

Fig. 8. Small-signal gain as a function of discharge electrical-energy density.

CO<sub>2</sub>-laser transition. A kinetics program was used together with fractional power-transfer calculations and the measured discharge power to calculate the gain. The good agreement for the time variation of the gain gives confidence that the performance of these devices can be predicted.

#### ACKNOWLEDGMENT

The equipment discussed in this paper was developed by Maxwell Laboratories, Inc., for a laser research program at the Institut de Mécanique des Fluides, Marseille, France. This research program was supported by the Direction des Recherches et Moyens d'Essais. The Garrett Corporation is gratefully acknowledged for using one of

their programs to calculate  $V_D$  and the fractional power transfer for our mixture. Discussions with S. Byron, G. Mullaney, A. Hoffman, and G. Vlases of Mathematical Sciences Northwest, Inc., and C. A. Fenstermacher and K. Boyer of LASL were most helpful.

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## Nonlinear Behavior of Solutions Illuminated by a Ruby Laser: II

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**Abstract**—The simultaneous temporal and spatial equations governing the light intensity and electronic molecular level population in a laser-illuminated medium were solved numerically for the cases of metal-free and chloroaluminum phthalocyanine. An energy model, consistent with the low-intensity spectroscopic data, was constructed, and the rate constants for transitions and absorption cross sections were varied to get simultaneous agreement with several independent literature experimental data at high irradiation intensities. The results, providing a self-consistent picture of the molecular rate constants within the assumed model, are compared with other results obtained by direct experimentation (where available) and to other approximate calculation methods.

#### I. INTRODUCTION

**S**OLUTIONS of many organic substances were shown to deviate from Beer-Lambert's absorption law when illuminated by an intense laser pulse [1]-[4]. These deviations, either positive or negative (namely, either bleaching [1] or coloring [1], [4]) can give a wealth of information regarding the dynamics of the excited levels, i.e., the various relaxation rates and cross sections coupling these states. Complementary measurements to the bleaching are the rate of recovery of the ground state population [2], [5]-[7], a phenomenon that is usually dominated by the triplet state lifetime, dynamical [8]-[13]

Manuscript received June 4, 1973; revised September 27, 1973.

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and spectral [14], [15] behavior of fluorescence under non-linear conditions, phosphorescence spectra [16], changes in the laser pulse shape during the transmission through the cell [2], [7], fluorescence delay time [17], etc. These data, accompanied by the low-intensity spectral data such as line shapes, quantum yields, and absorption cross sections from the ground state, can give us more detailed knowledge about the energy levels of the system and the rates of transfer among them.

Every interpretation of the results of experiments carried out at high laser intensity assumes an energy level model, and the experimental data are fitted to the level diagram using either 1) steady-state approximation; 2) thin-layer approximation; or 3) exact solution of the coupled spatial and temporal equations. In a previous paper [18] we compared the three methods and found under what conditions approximations 1) and 2) are valid and under what conditions they fail. In particular, it was shown that working under a certain approximation can usually explain one set of experiments while it fails to explain another set. Making an exact calculation can give a set of rate constants and extinction coefficients that fits in a self-consistent sense many of the experimental data described in the literature. This was indeed done in the case of cryptocyanine [18] solutions in methanol, on which a wealth of experimental information has been accumulated. In this paper we have done similar computations for another group of commonly used dyes, namely, metal-free phthalocyanine ( $H_2Pc$ ) and chloroaluminum phthalocyanine (CAP) [19]. The solvents commonly used are chloronaphthalene and pyridine. It should be noted that the often-used steady-state approximation completely fails in the case of  $H_2Pc$  due to the very slow decay of the triplet state, thus making the system's response time large compared to the exciting source duration. A minimum number of energy levels necessary to fit the experimental data considered was used in the schemes (see below). Since the available experimental data in "hole burning" are meager, we have considered our absorption bands to be homogeneously broadened [7], [11]. More detailed experimental data need schemes with more levels and more relaxation rates and cross sections coupling them.

