

# Optical quenching of coherence of states induced in optical transitions; saturation of the four-wave-mixing signal

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It is suggested that saturation of four-wave mixing and other phenomena involving coherent states of optical centers be regarded as a consequence of a universal optical quenching of coherence of states. In other words, coherent states of centers are put out of phase by photons of the same optical field which creates the coherence. It is shown in the particular case of an ethanol solution of rhodamine B that saturation of four-wave mixing can be described quantitatively over a broad range of the pump power density  $I_p$  in terms of this hypothesized optical quenching of the coherence of states. This hypothesis also makes it possible to determine the optical cross section for this quenching,  $\sigma_\delta$ . The value  $\sigma_\delta = 5.7 \times 10^{-12} \text{ cm}^2$  is found for an ethanol solution of rhodamine B. This figure is four orders of magnitude higher than the absorption cross section  $\sigma_\alpha = 2.2 \times 10^{-16} \text{ cm}^2$ . © 1995 American Institute of Physics.

Even the first papers<sup>1</sup> on the rate of phase relaxation in absorbing centers (molecules in solutions) by four-wave mixing pointed out that the efficiency of the process reaches saturation, which is seen as a decrease in the values of the conversion coefficient  $K$  as the pump power density  $I_p$  is raised. The coefficient  $K$  relates the ratio of the intensities of the signal wave ( $I_s$ ) and the probe wave ( $I_q$ ) to the power densities of the pump waves ( $I_{p1}$  and  $I_{p2}$ ):

$$I_s/I_q \propto K^2 I_{p1} I_{p2}. \quad (1)$$

At low pump power densities  $I_{p1}$  and  $I_{p2}$ , the measured coefficient  $K_{\text{exp}}$  is essentially independent of  $I_{p1}$  and  $I_{p2}$ , remaining proportional to the four-wave-mixing coefficient  $K_{\text{fps}}$ , which describes only the four-wave mixing (or “four-photon scattering”), and to the modulus of the third-order nonlinear polarizability:  $K_{\text{exp}} \propto K_{\text{fps}} \propto |\chi^{(3)}|$ . Relation (1), which was used in Ref. 2, and which is simpler than the other relations used in the literature (e.g., Ref. 1), is intended for use in studying the behavior of  $K$  as a function of the detuning  $\Delta\nu = \nu_1 - \nu_2$  in a narrow interval of small values of the pump power density  $I_p$ . For a study of saturation over a broad range of  $I_p$ , on the other hand, it is necessary to introduce some parameters which depend on  $I_p$ :

$$K_{\text{exp}} \propto K_{\text{fps}} n_0 / n(I_p) F(I_p). \quad (2)$$

Here  $n$  is the concentration of centers in the object, and  $n_0$  is the concentration of centers in the ground state, which are involved in the four-wave mixing and which determine the absorption coefficient of the object,  $\epsilon = n_0 \sigma_\alpha$ . The propagation function  $F(I_p)$  describes the losses of all the optical signals, ( $I_s$ ,  $I_q$ ,  $I_{p1}$ , and  $I_{p2}$ ) in the optically dense object under study. The dependence of the ratio  $n_0/n$  on  $I_p$ , which also describes the saturation of the absorption (a reversible photobleaching), is discussed below.

In Ref. 1 and several other papers, the saturation of four-wave mixing is attributed to the development of higher-order nonlinear processes which compete with the four-wave mixing. However, there is also a good probability that a saturation of the four-wave mixing is caused by an optical quenching of the coherence of states of optical centers which is induced in them by the coherent pumping. In the course of this optical quenching, a center  $M_c^*$ , which has acquired a coherent polarization in the course of the optical pumping, and which is subjected to even a small perturbation by a following photon of the same pump field, experiences a disruption of the phase of the train of oscillations

induced in it ( $M_c^* \xrightarrow{h\nu} M^*$ ). It therefore drops out of the coherent polarization wave which is propagating through the object. The optical cross section  $\sigma_\delta$  for the optical quenching of the coherence of the state of the center must be much greater than the cross sections  $\sigma_\alpha$  and  $\sigma_\gamma$ , for absorption and stimulated emission. In terms of its manifestations, the optical quenching of the coherence of states is similar to an optical quenching of fluorescence.<sup>3</sup> In terms of its mechanism, it is similar to a field-induced broadening of spectral lines, although the cross sections for that process and for the optical quenching of coherence may be different. We wish to stress that this optical quenching of coherence is essentially a universal effect and should be responsible for the influence of the pump power density on the efficiency of all phenomena which are governed by the involvement of coherent states of optical centers.

In this letter we use the example of a solution of rhodamine B to look at some experimental data which not only demonstrate complete agreement with the proposition that an optical quenching of coherence is responsible for the saturation of four-wave mixing but also make it possible to find the value of the optical cross section for the optical quenching of the coherence of a state of a center,  $\sigma_\delta$ .

