

LUMINESCENCE QUENCHING OF COMPLEX MOLECULES IN A STRONG LASER FIELD

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We have observed luminescence quenching of solutions in two-photon excitation by a ruby laser. The effective cross section of this process agrees with the assumption that the quenching is the result of a stimulated transition to high vibrational levels of the electronic ground state.

We measured the dependence of the luminescence intensity of luminescent solutions on the intensity of excitation with the ruby laser. The investigated solutions were transparent at the laser frequency, and the luminescence excitation was by two-photon absorption. We used a pulsed Q-switched ruby laser (rotating prism) with pulse duration approximately 30 nsec and an energy of several dozen Joules. The laser radiation was focused by a lens ($f = 7$ cm) inside a cell with the investigated solution. The luminescence was observed in a direction perpendicular to the laser beam with the aid of an ELU-FT photomultiplier. A filter (CuSO_4 solution) was placed in front of the photomultiplier. A small section (~ 5 mm) near the focus was focused on the photomultiplier window. The beam diameter on this section was approximately 0.3 mm and the power reached 5 GW/cm^2 . Further increase of the power led to breakdown (due apparently to dust particles). The solvents were ethyl alcohol and water, i.e., weakly-non-linear liquids. The geometry of the beam did not change with increasing power, and no self-focusing was observed.

The laser power was varied with the aid of filters. To monitor the power, part of the beam was deflected with a glass plate to a coaxial photocell. The signal from this cell and the luminescence signal from the photomultiplier were fed (through different delay lines) to an SI-11 oscilloscope. Another coaxial cell was placed at the exit of the laser beam from the cell and served to check the transmission and the absence of nonlinear absorption or scattering.

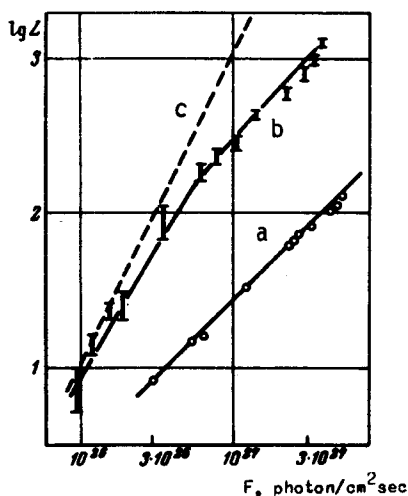


Fig. 1. Transmission (a) and luminescence intensity (b) vs. exciting flux F . The dashed curve (c) is a plot of formula (2).

Figure 1 shows, in a log-log scale, the results obtained for an alkaline solution of fluorescein in water (concentration 10^{-4} g/ml). The straight line a has unity slope and demonstrates the linearity of the transmission. This linearity agrees with the fact that the two-photon absorption is very small ($\sim 10^{-5} \text{ cm}^{-1}$, see [1]) and there is no appreciable nonlinear scattering. The slope of the dashed line equals 2. We see that the luminescence intensity first increases quadratically with the excitation power, and then the increase becomes gradually linear. A quadratic dependence should be observed for two-photon excitation. In the case when the beam was not focused, we obtained the quadratic excitation in the entire in-

vestigated power interval. The deviation from the quadratic law and the changeover to linearity should be attributed to quenching, which increases linearly with the intensity. As seen from Fig. 1, the deviation of the experimental points from the dashed line reaches one order of magnitude, i.e., the quenching is by a factor of 10.

Analogous results were obtained for alcohol solutions of acridine sulfate and 3-amino-phthalimide. No quenching was observed in a solution of anthracene in alcohol in the entire laser-power interval.

The luminescence kinetics is described in the case of quadratic excitation and linear quenching by the equation

$$dn/dt = \delta NF^2 - (1/\tau)n - \beta nF, \quad (1)$$

where N is the number of molecules per unit volume, n is the number of excited molecules (in our case $n \ll N$, $N \approx 10^{18} \text{ cm}^{-3}$, and $n \approx 10^{13} \text{ cm}^{-3}$), F ($\text{cm}^{-2} \text{ sec}^{-1}$) is the flux in photons, δ ($\text{cm}^4 \text{ sec}$) is the two-photon absorption coefficient, τ is the lifetime at the excited level, and β is the effective quenching cross section. In the case when the duration of the exciting pulse exceeds τ , it can be assumed that $dn/dt = 0$. (The same holds when the luminescence intensity is measured by determining the pulse maximum [2].) From this we get

