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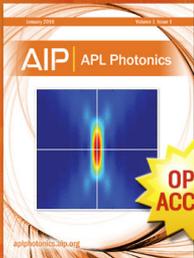
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# Nonlinear Behavior of Solutions Illuminated by a Ruby Laser

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The methods of calculating the deviations from Beer-Lambert's law and other related phenomena in solutions illuminated by a ruby laser are analyzed and criticized carefully. These methods include the steady-state and optically thin approximation as compared with the exact solution of a set of coupled differential equations which describe the temporal and spatial changes of the photons and populations of the various energy levels. Critical evaluation of the validity of the approximation is given. The computations are compared with the experimental data of Beer's law deviations, pulse shaping, recovery of the ground state after excitation, and blue and red fluorescence of solutions of cryptocyanine. A set of absorption cross sections and decay rates which fits best all these experiments is deduced.

## I. INTRODUCTION

Deviations from Beer-Lambert's law of various solutions illuminated by laser pulses have been measured extensively.<sup>1-7</sup> In all cases, solutions were shown to bleach (or to color)<sup>2</sup> when the intensity of the pulse is increased. These deviations from Beer-Lambert's law were interpreted in terms of excitation of various energy levels, thus reducing the number of molecules in the ground state and thus causing the absorption to deviate from the usual Beer's Law. These deviations, whether bleaching or coloring, depend on the various decay rates and absorption cross sections of the material investigated.

Measurements of these deviations can, therefore, give information about these decay rates and absorption cross sections, which is complementary to the information obtained by conventional spectroscopic methods.

There are other phenomena besides the deviations from Beer's Law that result from the changes in the population of the various energy levels. The measurement of these phenomena complement therefore the data obtained from the measurement of the aforementioned deviations. Of these phenomena we have chosen to study the changes in the original pulse shape, the rate of recovery of the ground state after the excitation, and the temporal behavior of the fluorescence.

The change in the pulse shape was measured by Andorn *et al.*<sup>1</sup> in the same experiments as the Beer's deviations were done.

Spaeth and Sooy,<sup>8</sup> measured the rate of recovery of the ground state of cryptocyanine after excitation, by observing the transmission of a probe beam through the cell. Müller and Pflüger<sup>9</sup> measured the blue fluorescence, namely fluorescence which originates from a second excited state, of this material and thus obtained information on the life times of higher levels.

In all these experiments the authors usually explained their own results, ignoring the results of others. It is the purpose of this paper to compare the results of various authors and also various computational methods, and thus to gain better understanding of the phenomena.

If one assumes an energy level scheme, the populations of the various levels are calculated according to the rate equations; once these are known, the change in light intensity and the change in the shape of the pulse are computed. Since the relevant differential equations are coupled, the calculations usually depend on some simplifying assumptions which may lead to errors.

The simplifying assumptions are (a) steady state, and (b) the absorption process is through a thin layer. It seemed worthwhile to do the calculations exactly, and thus to be able to compare the experimental data with a possible model, and also to be able to check where the various approximations made are valid, and under what conditions they fail. We have chosen to work mainly with solutions of cryptocyanine on which there is a wealth of data in the literature.

It should be noted that this method of finding the rate constants is an indirect one and obviously a direct method is preferable, but since the direct measurement of the decay rates is very difficult, a wealth of information can be obtained from this indirect method—regarding both the decay rates and the absorption cross sections of higher levels.

A method using picosecond pulses of a mode locked laser was used to measure directly lifetimes of various levels of colored dyes, especially azulene.<sup>10</sup> However, even this method is subject to assumptions about the energy level scheme used, and the negligibility of some rate constants involved. The indirect method described here, could serve as a consistency check for various relaxation rate constants measured by different techniques, since some experiments have different sensitivities towards the rate processes.

In Sec. II we discuss the general problem of transport of laser radiation through absorbing media, and present the method used for solving the relevant differential equations. In Sec. III we compare the exact solution to the various approximate methods and discuss the criteria of using them. In Sec. IV we fit a calculated model to the data found in the literature—these data include bleaching, narrowing, fluorescence, and recovering of original absorption.<sup>1,2,4,8,9</sup>

## II. TRANSPORT OF LASER RADIATION THROUGH MATTER

Transport equation of monochromatic photons through media is given by

$$(1/c)(\partial I/\partial t) + \nabla \cdot I = - \sum_{i>j} \sigma_{ij} \lambda (N_i - N_j) I + A_i \lambda N_i, \quad (1)$$

where  $N_i$  and  $N_j$  are the populations of the  $i$ th and  $j$ th levels, respectively,  $I$  the photon flux,  $\sigma_{ij} \lambda$  is the absorption cross section between level  $i$  and  $j$ , and  $A_i$  represents spontaneous emission rates from level  $i$  to a level which is located in the appropriate interval below it.

The values of  $N_i$  depend on rate equations such as

$$\partial N_i / \partial t = \sum_j \sigma_{ij} \lambda I (N_i - N_j) + \sum_{j>i} k_{ij} N_j, \quad (2)$$

where  $k_{ij}$  are the decay rates of upper levels  $j$  to lower level  $i$ , including both radiative and radiationless transitions, under the constraint  $\sum_i N_i = N_0$ , i.e., the total number of molecules  $N_0$  in all levels must be conserved, since we assume that no chemical changes are taking place.<sup>9</sup> The population change  $\partial N_i / \partial t$  of state  $i$  is described by the following processes: (1) Linear consecutive absorption processes; (2) stimulated emission at laser wavelength; (3) thermalization of excited states. Quite generally one should include in Eq. (1) photons from other wavelengths, but we shall avoid this needless complication in dealing with monochromatic laser radiation. We have also ignored in these equations, the molecular diffusion and simultaneous double photon absorption. The diffusion of large molecules as cryptocyanine is small, and on the short time scale (in the nanosecond range) they do not appreciably change their position.

The double photon absorption by virtual transitions, can be easily introduced into the equations by including terms which depend on  $I^2$ . The equations including these terms can be handled by the same methods described below. However, since strong one photon absorptions to higher levels are known to exist in cryptocyanine solutions, there is no point in including the weak simultaneous double photon processes.