A method using picosecond pulses of a mode-locked laser was used to measure lifetimes of various levels of colored dyes [20] and orientational relaxation rates of molecules in solutions of various solvents [21]. In this method, preassumption of energy level scheme and the negligibility of some rate constants is necessary to analyze the data. The indirect method described here could serve as a consistency check for various relaxation rates deduced by these techniques, since different experiments have different sensitivities towards the rate processes.

It seems, however, that an accurate description of some of the more modern picosecond work must be done along the lines described in this paper, namely, exact solution of the appropriate set of differential equations.

Amplification [22], i.e., an increase of intensity above its

initial value, can occur only if population inversion exists in the illuminated solution [ $N_i > N_j$  in (1)]. This may occur only if the solution under investigation is preexcited. It is possible to compute such processes by the same methods described in this paper by introducing the appropriate initial populations. The problem of preexcitation was treated earlier [18] in the cryptocyanine case.

## II. METHOD OF CALCULATION

The calculation scheme was described in detail earlier [18] and we shall present here only a brief outline.

The two sets of equations to be solved simultaneously for an  $n$ -level model are

$$\frac{\partial I}{\partial X} = \sum_{i>j} \sigma_{ij}(N_i - N_j)I \quad (1)$$

$$\frac{\partial N_i}{\partial t} = - \sum_j \sigma_{ij}(N_i - N_j)I + \sum_{i>j} k_{ji}N_j - \sum_{i<j} k_{ij}N_i, \quad i = 1, 2, \dots, n \quad (2)$$

where it is assumed that the illuminated volume has cylindrical geometry due to the small divergence of the laser beam, and all changes in intensity occur along its direction. Molecular diffusion processes [21] are assumed to be negligible on a time scale of laser pulsewidth. Simultaneous multiphoton processes, which become appreciable at higher intensities ( $>10^{10}$  W/cm<sup>2</sup>), can be included whenever desired by addition of terms with proper power of the intensity.

In these equations,  $I$  is the laser intensity in watts per square centimeters or in photons per seconds per square centimeters (a Gaussian pulse is taken for convenience in the computations);  $\sigma_{ij}$  (cm<sup>2</sup>) is the absorption cross section (related to the molar absorption coefficient  $\epsilon$  by  $\sigma = 3.83 \times 10^{-21} \times \epsilon$ ) from level  $i$  to level  $j$ ;  $k_{ij}$  (s<sup>-1</sup>) is the decay rate constant from level  $i$  to level  $j$ ; and  $N_i$  is the number of absorbing molecules of level  $i$  in unit volume, where  $\sum N_i = N_0$  is the total number of molecules per unit volume.

In order to solve these equations, one uses one of the following assumptions.

1) Steady state, in which (2) is equated to 0, and the various populations are inserted into (1), which is then integrated. The results depend only on the number of absorptions [2] and not on the detailed scheme. One can be very easily misled by an accidental agreement with experimental data.

2) Optically thin layer, in which one integrates (1) by assuming that the populations do not depend on position, but only on time. The values of the populations are obtained from the rate equation (2). This method is superior to the steady state, since it depends more explicitly on the individual decay rates and absorption cross sections. Its use, however, is limited to low absorbances, namely, when  $\sigma_{ij}(N_i - N_j) X \ll 1$ . For example, a solution with transmittance of 6 percent is calculated under this assumption with typical rate constants and a four energy level scheme to bleach under a pulse of 1 MW/cm<sup>2</sup> to 70-

TABLE I  
RATE CONSTANTS AND ABSORPTION CROSS SECTIONS OF METAL-FREE PHTHALOCYANINE; ENERGY LEVEL  
DIAGRAM IN INSERT TO FIG. 1

