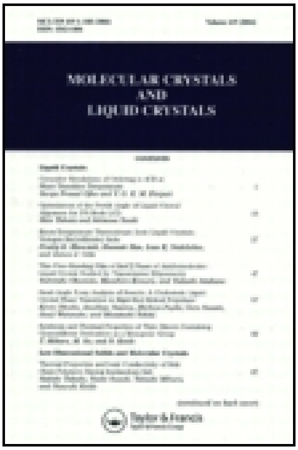

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A Probable Mechanism of Quantum Yield Enhancement for the Photostimulated Conformation Transitions in the Molecules of Liquid Crystals

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A mechanism is proposed and explanation is given of a new "gigantic" optical nonlinearity which has been experimentally discovered in nematic liquid crystals.[1] The suggested mechanism involves microscopic temperature fluctuations caused by the phototransitions of liquid crystal molecules. This results in the enhancement of the quantum yield of the process and considerable changes of the refractive index.

High optical nonlinearity of a new type was discovered in liquid crystals by the authors of Reference 1 and studied in detail in Reference 2. The effect was clearly manifested near the edge of the proper absorbtion band and was shown to be caused by the conformation transformations of molecules due to phototransitions induced by coherent radiation. Appreciable difference between the final state polarizability of phototransformed molecules and initial polarizability, gives rise to macroscopic changes of the refractive index. A probable mechanism of considerable enhancement of the nonlinear optic susceptibility is directly associated with the enhanced quantum yield of the process caused by the local temperature increase in the vicinity of phototransformed molecules of the liquid crystal. The conformation transition is induced by a quantum with energy much higher than thermal activation energy. Therefore, nonradiative relaxation of the photoexcited molecule into conformation or initial state can be accompanied by transfer of considerable extra energy to the environment and excitation of oscillation-rotation degrees of freedom of neighbour molecules, thus increasing the probability of their transition into new conformation states. The number of transformed molecules per one photon absorbtion act determines the effective quantum yield of the process. Inasmuch as it is greater than one, the optical nonlinearity is high.

The parameter of conformation cubic nonlinearity is given by[1]

$$\epsilon_2 \simeq 2\,\langle n\rangle \Delta n/E^2 \tag{1}$$

where Δn is the change of the mean refractive index, E^2 in the field intensity of the incident radiation. The induced change of the refractive index can be easily shown to be

$$\Delta n = \frac{2\pi}{\langle n \rangle} \Delta\beta \, N(J,T) \tag{2}$$

where $\Delta\beta$ is the difference between the polarizabilities of phototransformed and initial molecules. Δn mainly is governed by the concentration of photoexcited molecules $N(I,T)$ which depends on the temperature T and light intensity I.

Suppose a liquid crystal is exposed to two modulated light beams. We assume the law of intensity variation to be

$$I = I_o[1 - m \cos(2\pi X/\Delta)] \tag{3}$$

where $I_0 = I_1 + I_2$, $m = 2(I_1I_2)^{1/2}/I_0$, $\Delta = R/2 \cos\theta$, 2θ is the intersection angle of two coherent beams with intensities I_1 and I_2.

To find the concentration of photoexcited molecules, one has to bear in mind that each molecule that has absorbed a photon with energy $h\nu$, is desactivated for time τ, the energy being transferred to the environment and thus heating it locally. The process leads to the formation of active domains with elevated local temperatures which considerably increase the number of excited molecules. The sum volume of active domains at each time instant is much smaller than the whole volume of the medium, and hence the mean temperature only slightly differs from the initial temperature. Microscopic temperature fluctuations can be involved into consideration in the following way.

Equilibrium concentration of excited molecules for given local temperature is described by the formula

$$N_T = N_0 \exp(-E_a/T) \tag{4}$$

where N_0 is the total concentration, E_a is the activation energy.