Equation (1) is greatly simplified when dealing with collimated laser fluxes, in experiments which measure deviations from Beer's Law and pulse shapes.<sup>1</sup> In the first place, the second term on the left is changed to  $\partial I / \partial x$ , since there is no flux in other directions. The first term on the left describes creation (or destruction) of photons at constant spatial position. This occurs only through spontaneous emission (second term on the right), but since the latter is direction independent, in contrast to the induced emission, and is evenly distributed over  $4\pi$  steradians, the amount measured in the particular direction of the beam is small and can be ignored. Scattering processes have also been ignored for the same reason. This point has been ignored by

some authors<sup>11</sup> and introduces needless complications. Even after these simplifications, coupled differential equations are obtained which are usually solved by approximate methods described in Sec. III. We also ignore the self-focusing problem which is more pronounced in long cells.<sup>12</sup>

Equation (1) after the simplifications will take the form:

$$\partial I / \partial x = - \sum_{i>j} \sigma_{ij} (N_i - N_j) I. \quad (3)$$

It should be emphasized again that there is no analytical solution to Eqs. (2) and (3), even in the simplest case of only two levels, and one usually depends on one form of approximation or another which will be dealt with in the next section.

## III. METHODS OF CALCULATION

### A. Steady State

The values of  $N_i$  found from solution of  $\partial N_i / \partial t = 0$  and  $\sum_i N_i = N_0$  are introduced into Eq. (3), for  $\partial I / \partial x$  and the algebraic equation integrated.

As was shown elsewhere,<sup>1</sup> the integrated form of  $I = I(x)$  depends only on the number of levels connected by induced emission and absorption, all other levels and rates do not influence the mathematical form of the equation. In case of one absorption, this equation is

$$\ln(T/T_0) = (2/J) I_0 (1 - T) \quad (4)$$

and in case of two absorptions, the equation is:

$$\ln(T/T_0) = A \ln[(B + I_0)/(B + T I_0)] + (2/J) I_0 (1 - T), \quad (5)$$

where  $T$  and  $T_0$  are the measured and Beer's transmissions respectively,  $I_0$  the initial flux of photons, and  $A$ ,  $B$ , and  $J$  are constants which depend on all rate constants and absorption cross sections. Their exact form must be calculated for each model specifically.<sup>1</sup>

It must be borne in mind that the steady-state equations contain less information than the physical reality, since any model depends on more rate constants than the number of constants in Eqs. (4) or (5).

Choosing the correct set of rate constants from the experimental results is, therefore, somewhat arbitrary and depends very much on our physical intuition. This is the main objection to using this method in spite of its obvious simplicity.

### B. Optically Thin Method

One assumes that the cell is optically narrow enough so that the populations  $N_i$  do not depend on the position but only on the time.

Therefore, the solution is:

$$I_{\text{out}}(t) = I_{\text{in}}(t) \exp\left[- \sum_{i>j} \sigma_{ij} (N_i - N_j) l\right], \quad (6)$$

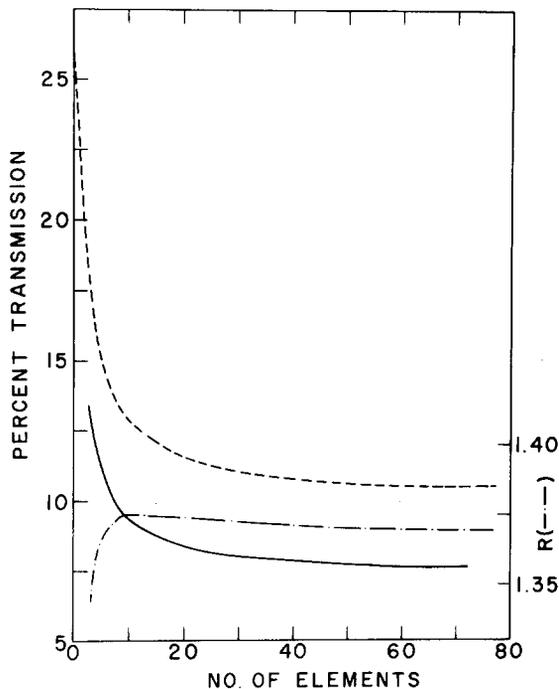


FIG. 1. Convergence test for the solution of Eqs. (2) and (3) for energy level scheme of Fig. 3. The rates and cross sections are those given in the text.  $I_0 = 5 \times 10^{25}$  photons/cm<sup>2</sup>·sec. Pulse width 20 nsec and initial absorbency 3.6. --- peak transmission; — energy transmission; - - - narrowing parameter: ratio between peak transmission to energy transmission.

where  $l$  is the cell length and  $N_i$  and  $N_j$  are the solutions of the rate Eq. (2).

This method is superior to the steady state method since it depends explicitly on all the rate constants and absorption cross sections. However, it is more time consuming. In many cases it gives reasonable results as we shall see below.

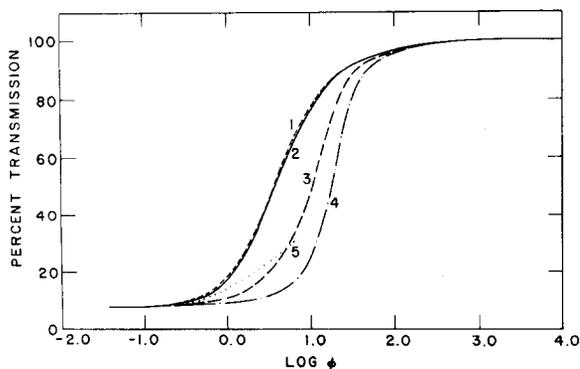


FIG. 2. Transmission vs intensity (reduced units) for two level system. (1), exact calculation  $D=178$  (using Ref. 4 values of  $k=7.05 \times 10^9$  and half-width 25 nsec); (2), steady state calculation  $D=0.25$ ; (3), optically thin,  $D=0.25$ ; (4), exact solution  $D=0.25$  (in 2, 3, 4,  $k=10^7$  sec<sup>-1</sup>); (5), experimental data of Ref. 4.