	$k_{21} \text{ sec}^{-1}$	$k_{34} \text{ sec}^{-1}$	$k_{31} \text{ sec}^{-1}$	$k_{41} \text{ sec}^{-1}$	$k_{32} \text{ sec}^{-1}$	$\sigma_{13} \text{ cm}^2$
This work*	$5 \times 10^8$	$9 \times 10^9$	$3 \times 10^9$	$10^6$	$10^{11}$	$2 \times 10^{-16}$
Literature values	$1.25 \times 10^8$ (9) <sup>b</sup> $1.31 \times 10^8$ (7) <sup>b</sup> $1.31 \times 10^9$ (7) <sup>h</sup> $7.15 \times 10^7$ (30) <sup>b</sup> $1.19 \times 10^8$ (30) <sup>g</sup>	$1.18 \times 10^9$ (7) $10^9$ (11) <sup>i</sup>		$< 2 \times 10^3$ (16) <sup>a</sup> $5.9 \times 10^3$ (26) <sup>f</sup> $1.39 \times 10^6$ (5) <sup>f</sup> $10^4$ (7) <sup>c</sup> $2 \times 10^6$ (7) <sup>d</sup> $6.7 \times 10^3$ (10) <sup>j</sup> $10^6$ (10) <sup>e</sup>	$2 \times 10^{11}$ – $2 \times 10^{12}$ (11)	$0.65 \times 10^{-16}$ (24) $2 \times 10^{-16}$ (8) $3 \times 10^{-16}$ (25) $3.6 \times 10^{-16}$ (27)(26)(14) $4.6 \times 10^{-16}$ (28) $5.8 \times 10^{-16}$ (11)(9)

\* These values are best fitted to all calculations of all the experiments discussed in the text.

<sup>a</sup> Estimate from phosphorescence of metal porphyrins at  $-77^\circ\text{C}$ .

<sup>b</sup> Radiative part only from integration on absorption band.

<sup>c</sup> Recovery of the original absorption, degassed sample.

<sup>d</sup> Same as footnote <sup>c</sup>, nondegassed sample.

<sup>e</sup> Room temperature.

<sup>f</sup> From decay rate of triplet absorption.

<sup>g</sup> From radiative lifetime and yield of 0.6.

<sup>h</sup> From radiative lifetime and yield of 0.1.

<sup>i</sup> From ratio of fluorescence yield at different pulsewidths.

<sup>j</sup> Measurement at  $-77^\circ\text{C}$ .

percent transmittance, while the exact calculation gives only 60 percent. The disagreement becomes more pronounced as the original transmittance decreases.

3) Exact calculation solves the simultaneous equations (1) and (2) numerically. The solution is done by the Runge-Kutta-Gill method and a full description is given elsewhere [18], [23]. The convergence of the method as a function of the number of spatial elements used is shown in [18, Fig. 1] for the cryptocyanine case. Similar results were obtained in the case of both  $\text{H}_2\text{Pc}$  and CAP.

In this paper we made computations for metal-free phthalocyanine and chloroaluminum phthalocyanine. For the two compounds there is a wealth of data in the literature, both for usual low-level energy spectroscopy and laser irradiation effects.

### III. METAL-FREE PHTHALOCYANINE ( $\text{H}_2\text{Pc}$ )

In order to establish a reasonable energy level scheme, the following facts were taken into account.

1) The singlet manifold contains two excited states at 699 nm and 325 nm. The measured cross section (given in Table I) is quite controversial, the discrepancy in the various sources in the literature [3], [8], [11], [14], [15], [24]–[27] probably being due to difficulties in dissolving the material. The value chosen for our calculations is  $2 \times 10^{-16} \text{ cm}^2$ . No significant changes were obtained when this value was slightly altered.

2) There is evidence for the existence of a triplet manifold [5], [9], [10], [27], [28]. These authors measured directly the decay rate constant of the triplet state to be  $10^6 \text{ s}^{-1}$  or less (depending on whether the sample was degassed or not, on temperature, and on the presence of impurities) and estimated the absorption cross section of the

triplet-triplet absorption to be  $10^{-18} \text{ cm}^2$ . No evidence for phosphorescence has been observed; however, it was detected in similar compounds [16] with decay time of approximately  $5 \times 10^{-4} \text{ s}$  at low temperatures.