$$n = \delta NF^2 / [(1/\tau) + \beta F]. \quad (2)$$

The luminescence intensity L is proportional to the number of excited molecules, and consequently this formula gives the $L(F)$ dependence. The effective cross sections β were determined by comparing the experimental curves with this dependence. If $F_{1/2}$ is the flux at which quenching by a factor of 2 takes place, then $\beta = 1/\tau F_{1/2}$. The table lists the results obtained for the four investigated solutions. In estimating the flux we disregarded the uneven distribution of the power over the beam cross section, and therefore the absolute value of β may be subject to appreciable errors.

The quenching may be due to absorption of the laser light by the molecules of an excited electronic level. It is well known, however, that in complex molecules transitions to higher states usually produce a non-radiative transition to the first excited state, and not to the ground state, so that such a process does not lead to quenching. We therefore propose

| Substance | $F_{1/2}$ $\times 10^{-26}$ | τ , nsec* | $\beta \times 10^{20}$, cm^2 | $\sigma_n \times 10^{18}$, cm^2 * | β/σ_n |
|---------------------|--------------------------------|-------------------|---|--|------------------|
| Fluorescein | 3 | 4 | 80 | 100 | 0.008 |
| Acridine | 10 | 30 | 3 | 2.4 | 0.014 |
| 3-amino-phthalimide | 12 | 12 | 7 | 12 | 0.006 |
| Anthracene | >200 | 4 | < 1 | - | - |

* The values of τ and σ_n (effective absorption cross section) were taken from published data.

that the observed quenching is due to stimulated emission induced by the laser light. This is accompanied by emission of a quantum at the ruby frequency, and the molecule goes over to

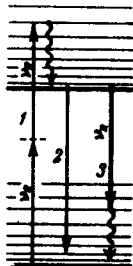


Fig. 2. Transition scheme, ν_R - ruby frequency; 1 - two-photon absorption, 2 - luminescence, 3 - stimulated emission with subsequent radiative transition.

higher vibrational levels of the electronic ground state. This is followed by a non-radiative transition to lower vibrational levels, and consequently such a process leads to luminescence quenching (Fig. 2).

To estimate the value of β that follows from such a scheme we can compare the effective cross section of the stimulated transition with the probability of the spontaneous transition at the same frequency. Using the relation between the Einstein coefficients and assuming that the absorption and luminescence spectra obey the mirror-symmetry law [3], we obtain the following formula

$$\frac{\beta(\nu_R)}{\sigma_a(\nu_a)} = \frac{\nu_\ell^3}{\nu_R^2 \nu_a} \frac{A(\nu_R)}{A(\nu_\ell)}, \quad (3)$$

where ν_R is the ruby frequency, ν_a and ν_ℓ are the frequencies of the maxima of the absorption and luminescence spectra, $\sigma_a(\nu_a)$ is the effective absorption cross section at the maximum, and $A(\nu_\ell)$ and $A(\nu_R)$ are the intensities (the numbers of quanta) in the luminescence spectrum at the maximum and at the ruby frequency. The frequency-dependent factor is equal to 1.6 (for fluorescein). Thus, the ratio of the effective quenching cross section to the absorption cross section at the maximum is of the order of the ratio of the luminescence intensities at the ruby frequency and at the maximum.

We know of no exact measurements of the remote long-wave tails of the luminescence spectra of the investigated substances (such measurements are quite difficult). However, from the long-wave tail of the luminescence spectrum we can conclude that the ratio $A(\nu_R)/A(\nu_\ell)$ is of the order of 0.01. This agrees with the obtained β/σ_n ratios (see the table). For anthracene, this ratio should be smaller, since its spectra are located at shorter wavelengths. No quenching is therefore observed in anthracene.

In conclusion, it can be noted that the observed quenching possibly hinders two-photon excitation of generation in the solutions, since it influences the population of the excited level.

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 [2] M. D. Galanin, V. N. Smorchkov, and Z. A. Chizhikova, *Opt. Spektrosk.* 10, 296 (1965).
 [3] B. I. Stepanov and V. P. Gribkovskii, *Vvedenie v teoriyu lyuminesentsii* (Introduction to Luminescence Theory), Minsk, 1963.