### C. Exact Solution

Equations (2) and (3) are solved numerically for a particular energy level scheme, namely for a given set of decay rates  $k_{ij}$  and absorption cross sections  $\sigma_{ij}$ .

The cell length is divided into many elements of width  $\Delta$  in such a way that  $\sigma_{ij}N_i\Delta \ll 1$ , (usually taken as 0.01), namely each element is optically thin. For each thin element the set of Eq. (2) is solved by the Runge-Kutta-Gill method with variable time increment and error control. At all times, the time increment is kept smaller than the smallest relaxation time  $k_{ij}^{-1}$  of the system. The solution for the  $n-1$  element is used to calculate the pulse going out from this element and entering element  $n$  [according to Eq. (6) putting  $\Delta$  instead of  $l$ ].

Since bleaching occurs, the optically thin condition can still be maintained within each element for larger  $\Delta$ 's. The program provides for such variations in the element width.

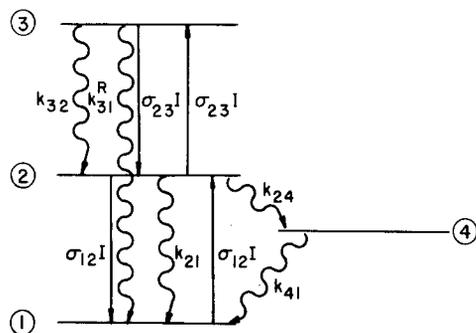


FIG. 3. Four energy level diagram with two absorptions and one triplet.

The initial pulse entering the cell is either Gaussian shaped, or the experimental one. The program calculates: (a) Energy level populations at each point of the cell as a function of time; (b) laser intensity time profile after every element of the cell; (c) transmission—both peak pulse and total energy (namely the ratio of the areas of the transmitted and incident pulses); (d) the temporal behavior of the total fluorescence from the cell—by integrating the number of molecules  $[N_i(x, t)]$  in the fluorescing level, on the cell length; (e) “mean free path” of a photon, namely, the distance in which the transmission is reduced to 50%.

The calculations were done on a C.D.C. 6600 computer at the Tel-Aviv Computational Center.

In Fig. 1 the check for the convergence of the method is shown. This is done by calculating the transmission for increasing number of elements in the cell. It is seen that 50 elements are enough to bring the transmission within 1% of the final one, even for the high absorbency shown in this particular example. The change of shape of the pulse, namely the ratio of peak to energy trans-

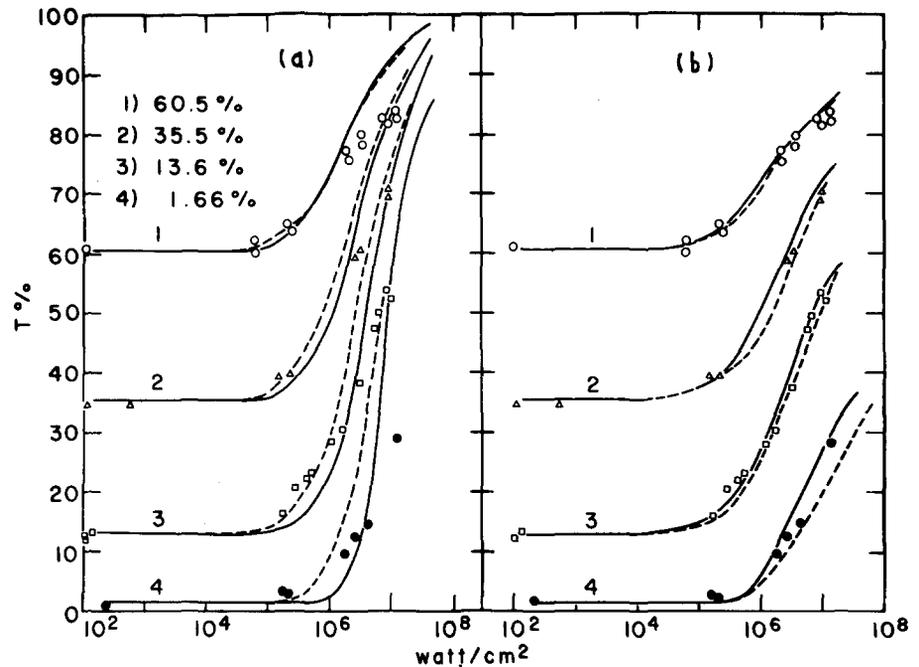


FIG. 4. Energy transmission vs laser intensity from Ref. 2 experiments. (a) Model and rate constants of Ref. 2 Fig. 9. (b) Model of Fig. 3 with rate constants of this work.  $\circ$ ,  $\Delta$ ,  $\square$ ,  $\bullet$ , experimental points of Ref. 2. — exact calculation; --- thin optics calculation.

mission converges even faster. It should be noted that the case of one element is identical to the optically thin method since  $\Delta=l$ . It is seen that in the example shown, the optically thin method fails completely and erroneous results are obtained.

In order to gain some feeling into the usefulness of the various approaches, we calculated a simple two level system in steady state, optically thin assumptions, as compared with the exact solution. Figure 2 shows the transmissions vs peak intensity in reduced units.

The transmission depends on the peak intensity [which in terms of reduced units is described by  $\phi = (2\sigma/k)I_0$ ], the pulse shape (described by its width  $D$  in units of  $k^{-1}$  the reciprocal decay rate) and the initial transmission  $T_0$ . In every two level calculation the transmission increases with intensity from its initial value  $T_0$  to the value of total bleaching  $T=100\%$ , as one can see intuitively. The steady state method is obviously, as its name implies, independent of the pulse shape. The exact calculation approaches the steady state as  $D$  increases, i.e., as the pulse width approaches the half-life of the level, one can safely use the steady state as an approximation. The thin optics assumption is seen to be a somewhat better approximation than the steady state one for the case of narrow pulses.