3) Increase of temperature causes a drastic decrease in the fluorescence yield [10]. This type of behavior cannot be explained by a scheme that takes all rates as temperature independent and ignores completely such features as nature of solvent, interaction of solvent-solute, etc. However, since a change in the fluorescence yield is observed, we have to assume that the absorbed laser irradiation leads to some vibronically excited level of the first singlet. The nature of this vibronic state, and of course its decay rates, depends on the nature of the solvent and its interaction with the solute molecules, and therefore on the temperature. We have not tried to calculate this temperature dependence, but have assumed that the absorption leads to some undefined vibronic level. Similar conclusions were obtained by Pine [29] in the case of cryptocyanine.

4) The very small cross section of the triplet-triplet absorption relieves us of the necessity to include transitions to an excited triplet in our scheme, because none of the experiments described in this paper will reveal its existence. In spite of this we have also tested a scheme that includes triplet-triplet absorption. A cross section as low as  $10^{-18} \text{ cm}^2$  does not affect at all the results described below, while a larger cross section does not conform with other results and with the results of direct measurement [27].

5) The integrated absorption spectra in the absorption region of the  $B_{lu}$  singlet reveals a radiative rate constant of  $1.25 \times 10^8 \text{ s}^{-1}$  obtained by Kosonocky *et al.* [9] and  $7.15 \times$

$10^7 \text{ cm}^{-1}$  obtained by Gouternam *et al.* [30]. The fluorescence quantum yield was measured by the latter authors to be 0.6, which implies a total decay rate of the fluorescing level at  $1.3 \times 10^8 \text{ s}^{-1}$ .

All these low-intensity data suggest a minimal model of four levels. The experiments described below were fitted by calculation according to the scheme shown in the insert to Fig. 1.

#### A. Saturation of Transmission (Kosonocky *et al.* [9]–[11])

A solution of phthalocyanine was irradiated by a ruby laser and the transmission of the sample was measured at right angles by a low-intensity source. Fig. 1 shows the experimental results and the calculated curve according to the rates of Table I. This was done both in a steady-state approximation with the author's rates [11] and by an exact calculation with these same rates. Although a good agreement was obtained between experimental points and a steady-state model with adjustable parameters (plot 1), the exact calculation with the same parameters (plot 3) deviates largely from experiment. The rate that yields a best fit in our model by means of exact solution (Table I) produces a fair agreement with the experiment (plot 2). The sensitivity of the calculation to the model and the parameters will be discussed below.

Gires [8] obtained residual transmission at very high intensities; however, the author himself claims that the explanation to this residual absorption is due to overheating of undissolved particles. The possibility of dissociation of the phthalocyanine molecules was also previously discussed [31].

#### B. Transmission Measurements

Giuliano and Hess [1] measured the transmission of the ruby laser itself through  $\text{H}_2\text{Pc}$  solutions. Very good agreement is seen in Fig. 2 between the calculation based on rates of Table I and experimental data.

#### C. Saturation of Fluorescence (Kosonocky *et al.* [9]–[11], Gires [8])

In the same setup of the previous experiment, Kosonocky *et al.* [9]–[11] measured the fluorescence at right angles to the direction of ruby irradiation. The four plots of Fig. 3 show experimental, steady-state, and exact calculation according to the author's [9]–[11] parameters adjusted to the steady-state model. Again, the exact calculation with steady-state parameters that were selected to yield best fit with the experiment does not agree well with the experiment. In turn, the parameters employed in the four energy levels (Table I) yield satisfactory agreement with experiment through exact calculation.

In Fig. 4 the experimental results of Gires [8] are shown together with the calculated ones. Exact calculation and steady-state approximation in this case of a two-level system yield similar results, since the conditions for the validity of the approximation [18] are fulfilled (short