Curve 1 in Fig. 1 shows the saturation of four-wave mixing in an ethanol solution of rhodamine B as a plot of the ratio of measured values of the conversion coefficient,  $\bar{R}_{\text{exp}}$ ,

$$\bar{R}_{\text{exp}} \left( \frac{I_p}{I_{pt}} \right) = \frac{\bar{K}_{\text{exp}}(I_p)}{\bar{K}_{\text{exp}}(I_{pt})},$$

versus the power density of the pump light,  $I_p$  (the notation will be explained below). Curve 1 is plotted from data obtained by Spiro and the present author<sup>2</sup> on the internal structure of the continuum in the spectra of a group of rhodamines. A few comments about the experimental conditions are necessary here. In those experiments, laser pump pulses produced roughly equal power densities  $I_{p1} \approx I_{p2}$  in the object and also equal durations  $\Delta t_1 = \Delta t_2 = 10$  ns. If the duration of an excited state of rhodamine B in solution is  $\tau = T_1 = 3.35$  ns, it is thus possible to treat the four-wave mixing in this system as a

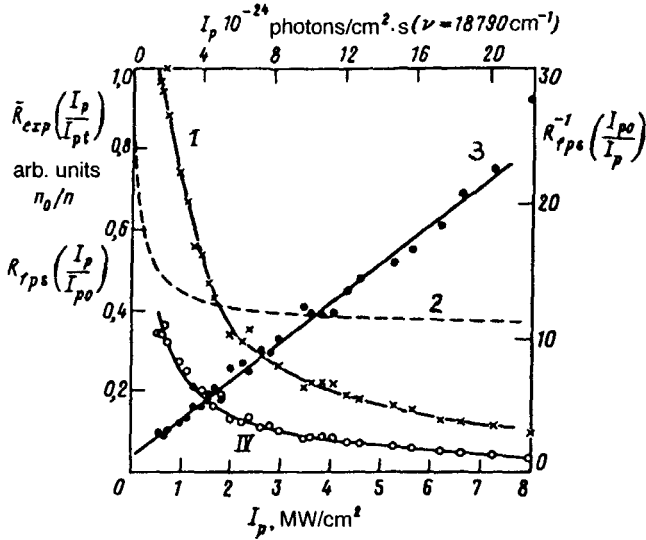


FIG. 1. Ethanol solution of rhodamine B. Saturation of four-wave mixing. Dependence on the pump power density  $I_p$ . 1—Average ratios of experimental values of the total conversion coefficients,  $R_{\text{exp}}(I_p/I_{pt})$ , in arbitrary units; 2—calculated values of the fraction of rhodamine B molecules in the electronic ground state,  $n_0/n$  (saturation of absorption); 3—reciprocal values of the ratio of the four-wave-mixing coefficients,  $R_{\text{fps}}^{-1}(I_p/I_{p0})$ , in absolute units; 4—ratios of the four-wave-mixing coefficients,  $R_{\text{fps}}(I_p/I_{p0})$ , in absolute units.

quasisteady process. The probe wave  $I_q$  was one of the pump waves:  $I_q = I_{p1}$ . The use of the notation  $I_q = I_{p1} = I_{p2}$  as  $I_p$  simplifies the discussion below. Values of  $K_{\text{exp}}$  were found in the experiments of Ref. 2 and in calculations from

$$K_{\text{exp}}^2 = \frac{I_s}{I_q I_{p1} I_{p2}} = \frac{I_s}{I_p^3}. \quad (3)$$

The frequency of the pump light was  $\nu_1 = 18\,790\text{ cm}^{-1}$ ; a detuning  $\Delta\nu = 1\text{ cm}^{-1}$  was sufficient for spatial selection of the  $I_s$  pulse. All four pulses— $I_{p1}$ ,  $I_{p2}$ ,  $I_q$ , and  $I_s$ —are close together near the peak of the absorption band of rhodamine B and have essentially equal absorption cross sections  $\sigma_\alpha = 2.2 \times 10^{-16}\text{ cm}^2$  and stimulated-emission cross sections  $\sigma_\gamma = 1.25 \times 10^{-16}\text{ cm}^2$ . The layer of solution under study had an optical density  $D = 0.9$  at a thickness  $l = 0.1\text{ mm}$ . Three processes develop along the beam direction in this optically dense layer: four-wave mixing, absorption of all the waves, and photobleaching. There are complex interactions among these processes. These interactions require some discussion.