#### IV. CRITIQUE OF PREVIOUS RESULTS

Several authors examined different energy schemes in order to explain their results. We have checked each of the proposed models with the best parameters given by the authors, by making the exact calculations and the calculations based on one or more of the simplifying assumptions. In each case there are some discrepancies,

as will be shown in the following discussion. As a consequence of this discussion, we have chosen to work with the simplest model, 4 levels, two absorptions and one triplet, Fig. 3, consistent with the experimentally proven features and have found the best set of parameters in order to fit as many experiments as possible. The results are summarized in Table I.

Degiorgio and Potenza<sup>4</sup> tried to explain their transmission results on the basis of the steady-state two level model (Fig. 2). Since their pulse is wide compared with the decay rate, the steady-state calculation is valid, but it falls widely apart from the experimental results. Moreover, no other decay rate can be found to fit this data—the two level scheme is therefore definitely incorrect. Better fit was obtained by Giuliano and Hess<sup>2</sup> by introducing more intermediate levels using steady state and the optically thin methods. Some of their calculations include absorption from excited states, but these calculations are incomplete since they do not include conservation of matter. Figure 4(a) reproduces the experimental results of those authors together with the calculated points according to the thin optics assumption and exact integration. The two calculations do not differ appreciably since the authors have done the experiments with relatively low absorbances.

At very high intensities, the two methods converge, since bleaching reduces the transmission and makes the sample optically thin. It is seen that there is a discrepancy between the experimental transmission curve, and both the exact and optically thin calculations manifested mainly in the top graph. For the present energy scheme, this discrepancy cannot be accounted for by another choice of parameters. A different scheme which

TABLE I. Summary of rate constants and absorption cross sections, used in this work.

Author	$\sigma_{12}^{a,m}$	$\sigma_{23}^a$	$k_{21}^b$	$k_{32}^b$	$k_{24}^b$	$k_{41}^b$	$k_{31}^{R\ b}$	Figure	FWHM (nsec)
Degiorgio, Potenza <sup>d</sup> <sup>e</sup>	$5 \times 10^{-16}$	...	$7.05 \times 10^9$	...	...	...	...	2 Plot 1	25
... <sup>d</sup>	$5 \times 10^{-16}$	...	$10^7$	...	...	...	...	2 Plot 2, 3, 4	25
Giuliano, Hess <sup>2</sup> <sup>e</sup>	$5 \times 10^{-16}(\sigma_{13})$	...	$10^{10}$	$10^{11}$	$8 \times 10^8$	$2 \times 10^8$	...	4(a)	69.5
Andorn, Bar-Eli <sup>1</sup>	$5 \times 10^{-16,m}$	$1.25 \times 10^{-14}$	$4.9 \times 10^{10}$	$5 \times 10^{13}$	$10^9$	$10^7$	...	5(a), 6(a), 7	19
Spaeth, Sooy <sup>8,f</sup>	$5 \times 10^{-16}$	...	$2.3 \times 10^{10}$	...	$1.8 \times 10^9$	$10^7$	...	8	27
This work <sup>g</sup>	$5 \times 10^{-16}$	$3.1 \times 10^{-16}$	$5 \times 10^9$	$1.0 \times 10^{11}$	$1.4 \times 10^8$	$7 \times 10^7$	$0.95 \times 10^6$	2 Plot 1, 4, 4(b), 5(b), 6(b) 7, 8, 9, 10	...
Literature estimates	$5 \times 10^{-16}$	$10^{-16}, 10^{-14,h}$	$1.2 \times 10^{10,i}$ $2 \times 10^{10,j}$ $5 \times 10^8,k$ $\geq 10^7,l$	$5 \times 10^{12}$	$5 \times 10^8$	$5 \times 10^6, 5 \times 10^7 \text{ }^l$	$2.4 \times 10^7 \text{ }^b$	...	...

<sup>a</sup> Units  $\text{cm}^2$ .<sup>b</sup> Units  $\text{sec}^{-1}$ .<sup>c</sup> Model contains two levels only.<sup>d</sup> Steady-state deviates if pulse narrows compared to  $k_{21}$ .<sup>e</sup> Absorption to level 3 which is vibrational level of level 2 (Ref. 2 Fig. 9).<sup>f</sup> Parameters for solution in propanol.<sup>g</sup> Best fit to data of Refs. 1, 2, 8, 9, 16.<sup>h</sup> Reference 1.<sup>i</sup> References 2 and 21.<sup>j</sup> Reference 22.<sup>k</sup> References 13 and 23.<sup>l</sup> Reference 7.<sup>m</sup> Measured from spectrum of Ref. 1.