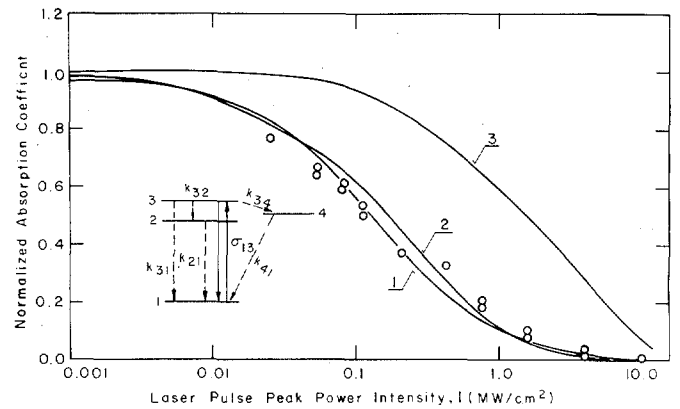


Fig. 1. Absorption coefficient versus laser intensity of  $\text{H}_2\text{Pc}$ . Plot 1—three-level steady-state calculation [11]; plot 2—exact calculation with model (insert) and rates of Table I; plot 3—exact calculation with steady-state parameters and model [11];  $\circ$ —experimental points. Experimental data from [9], [11]—laser pulsewidth 30 ns,  $\text{OD}_0 = 0.3$ .

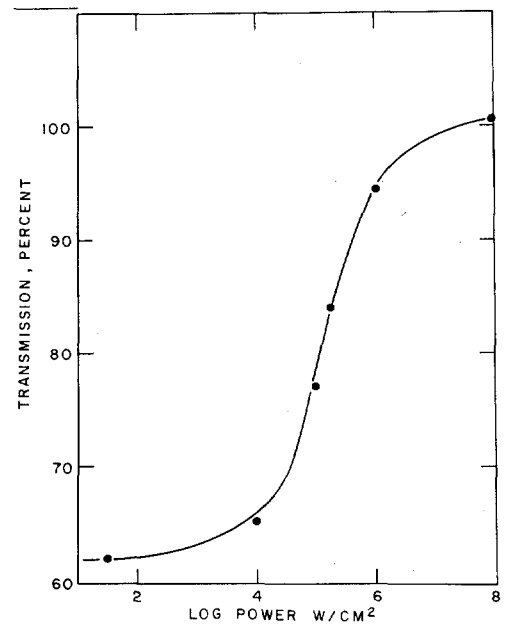


Fig. 2. Transmission versus laser intensity of  $\text{H}_2\text{Pc}$ . Solid line data of [1], points calculated according to model (insert to Fig. 1, parameters of Table I). Laser pulsewidth 43 ns.

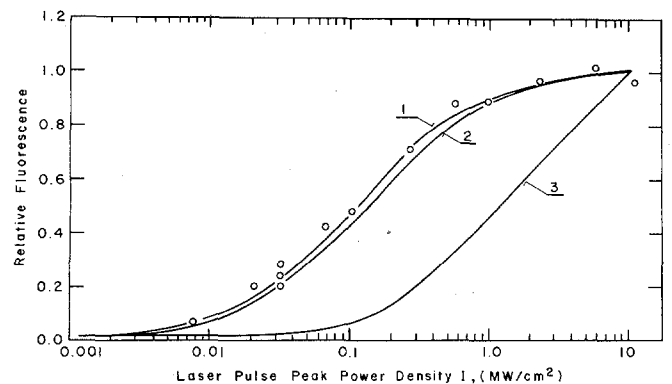


Fig. 3. Fluorescence versus laser intensity of  $\text{H}_2\text{Pc}$ . Plot 1—steady-state calculations (same as Fig. 1); plot 2—exact calculation with proposed model; plot 3—exact calculation with parameters fitted by steady state [9], [11];  $\circ$ —experimental points. Data from [9], [11]—laser pulsewidth 30 ns,  $\text{OD}_0 = 0.3$ .

