Broadening of the S_2-S_0 luminescence spectrum of a rhodamine 6G solution during intense laser excitation

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An intense spectral broadening has been observed in the luminescence from the second excited electronic state, S_2, of the rhodamine 6G molecule at an excitation intensity 10^{29}–10^{30} photons/(cm^2·s). This broadening is attributed to a buildup of vibrational energy when the average time between excitation events is shorter than the vibrational relaxation time τ_r. This relaxation time is estimated to be $\tau_r = (3 \pm 1) \times 10^{-13}$ s.

During the ordinary luminescence of dye solutions with a nanosecond lifetime, the excess vibrational energy which results from the excitation becomes redistributed among all the vibrations and is transferred to the surrounding solvent in a time short in comparison with the lifetime. The luminescence thus comes from an equilibrium vibrational state corresponding to the temperature of the medium. In general, however, the high-lying electronic states of complex molecules have very short lifetimes, on the order of 10^{-12}–10^{-13} s—comparable to the vibrational relaxation time. We have previously[1] determined the quantum yield of the luminescence from the second electronic excited level, S_2, to the ground level, S_0, for rhodamine 6G. Specifically, we found this quantum yield to be 10^{-5}, and we found the lifetime of the S_2 state to be $\tau_2 = 2 \times 10^{-13}$ s. This lifetime is determined by the high probability for a radiationless S_2-S_1 transition. It was also mentioned in Ref. 1 that the spectrum of the S_2-S_0 luminescence is much broader than the corresponding absorption band. This broadening was explained on the basis that there is not enough time for vibrational relaxation to occur over the lifetime in the S_2 level.

We proposed a two-step method[1] for exciting the S_2-S_0 luminescence. In the case of rhodamine 6G, the second harmonic of a neodymium laser ($\lambda = 0.53$ μm) can be used for excitation to the S_1 level, while the fundamental frequency of this laser ($\lambda = 1.06$ μm) can be used for the S_1-S_2 excitation (Fig. 1). The lifetime in the S_1 level is $\tau = 4.2$ ns. The initial state, S_1, of the S_1-S_2 transition is thus an equilibrium state. If the intensity of the excitation in the S_1-S_2 channel is high enough that the average time between excitation events of a given molecule becomes shorter than the vibrational relaxation time, then the S_1-S_2 transition will originate from a nonequilibrium state, and we can expect an additional spectral broadening. To excite the luminescence we used a TYAG-Nd laser with an unstable resonator, which produces a train of five or six pulses with a length of 25–30 ps, a total energy up to 30 mJ, and a divergence near the diffraction level. The intensity of the fundamental frequency of the laser was varied by means of filters F_1 (Fig. 2) without changing the intensity of the second harmonic. Photomultipliers P_1, P_2, and P_3 monitored the energy in the fundamental frequency, in the second harmonic, and in the S_2-S_0 luminescence. The light was focused on the cell

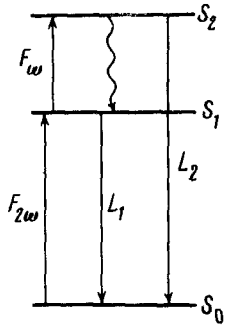

FIG. 1. Level and transition scheme. $F_{2\omega}$, F_ω—Excitation by the second harmonic and by the fundamental frequency of the laser; wavy arrow—radiationless transition; L_1-ordinary luminescence; L_2—S_2-S_0 luminescence.

holding the solution by a lens with a focal length of 1 m. The absolute intensity was determined from the energy of the laser pulse, the known duration, and measurements of the energy distribution over the beam cross section. The experiments were carried out for an ethylene glycol solution of rhodamine 6*G* with a concentration of 10^{-5}M.

Figure 3 shows the measured luminescence spectrum for a relatively low excitation level and for an excitation level an order of magnitude higher [$\sim 5\times 10^{29}$ photons/(cm^2·s)]. The spectral broadening is quite substantial: The half-width increases by 1500 cm^{-1}. This pronounced broadening cannot be explained by a quasiequilibrium "heating" of the molecule by the light: Measurements of the spectrum when the solution was heated to 180 °C, with "weak" excitation, revealed no broadening within the error of these measurements. It must apparently be assumed that in the case of intense excitation the energy released during the radiationless S_2-S_1 transition does not have time to become redistributed over the molecule before the next excitation event. The next S_1-S_2 excitation event forces the molecule into a vibrationally excited state. This state does not manage to relax over the brief lifetime in the S_2 level, so that the spectrum becomes broader.

To evaluate the relaxation time we need to find the average time between excitation events at that intensity at which the spectral broadening first appears. Denoting

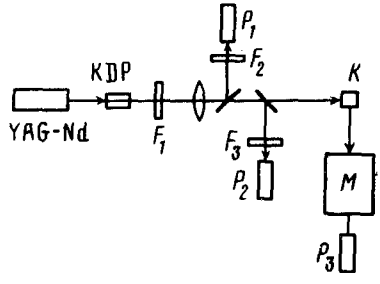

FIG. 2. Experimental arrangement. F_1, F_2, F_3—Light filters; P_1, P_2, P_3—photomultipliers; M—monochromator; K—cell holding the dye solution.

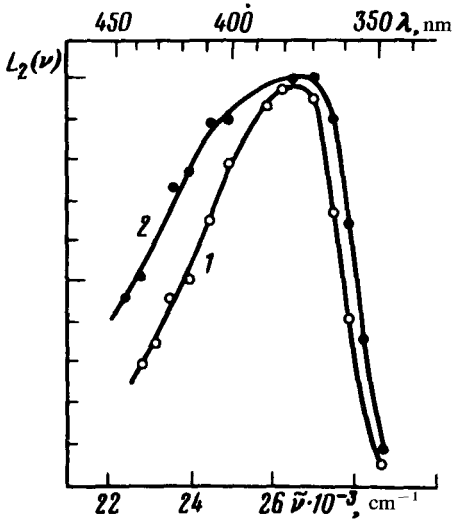

FIG. 3. Spectra of the S_2-S_0 luminescence. 1—Excitation intensity of 5×10^{28} photons/(cm^2·s); 2—5×10^{29} photons/(cm^2·s). These intensities are given in arbitrary units, proportional to the number of photons per frequency interval.

by F the flux density (the number of photons per square centimeter per second) and by σ the effective absorption cross section, we can write the average time between excitation events as $\bar{t} = 1/\sigma F$ in the absence of saturation. In the case of saturation, $\bar{t}$ approaches τ_2. The S_1-S_2 absorption cross section was found in Ref. 1 to be $\sigma = 2\times10^{-17}$ cm^2. Measurements of the dependence of the luminescence intensity on the excitation intensity show that saturation—a deviation from linearity—is not observed up to $F \approx 1.5\times10^{29}$ cm^{-2}·s^{-1}. The spectral broadening becomes noticeable at a slightly higher intensity. We can thus estimate the relaxation time τ_r from the value $F = 1.7\times10^{29}$; we find $\tau_r = \bar{t} = 3\times10^{-13}$ s. The possible error of this estimate depends primarily on the uncertainty in F, which we estimate to be $\pm$ 50%.

We should point out that this estimate of the vibrational relaxation time shows that for the dye molecule this time is considerably shorter than the vibrational relaxation time of simpler molecules, for which direct measurements yield τ_r values on the order of picoseconds or tens of picoseconds (see Ref. 3, for example).

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[2]M. D. Galanin and Z. A. Chizhikova, Zh. Prikl. Spektrosk. **37**, 1010 (1982).
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