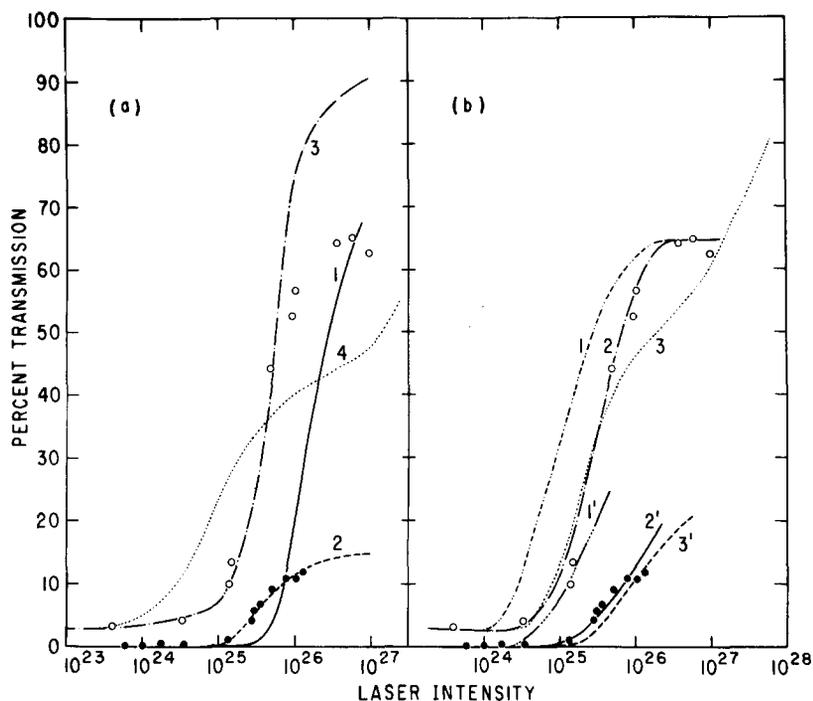


FIG. 5. Transmission vs laser intensity. Experimental points of Ref. 1. Energy scheme of Fig. 3. ●,  $OD_0=3.6$ ; ○,  $OD_0=1.55$ . (a) Reference 1 parameters.  $OD_0=3.6$ . —, exact calculation; ---, steady state approximation;  $OD_0=1.55$ . - · - ·, exact calculation; · · ·, steady state approximation. (b) Parameters of this work.  $OD_0=3.6$ . —, exact calculation; ---, steady state approximation; - · - ·, thin optics approximation.  $OD_0=1.55$ . - · - ·, exact calculation; · · ·, steady state approximation; - · - ·, thin optics approximation.

includes absorption from the excited state can overcome this discrepancy as was shown earlier.<sup>2,6</sup>

Although this thin layer assumption seems fairly adequate, one can see the deviations at high absorbancies, which became even more pronounced in Ref. 1; moreover, it is impossible to account for other experimental features such as anomalous blue fluorescence, rate of recovery of ground state, etc., as mentioned above. The results of Ref. 1 are reproduced in Fig. 5.

Using the scheme depicted in Fig. 3, a second absorption was included, with steady-state assumption. (The authors model differs slightly from that of Fig. 3 by an additional vibrational level to the first excited level, but this does not introduce significant differences, since the vibrational level was taken by Andorn *et al.*, to relax very rapidly to the first excited state.)

It is seen that the set of parameters adjusted to fit the experimental data under steady state assumption in one case ( $OD_0=3.6$ ) does not predict the correct results in the other case ( $OD_0=1.55$ ). Moreover the agreement of the steady state calculation to the experimental data is very misleading since the exact calculation with the same parameters yields quite different results. The inclusion of a triplet state, known to play an important role in the processes of molecular relaxation (see below), makes the response time of the system comparable or even larger than the laser widths, causing the gross discrepancy of steady-state calculation. In a similar way, in the case of the two level system (Fig. 2) a steady-state approximation is valid provided the response time of the system is short compared to the laser pulse width.

Since the initial absorbency in the work of Andorn

*et al.*,<sup>1</sup> is much higher than in the experiments of Ref. 2, one can see the complete failure of the optically thin approximation. In Fig. 5(b) this latter approximation is compared with the exact calculation (the set of parameters is the best one given in Table I). The optically thin approximation overestimates the transmission (as can also be seen in Fig. 1).

These authors also measured the change of the transmitted pulse shape. In Fig. 6 the narrowing of the pulse (defined as the ratio of peak pulse to area transmissions) is plotted vs the intensity of the pulse. While the steady-state method yields results which have the same behavior as the experimental data, the exact calculation with the same rate constants show qualitative differences. The maximum narrowing appears at much higher intensity, and also a widening effect ( $R < 1$ ) is seen at medium intensities [Fig. 6(a)]. In Fig. 7 the behavior of a single pulse is reproduced. Again while the steady-state approximation yields a satisfactory solution, the exact calculation employing the same parameters differs widely both from the experimental and the steady-state calculation. The transmitted pulse is wider (not narrower) and much more asymmetric than the incident one.

Spaeth and Sooy<sup>8</sup> have examined the rate of recovery of the ground state, by measuring the transmission at the laser wavelength of a pre-excited sample. They conclude that another level exists, probably a triplet, via which part of the excitation reverts to the ground state. Their model includes one absorption and a triplet.

Figure 8 reproduces their experimental results and the calculated ones both with the authors model and with the model of Fig. 3 and the best parameters

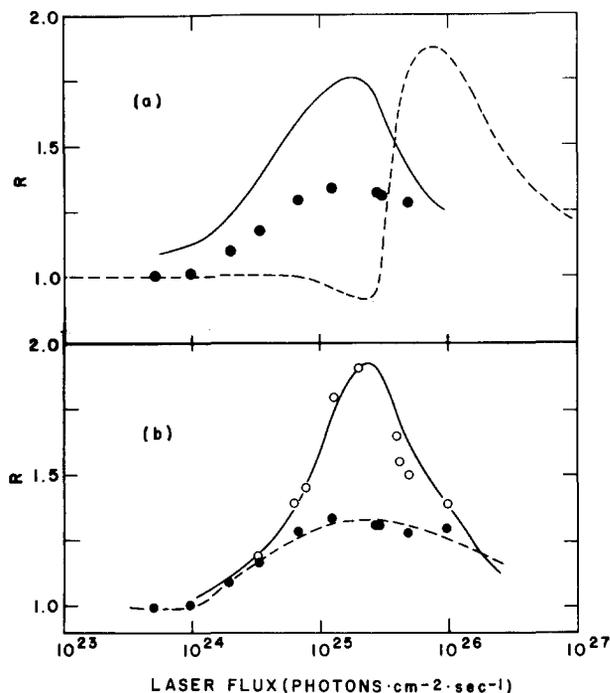


FIG. 6. Narrowing parameter  $R$  (ratio of pulse peak/pulse energy) vs laser energy. Experimental points Ref. 1. (a) Parameters of Ref. 1. —, steady state; ---, exact calculation; ●, experimental points  $OD_0=3.6$  Ref. 1. (b) Parameters of this work. —, calculated  $OD_0=5.4$ ; ○, experimental  $OD_0=5.4$ ; ---, calculated  $OD_0=3.6$ ; ●, experimental  $OD_0=3.6$ .

described below. The parameters of the chopped exciting pulse and the probe pulse were also taken from the above reference. It is clearly seen that although their main conclusion is probably correct, namely the existence of an intermediate triplet state, their model and rate constants are probably in error.

Similar conclusions were obtained by Pine<sup>13</sup> from the temperature behavior of cryptocyanine fluorescence. The existence of the triplet can therefore be definitely concluded from the last two experiments.