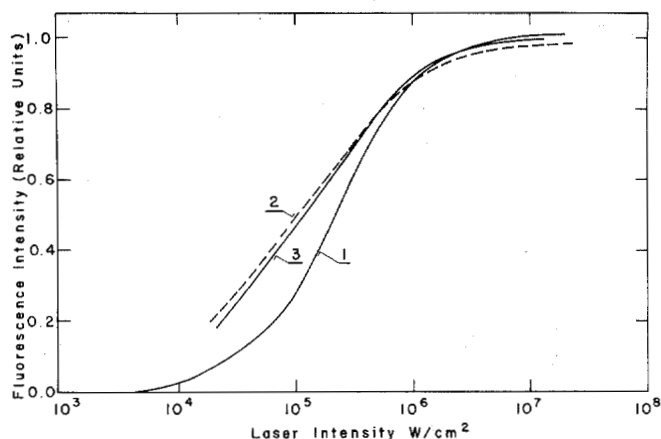


Fig. 4. Fluorescence versus laser intensity of  $H_2Pc$ . Plot 1—exact calculation with parameters fitted by steady state, parameters and energy scheme (two levels) of [8]; plot 2—experimental data of [8]; plot 3—exact calculation with proposed model and rates of Table I. Laser pulsewidth 30 ns,  $OD_0 = 1.22$ .

lifetimes compared to the laser pulsewidth); however, the existence of a slow-decaying triplet state contradicts this assumption and thus causes the steady-state and exact calculation to deviate from the experimental behavior (Fig. 4, plot 1). The four energy level scheme, on the other hand, yields agreement with experiment (plot 3). Another phenomenon observed experimentally during saturation of fluorescence [10] is the broadening of the fluorescence time profile under high-flux irradiation. This was attributed by the authors to the existence of a long-lived delayed fluorescence component due to consecutive absorption of a second photon at ruby wavelength either by the excited singlet or by the triplet. Such an explanation turns out to be unnecessary in our model, since broadening of the fluorescence time profile in this model results directly from the calculations.

#### D. Absolute Fluorescence Intensity (Kosonocky et al. [9])

The integration of the time profiles of the population of level 2 over the spatial elements along the cell is proportional to the measured fluorescence intensity  $F = k_{21}^R N_2$ , where  $k_{21}^R$  is the radiative rate from level 2 to the ground state (level 1). The measured peak integrated fluorescence flux generated by a known ruby pulse [9] divided by the calculated peak integrated population with the former constants gives  $k_{21}^R = 1.2 \times 10^8 \text{ s}^{-1}$ . This value should be compared with the value  $1.25 \times 10^8 \text{ s}^{-1}$  to  $7.15 \times 10^7 \text{ s}^{-1}$  obtained from the integration of the absorption curve [9], [30]. These radiative lifetimes are based on integration of the spectra and are therefore liable to the same experimental errors as the measurement of the extinction coefficient. The total decay rate depends on the standard used for calibrating the fluorescence yields [30], [32]. Taking these facts into account, our results are well within the experimental error.

Kosonocky et al. [10] measured the ratio between fluorescence peak intensities for excitation with two different laser pulsewidths: 20 ns and 80 ns, in order to

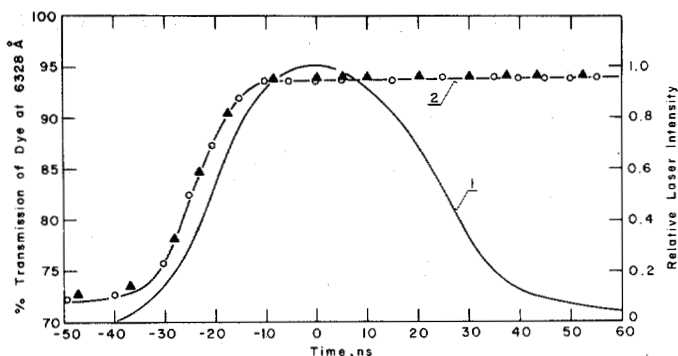


Fig. 5. Transmission of  $H_2Pc$  at 6328 Å versus time. Plot 1—ruby laser pulse shape;  $\circ$ —experimental data of [7];  $\Delta$ —calculated points with proposed model and Table I parameters. Laser peak intensity 2.6 MW/cm<sup>2</sup>,  $OD_0(6943 \text{ Å}) = 0.3$ ,  $OD_0(6328 \text{ Å}) = 0.14$ .

determine from the fluorescence ratio thus obtained (= 17) the intersystem crossing (ISC) rate constants. The magnitude of this constant invoked by steady-state calculations [10] combined with this result was  $10^9 \text{ s}^{-1}$ . Their results could not be reproduced by us, even when varying  $k_{21}$  between  $10^8$ – $10^{11} \text{ s}^{-1}$ ,  $k_{34}$  between  $10^8$ – $10^{10} \text{ s}^{-1}$ , and also by assuming excited-state absorption from level 2 with cross section between  $10^{-17}$ – $10^{-15} \text{ cm}^2$ . Instead, the maximum ratio obtained did not exceed 3.2.

