = 10^{-3}$ mole/l) at wavelengths λ_{exc} = 600 nm (1), 530 nm (2), and 460 nm (3) and the spectrum of the afterglow duration (B).

length of 460 nm differs by a factor of > 2.5 from that at the wavelength of 600 nm. Analogous results were obtained for the 4-amino-N-methyl phthalimide molecules.

The observed "upward" relaxation of the fluorescence spectra can be explained in terms of the nonuniform orientational broadening of spectra of complex organic molecules in polar solvents, which was described in Refs. 6 and 7. According to Refs. 6 and 7, the polar dye solutions, in addition to the equilibrium solvate configurations, have an unbroken statistical set of nonequilibrium configurations, which are distinguished by higher energies of the orientational interaction and hence by lower energies of the electronic transition of the dye molecule. In hard matrices (frozen solutions, polymeric media) such an assembly of configurations does not vary in time, i.e., the nonuniform broadening of spectra is fixed. Experimentally it is exhibited by "bathochromic luminescence,[7]" which consists in the shift of the stationary fluorescence spectrum into the red region as a result of transition from the Stokes to the anti-Stokes-line excitation. The anti-Stokes-line excitation in the liquid solutions used by us also selectively excites the solvates in the configurationally nonequilibrium state. Their luminescence initially is characterized by a spectrum which is shifted to the long-wave region relative to the equilibrium position and then in the course of time the configuration of the solvates is brought to the equilibrium state, which is accompanied by a decrease in the energy of the orientational interaction and an increase in the electronic energy of the dye molecule. This process occurs in the observed short-wave shift of the fluorescence spectrum during the emission.

It should be noted that an analogous short-wave shift of the fluorescence spectrum should be observed in nonviscous solutions (when $\tau_r \ll \tau^*$) but in a shorter time interval. Thus Bushuk *et al.*[8] observed during 200-psec a short-wave shift (by 6 nm)

of the amplification spectra as a result of an anti-Stokes-line excitation of an unsubstituted rhodamine in ethanol.

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