One can deduce from these calculations that (a) a second absorption to a higher excited state is needed

to explain the results, and (b) an incorrect choice of parameters combined with an approximate solution of the equations can result in a misleading fit to the experimental data. Moreover, as discussed below, a correct set combined with an approximate method of computation can also result in a misfit to data; (c) as a result of using an approximate solution, the best parameters of one experiment do not usually fit all other experiments. The simplest model with a set of parameters which will best describe all the above experimental data is, therefore, described below.

## V. A SIMPLE METHOD

The energy level scheme shown in Fig. 3 is the simplest one which conforms with the experimental evidence: (a) It contains an intermediate triplet level.<sup>8,13</sup> Attempts to measure delayed fluorescence<sup>9</sup> and phosphorescence<sup>7</sup> in cryptocyanine, and thus to prove directly the existence of a triplet state were unsuccessful; however, it was found in other cyanine dyes.<sup>14</sup> (b) It has a second absorption as suggested earlier<sup>1,2,6,7</sup> and shown also in this work. Further evidence that such absorption participates in laser absorption experiments was given by Müller and Pflüger<sup>9</sup> who measured the anomalous "blue" fluorescence of cryptocyanine. This material manifests normal "red" fluorescence<sup>15</sup> at 740 nm when excited to its first singlet, but when laser excited, an additional "blue"—460 nm—fluorescence<sup>16</sup> appears. This radiation is probably emitted from a second excited singlet state. This state is populated by a second absorption from the first excited singlet. Similar "blue" fluorescence was discovered in phthalocyanines.<sup>17</sup> Also the spectrum of cryptocyanine shows an absorption in the uv region, a fact that supports the suggestion of a second singlet. We have used this model and found a set of parameters that will best fit the experimental data given in the literature.

The experimental data we have chosen to fit are the following: (a) Bleaching and deviations from Beer's law.<sup>1,2</sup> (b) Shaping the laser pulse traveling through the solution.<sup>1</sup> (c) Rate of recovery of the original

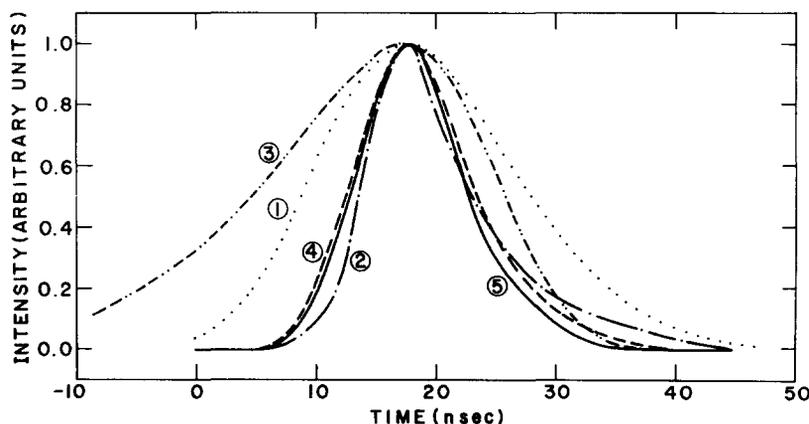


FIG. 7. Incident, transmitted and calculated pulse shapes  $OD_0=5.4$  (experimental Ref. 1). ···, incident pulse; -·-·, transmitted pulse. Parameters of Ref. 1. ---, exact calculation; - - - steady state approximation parameters of this work; —, exact calculation.

absorption.<sup>8</sup> (d) Intensity and temporal dependence of the "blue" fluorescence.<sup>9,16</sup> (e) Intensity and temporal dependence of the "red" fluorescence.<sup>9</sup>

(a) *Deviations from Beer's law.* In Figs. 4(b) and 5(b) we see the experimental and calculated curves of Refs. 1 and 2. The rate constants used for the calculation are given in Table I. Also given in these figures are the approximate calculations, namely steady state and thin optics, with the same set of parameters. Both approximate methods deviate quite appreciably from the exact calculation, approximations became good at very low intensities since then the levels populations do not change very much. The thin layer approximation also approaches the exact calculation when the intensity is very high since, under bleaching conditions, there is a constant difference which is time independent between the level populations; thus the laser pulse is not further attenuated. The advantages of the exact calculation compared to the approximate solutions is clearly demonstrated.

(b) *Pulse shaping.* It was previously shown<sup>1,2</sup> that the pulse changes its shape and usually narrows while passing through the sample. The narrowing effect is best measured by the ratio of intensity to energy transmissions. This ratio equals one when the pulse does not change its shape. In Fig. 6(b) we plot this ratio against laser intensity. During variation of the rate and absorption parameters, it was observed that the shaping effect is particularly sensitive to  $\sigma_{23}$ . Increasing the excited state absorption reduces the amount of narrowing and can even result in pulse broadening at high  $\sigma_{23}$  values. In the three level system ( $\sigma_{23}=0$ ) the narrowing effect is thus more pronounced than the corresponding value in a four level system. The intersystem-crossing rate constant  $k_{24}$  has relatively small narrowing effect, thus small  $k_{24}$  (approach to two level system) favors higher  $R$  values. Short first excited singlet lifetimes  $k_{21}$ , also

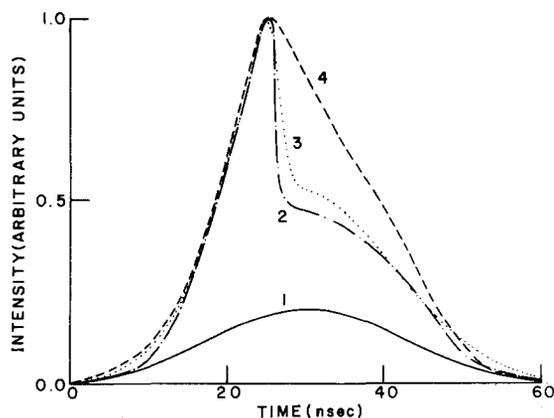


FIG. 8. Transmitted pulse shape of a pre-excited cryptocyanine. —, transmission of probe pulse through unexcited cell, ---, transmission of probe pulse through excited cell; experimental; ···, calculated with model of Fig. 3; - · - ·, calculated with the model and rates of Ref. 8.