The large optical density of the layer, primarily the absorption of light in it, gives rise to a threshold pump power density  $I_{pt}$ , which is determined by the energy expended on maintaining the concentration ratio  $n_0/n$  corresponding to the value of  $I_p$  in the course of the photobleaching. It is also determined by the need to support generation of a signal wave with an intensity  $I_s$  sufficient for observation against the noisy background. Finally, it is determined by the shape of the initial part of the quenching curve (more on this below). Accordingly, curve 1 in Fig. 1—starting from the threshold power density

$I_{pt} \approx 0.5 \text{ MW/cm}^2 [1.5 \times 10^{24} \text{ photons}/(\text{cm}^2 \cdot \text{s})]$ , at which a measurable signal arises—represents the dependence on the pump power density  $I_p$  of the experimental values of the ratio  $\bar{R}_{\text{exp}}(I_p/I_{pt}) = \bar{K}_{\text{exp}}(I_p)/\bar{K}_{\text{exp}}(I_{pt})$  averaged over the layer. This is the ratio of the constants  $\bar{K}_{\text{exp}}$  determined from measurements of the resultant signal  $I_{ss}$  generated in the optically dense layer. This signal  $I_{ss}$  may be thought of as the sum of the signals  $I_{si}$  generated in  $m$  thin sublayers with values  $n_{0i}$ ,  $I_{pi}$ , and  $F_i$  in each sublayer  $i$ . The values of  $\bar{R}_{\text{exp}}(I_p/I_{pt})$  averaged over the interval  $I_p - I_{pm}$  are obviously expressed in arbitrary units here; the units depend on the threshold power density  $I_{pt}$  and the optical density of the  $D$  layer.

However, we wish to stress that in order to analyze these phenomena we need to know the  $I_p$  dependence of the ratio

$$R_{\text{fps}}\left(\frac{I_p}{I_{p0}}\right) = \frac{K_{\text{fps}}(I_p)}{K_{\text{fps}}(I_{p0})},$$

expressed in absolute units for an optically thin layer with constant values of  $n_0$ ,  $I_p$ , and  $F$ . Here  $K_{\text{fps}}(I_{p0})$  is the value of the four-wave-mixing coefficient for a low power density  $I_{p0}$ , with essentially no optical quenching of coherence.

The conversion from the resultant values of  $\bar{K}_{\text{exp}}(I_p)$ , for the complex signal from the optically dense layer, to the values of  $K_{\text{fps}}(I_p)$ , for a signal from an optically thin layer, is described by

$$K_{\text{fps}}(I_p) = C(I_p) \bar{K}_{\text{exp}}(I_p). \quad (4)$$

The coefficient  $C(I_p)$  in this conversion depends on the distribution of  $n_0$  along the beam in the optically dense layer. Again,  $n_0$  is the concentration of rhodamine molecules in the ground state, which are directly involved in the four-wave mixing [see Eq. (2)]. These ground-state molecules also determine the value of the function  $F(I_p)$ , which reflects the decrease, due to absorption in the object, in the intensities  $I_{p1}$ ,  $I_{p2}$ , and  $I_q$  between the entrance surface and layer  $i$  and also in the intensity  $I_{si}$  from the  $i$ th layer to the exit surface. The value of  $n_0$ , which is determined by photobleaching, depends on  $I_p$ . The actual functional dependence,

$$\frac{n_0}{n} = \frac{2\sigma_\alpha I_p + T_1^{-1}}{2(\sigma_\alpha + \sigma_\gamma)I_p + T_1^{-1}}, \quad (5)$$

which follows from simple kinetic considerations for a two-level scheme of electronic states of the rhodamine B molecule in the steady state, is shown by curve 2 in Fig. 1. Here we have taken into account the circumstance that the sum of power densities  $I_b = I_{p1} + I_{p2}$  is involved in the incoherent photobleaching process (as in the optical quenching of coherence).

Values of the conversion coefficient  $C(I_p)$  were determined for each pump power density  $I_p$  as the ratio of  $I_{s1}$ , the power of the signal wave from the first thin sublayer along the beam path, to the power  $\sum_m I_{si}$ , of the signal from all  $m$  sublayers forming the optically dense layer under study. The values of  $I_{si}$  were calculated from Eqs. (3) and (2)

with the help of (5) for determining  $n_{0i}$  and thus the optical parameters of the process for sublayer  $i$ . The coefficients  $C(I_p)$  were calculated in the second approximation with  $m=5$ .