A unit volume of the medium, exposed to radiation of intensity I, absorbs per one second $I\alpha/h\nu$ photons, where α is the absorbtion coefficient. Each photon can create one active domain containing N_a molecules. Thus, the concentration of photoexcited molecules is

$$N = \frac{I\alpha}{h\nu} k \tag{5}$$

where k is the effective quantum yield of the process:

$$k = \frac{\tau}{t_1} \int_0^{t_1} dt N_a(t) \exp(-E_a/T) \tag{6}$$

Here $T(t)$ is the temperature in the center of the active domain, t_e is the time required for the relaxation of local temperature to the environment temperature.

The quantities $N_a(t)$ and $T(t)$ satisfy the relation which determines energy balance of the process under consideration[3]:

$$h\nu = C_a N_a(t)\,(T(t) - T_o) \tag{7}$$

where C_a is the characteristic dimensionless heat capacity per one molecule, T_o is the medium temperature.

Having assumed that the spreading of active domains is not caused by any processes other than thermal conduction, we can estimate the number of molecules contained in each domain by the formula

$$N_a(t) = \frac{4}{3}\pi N_o\,(4\chi t)^{3/2} \tag{8}$$

where χ is the thermal conductivity coefficient. We change the integration variables in the integral (6) and perform the integration. Then the parameter of conformation cubic nonlinearity is given by

$$\epsilon_2 \simeq 4\pi\Delta\beta\left(\frac{4}{3}\pi N_o\right)^{-2/3}\frac{\alpha\, C_a}{h\nu}\,\frac{\tau}{t_1}\,\frac{1}{\chi}\left(\frac{h\nu}{C_a E_a}\right)^{5/3} S\left(\frac{T_o}{E_a}\right) \tag{9}$$

where the function $S(T_0/E_n) = 1$ if $C_aE_a/h\nu << 1$ and $S(T_0/E_n) = (2/3)(E_a/T_0)^{2/3}$ $\exp(-E_a/T_0)$ if the inverse inequality occurs.

For the experimental values $E_a = 75$ kj/mole, $\nu = 4.5\ 10^{15}\ \mathrm{s}^{-1}$, $\alpha \simeq 25\ \mathrm{cm}^{-1}$, $\chi \simeq 2\ 10^{-3}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$; $\Delta\beta \simeq 6\ 10^{-40}\ \mathrm{fm}^2$, $\tau = 1$ s, $t_1 \simeq 10^{-11}$, we obtain $\epsilon_2 \simeq 1\ \mathrm{cm}^3/\mathrm{erg}$. The effective quantum yield of the process for the mechanism under consideration is $k = 6 - 8$.

This mechanism was proposed earlier in Reference 4 and confirmed experimentally in Reference 5. The authors applied the method of two beam refraction and discovered that one light quantum excited several (6–8) conformers. Inasmuch as luminescence does not occur, this observation enables one to suggest just the proposed mechanism. "The possibility of its occurrence was confirmed by independent dynamical hologram recordings, with the admixture of conformly stable tetrazen molecules."[5]

We draw the reader's attention to one more probable effect associated with the influence of microscopic temperature fluctuations. The scattering of light with wavelength close to the edge of the absorbtion band must cause the growth of the extinction coefficient[6]

$$f = \frac{2\omega^4}{3c^4}\,\frac{T^2}{\rho C_v}\,\Delta\beta\left(\frac{\partial N}{\partial T}\right)^2 \tag{10}$$

The extinction coefficient depends on the intensity and hence relative contribution in scattering, with regard to the effect of microscopic temperature fluctuations, is given by the expression

$$R = \frac{N}{N_T} = \left(\frac{4}{3}\pi N_0\right)^{-5/3} \frac{I\alpha}{h\nu}\frac{\tau}{t_s}\frac{1}{\chi}\left(\frac{h\nu}{C_a E_a}\right)^{5/3} \exp\left(\frac{E_a}{T_0}\right) S\left(\frac{T_0}{E_a}\right) \qquad (11)$$

Thus, the mechanism of molecular phototransformations in liquid crystals stimulated by microscopic temperature fluctuations can be responsible for the large coefficient of optical nonlinearity. Theoretical estimates are in qualitative and quantitative accordance with the experimental data.

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