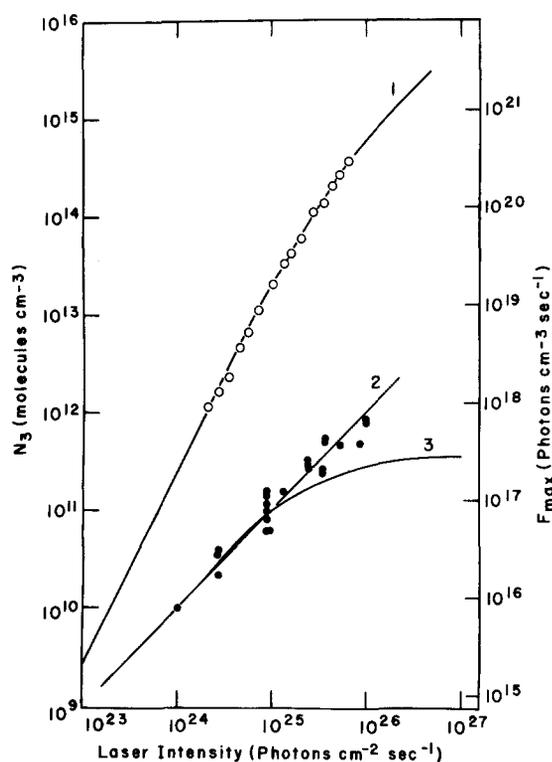


FIG. 9. ○ Intensity dependence of blue fluorescence Ref. 16 to scale. ● Intensity of red fluorescence (Ref. 9—arbitrary scale). (1) Calculated population of level 3—to scale. (2) Best straight line through experimental points (Ref. 9). (3) Calculated population of level 2.

tend to increase  $R$ . This ratio is therefore a very sensitive method for determining the rates because a slight change in the constants gives a very large change in the pulse shape. Figure 7 shows the whole pulse together with the calculated one. It should be mentioned that narrowing effects in cryptocyanine are pronounced only at high optical density solutions,<sup>1</sup> a fact making the optically thin method inadequate for calculating these effects. The steady-state method, assuming usually that the exciting pulse is very wide, is shown to predict rather poorly the shaping effects.

Huff *et al.*<sup>18</sup> base most of their conclusions on the laser pulse shaping in indanthrone solutions, on the data analyzed by the steady-state assumption. It is seen that erroneous conclusions regarding decay rates can be obtained which will fit the data quite well. One should always proceed with caution while using either approximation.

There is experimental evidence that the high intensity pulse lags for about 5 nsec behind the low intensity one. It was not possible to measure this effect accurately.<sup>19</sup> A similar lag was obtained in the exact calculations. This lag will not appear at all under the steady-state calculation, but could be predicted by the optically thin method. Since this effect is more pronounced at high absorbencies, this method will not be useful in calculating the lag. An accurate measurement

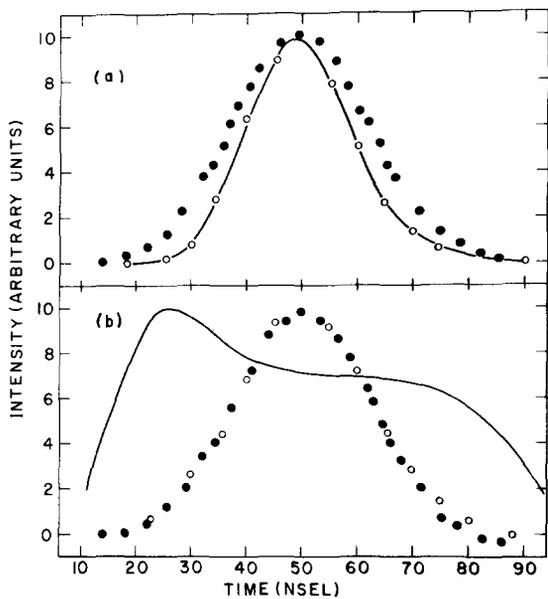


FIG. 10. (a) ●, laser pulse 1 MW/cm<sup>2</sup> peak intensity; ○, blue fluorescence calculated; —, blue fluorescence experimental. (b) ●, laser pulse; ○, Red fluorescence calculated and experimental  $I_0=1$  MW/cm<sup>2</sup>; —, Red fluorescence calculated  $I_0=57$  MW/cm<sup>2</sup>.

of this effect will be very useful for the accurate knowledge of the parameters.

(c) *Recovery data.* In Fig. 8 the results of Spaeth and Sooy<sup>8</sup> are shown together with the calculated ones. The agreement is as good as one can expect under the circumstances.

The results of these experiments depend mainly on the ratio of the decay rates from the first singlet and on the lifetime of the triplet. The exact calculations confirm the results of Gires<sup>7</sup> and Spaeth and Sooy<sup>8</sup> for triplet decay rate, and gave reasonable branching ratio, namely,  $k_{21}/k_{24}=50$ .

The other parameters—second absorption and decay

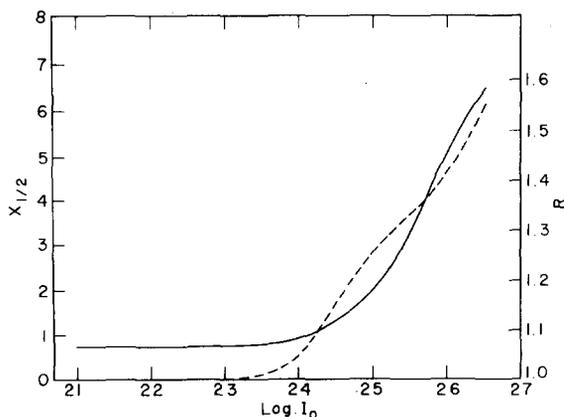


FIG. 11. —, mean free path of photon vs laser intensity; ---, maximum pulse narrowing vs laser intensity.

rate from the second singlet, have very little influence on the results of this experiment.