Using (5), we transformed from the set of average values  $\bar{R}_{\text{exp}}(I_p/I_{p1})$  (curve 1) to the set of values  $\bar{R}_{\text{fps}}(I_p/I_{p1})$  for sublayer  $l$ . The latter values are expressed in arbitrary units, like  $\bar{R}_{\text{exp}}$ . The set of reciprocal values  $R_{\text{fps}}^{-1}(I_{p1}/I_p)$  conforms completely satisfactorily to a linear dependence on  $I_p$  (the points on line 3 in Fig. 1), which is required by the equation for the optical quenching of coherence [Eq. (6b)]:

$$R_{\text{fps}}\left(\frac{I_p}{I_{p0}}\right) = \frac{K_{\text{fps}}(I_p)}{K_{\text{fps}}(I_{p0})} \sim \frac{n_c^*}{n^*} = \frac{T_2^{-1}}{2\sigma_\delta I_p + T_2^{-1}} \quad (6a)$$

or

$$R_{\text{fps}}^{-1}\left(\frac{I_{p0}}{I_p}\right) = 1 + 2\sigma_\delta T_2 I_p. \quad (6b)$$

Expressions (6) were derived from simple kinetic relations under the assumption that the four-wave-mixing coefficient  $K_{\text{fps}}(I_p)$  is a linear function of the concentration of coherently excited centers,<sup>1)  $n_c^*(I_p)$ .</sup>

The conversion from the relative values  $R_{\text{fps}}^{-1}(I_{p1}/I_p)$  to the absolute values  $R_{\text{fps}}^{-1}(I_{p0}/I_p)$  is made by replacing the arbitrary scale to which line 3 in Fig. 1 is plotted by an absolute scale, with the value of  $R_{\text{fps}}^{-1}(I_{p0}/I_p)$ , taken as the new unit of the scale, at the point at which the continuation of this straight line intercepts the ordinate.<sup>2)</sup> This change in scale has been carried out for line 3 in Fig. 1; the resulting absolute values of  $R_{\text{fps}}^{-1}(I_{p0}/I_p)$  have been used to plot the curve for optical quenching of coherence (curve 4 in Fig. 1), which represents Eq. (6a).

The basic results of this study, however, are shown by line 3 in Fig. 1.

In the first place, the good agreement between the experimental data and Eq. (6b) proves that specifically the optical quenching of the coherence of states is the main cause of the saturation of the four-wave mixing. In addition, being universal in nature, the optical quenching of coherence is the reason why the pump power density affects the efficiency of various phenomena involving coherent states. The optical quenching of coherence sets in at low values of the pump power density  $I_p$  and develops up to high values of this power density, at which effects of higher order come into play along with the optical quenching of coherence and cause deviations from line 3 in Fig. 1, starting at about  $I_p = 7-8 \text{ MW/cm}^2$ .

Second, from line 3 we can directly find the cross section for the optical quenching of the coherence of rhodamine B molecules in ethanol:  $\sigma_\delta \approx 5.7 \times 10^{-12} \text{ cm}^2$ . This figure is four orders of magnitude larger than the absorption cross section  $\sigma_\alpha = 2.2 \times 10^{-16} \text{ cm}^2$ . We should stress that studies of the cross section for optical phase relaxation,  $\sigma_\delta$ , hold promise for learning about the details of photophysical processes in molecules.

The accuracy of this estimate of the cross section  $\sigma_\delta$  is determined primarily by the simplifying assumptions adopted in the analysis of the experimental data. Among these assumptions are that the four-wave mixing is a quasisteady process, that the states of the

rhodamine B molecule can be described by a two-level scheme, that average values of  $I_p$  can be used (i.e., that the pump pulses are square), that the four-wave mixing coefficient  $K_{\text{fws}}$  is a linear function of the concentration of coherently excited centers,  $n_c^*$ , and, finally, that it is legitimate to extrapolate curve 3 to the ordinate. These approximations were discussed to some extent in the text above. Since methods for appraising the accuracy and improving it for all these assumptions have been developed quite well, the values of  $\sigma_\delta$  can evidently be determined quite accurately.

Even for the least favorable estimates of the errors, the estimate of  $\sigma_\delta$  given above is correct in order of magnitude.

On the other hand, the primary result of this study—the assertion and proof that an optical quenching of the coherence of states plays a governing role in the saturation of coherence processes—remains valid, regardless of the assumptions adopted above to simplify the analysis of experimental data.

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<sup>1</sup>Evidence in favor of this proposition comes from the agreement of Eq. (6b), which is based on the assumption  $K_{\text{fws}} \propto n_c^*$ , with experimental data. This fact may be useful for explaining the mechanism for the four-wave mixing. As was pointed out earlier, the power density actually involved in the incoherent process of optical quenching of coherence is  $I_\delta = I_{p1} + I_{p2}$ .

<sup>2</sup>This linear extrapolation does not convey the nonlinear behavior of  $R_{\text{fws}}^{-1}$  as a function of  $I_p$  in the region  $I_p < 0.5(\sigma_\delta T_2)^{-1}$ , in which the interval between encounters of a pump photon with optical centers is greater than  $T_2$ , the lifetime of the coherence of a center. It can nevertheless be shown that the intersection point under consideration here is also the beginning of a sublinear quadratic dependence, which converts into straight line 3 near  $I_p = 0.5(\sigma_\delta T_2)^{-1}$ .

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