(d) *Blue fluorescence.* The dependence of the blue fluorescence photon density on laser intensity was measured by Zunger and Jortner<sup>16</sup>; their results are reproduced in Fig. 9. These values depend on the population of second singlet  $F_{max}=k_{31}^R N_3$ , where  $F_{max}$  is the maximum fluorescence photon density at each intensity,  $N_3$ —the population of level 3, summed over the sample volume and  $k_{31}^R$ —the radiative decay rate from level 3 to level 1. The population  $N_3$  calculated from our model is given in the same figure and fits very well with the experimental points. The value of  $k_{31}^R=0.95 \times 10^6$  sec<sup>-1</sup> is obtained by this method and should be compared to  $k_{31}^R=2.4 \times 10^7$  sec<sup>-1</sup> given by Andorn

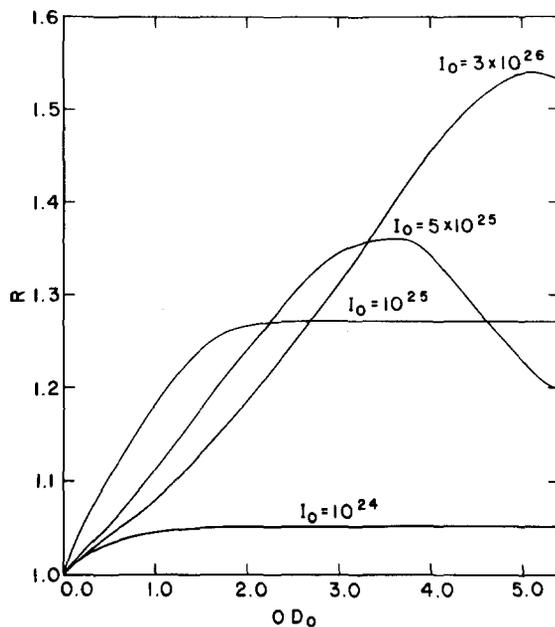


FIG. 12. Pulse narrowing vs initial absorbency.

*et al.*,<sup>1</sup> calculated from integration of the 310 nm band. This is a very good agreement considering the inaccuracies in the integration of the spectrum.

The plot has a slope of 2 at low intensities indicating an  $I^2$  dependence, and then decreases, since there is a greater influence to induced emission. Similar behavior is expected in the case of simultaneous double photon absorption and only accurate measurements of deviation from  $I^2$  dependence at higher intensities together with appropriate calculation can decide between the two alternatives. The parameter governing mostly the fluorescence  $I$  dependence is  $\sigma_{23}$ . Measurements of the saturation effect of the fluorescence at very high intensities will thus provide a better means to estimate  $\sigma_{23}$ .

The temporal behavior of the fluorescence pulse was measured by Müller and Pfüger<sup>9</sup> and their results are reproduced in Fig. 10(a). The agreement between the

calculated and experimental points is very good. The ratio between the width of laser and fluorescence pulses is  $\sqrt{2}$ , as is expected from the  $I^2$  dependence, and confirmed by experiment.<sup>9</sup> A similar temporal dependence is expected if a mechanism of simultaneous two photon absorption is assumed, if the first excited singlet has a short relaxation time.

It should be noted, however, that we have based our calculation on lower laser intensities than used by the authors (1 MW/cm<sup>2</sup> instead of 10 MW/cm<sup>2</sup>). No set of parameters could reproduce their results, since at higher intensities there is always widening of the fluorescence pulse as the  $I$  dependence decreases. We were unable to explain this discrepancy.

(e) *Red fluorescence.* The intensity of the red fluorescence is linearly dependent on laser intensity as measured by Müller and Pflüger,<sup>9</sup> and by Gires.<sup>7</sup> This linear dependence is shown in Fig. 10. The coordinates are arbitrary and therefore no value of  $k_{21}R$  can be deduced. Again, at very high intensities the slope decreases from the value of 1 in contradiction with Ref. 9.

Since the coordinates are arbitrary, one can obtain consistency with the authors' results by changing the abscissa. However, this means decreasing the authors' maximum laser intensity to the value of 1 MW/cm<sup>2</sup> (compare with the results of the blue fluorescence).

The temporal behavior is shown in Fig. 10(b), again basing the calculations on 1 MW/cm<sup>2</sup> peak laser pulse. At higher intensities, the red fluorescence pulse is distorted as observed experimentally by Gires<sup>7</sup> in cryptocyanine and by Kosonocky *et al.*<sup>20</sup> in phthalocyanine at the same intensities.

In conclusion, there are a few points worth mentioning in addition to those discussed above.

(a) *Mean free path of a photon.* The bleaching effect can be demonstrated most effectively by plotting the distance through which the initial intensity is halved in laser intensity. In Fig. 11, this "mean free path" ( $X_{1/2}$ ) of the photon is plotted. At low intensities its value is  $\ln 2$  [in units of  $(\sigma_{12}N_0)^{-1}$ ] and this value increases very fast when intensity increases beyond  $10^{24}$  photons cm<sup>-2</sup>·sec<sup>-1</sup>.

(b) *Narrowing parameter.* A plot of the narrowing parameter ( $R$ ) vs the initial absorbency shows a flat maximum, Fig. 12. The maximum increases with the intensity. When this maximum narrowing is plotted vs the intensity, a curve similar to the  $X_{1/2}$  curve is obtained (Fig. 11). These graphs have a practical value: they indicate the price in intensity one has to pay in

order to gain a desired amount of narrowing. Moreover, it is seen, again, that the narrowing effect is more pronounced at those intensities where the optically thin approximation fails—namely, those intensities in which the  $X_{1/2}$  value deviates appreciably from  $X_{1/2}^0$ .

(c) *Singlet-triplet ratio.* The ratio between the populations of the first singlet and triplet is a monotonously decreasing function of time in spite of the fact that  $k_{21} > k_{24}$ . The triplet population overcomes the singlet before the laser pulse reaches its maximum and remains so until the end. It is, therefore, important to quench the triplet as fast as possible in order to populate the singlet, as needed, for instance, in dye lasers.

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