#### E. Time-Dependent Transmission Curves (Hercher et al. [7])

The transmission of an He-Ne laser at 6328 Å was measured at right angles to the main ruby laser as a function of time. Since there is no change in the absorption curve shape during the bleaching process (homogeneous band broadening), we have to introduce the ratio 2:1 between the absorption cross sections at 6943 Å and 6238 Å, respectively, into the calculations. Fig. 5 shows the experimental and calculated transmission together with the exciting laser pulse. The transmission is seen to rise with the laser pulse and remains constant at the highest level ( $\approx 93$  percent) long after the laser decays. Calculation shows that this value is very sensitive to the lifetime of the first singlet ( $k_{21}$ ) and to the ISC rate ( $k_{34}$ ). There is no influence of the lifetime of the triplet ( $k_{41}$ ) since any reasonable value, such as  $10^8 \text{ s}^{-1}$  or smaller, leaves the calculated curve unchanged. The decrease of the ISC rate will cause the lifetime of the singlet to be the dominant rate, and this will cause the transmission to follow the laser pulse. On the other hand, a value too large for the ISC rate will cause a decrease in the singlet population and, therefore, a decrease in the transmission from the experimentally measured value.

#### F. Discussion

Table I summarizes all the relevant parameters, those given by previous authors and those calculated in this work. The energy level scheme is shown in the insert to Fig. 1.

Values of  $10^6 \text{ s}^{-1}$  and lower were used by many authors

[5], [7], [9] for the triplet decay rate. A value of  $4.05 \times 10^3 \text{ s}^{-1}$  was measured [9], [27] and similar values were estimated for similar compounds [16]. The differences among the various results are due probably to different experimental conditions, namely, different temperatures and different degassing methods. Since even the fastest rate ( $10^6 \text{ s}^{-1}$ ) is much slower than the other relevant rates, we have used this value, although it may be taken as an upper limit.

A model with singlet-singlet absorption was tested. Agreement could be obtained only with cross sections much smaller than that of the first absorption. The results thus obtained do not differ from those of the proposed model, and thus we can safely ignore the second absorption, unlike the CAP case (see Section IV). In the latter case, experiments were conducted with very high intensities, and thus the existence of the second absorption was more pronounced.

The time-dependent transmission measurements are particularly sensitive to the second absorption. However, this sensitivity is more apparent at higher intensities than used [7]. It is useful, therefore, to conduct such measurements at very high intensities (10–100 MW/cm<sup>2</sup>) in order to obtain meaningful results for the second absorption (if any).

The delay time of the pulse in the solution is sensitive to  $k_{21}$  (increase by a factor of 5 causes a delay of 12 ns). A precise measurement of the delay time will give a better value for this rate.

#### IV. CHLOROALUMINUM PHTHALOCYANINE (CAP)

This compound is most suitably described by a scheme that has two absorptions and a triplet state. Its spectrum shows the existence of a first excited singlet at  $14\,400 \text{ cm}^{-1}$  and a second singlet at  $27\,000 \text{ cm}^{-1}$  above ground level [33]. The cross section for absorption to the first singlet is  $3 \times 10^{-16} \text{ cm}^2$  [4], [8], [34]. It emits a strong red fluorescence with  $\lambda_{\text{max}} = 700 \text{ nm}$  and has a blue fluorescence at  $\lambda_{\text{max}} = 400 \text{ nm}$  [12]. Thus the model chosen conforms to the main experimental results. We have ignored triplet-triplet absorption, as we have done in the case of the H<sub>2</sub>Pc, since it introduces two extra redundant parameters, which seems unjustified in view of the available experimental data. The energy level diagram is shown in the insert to Fig. 6.

##### A. Transmission

In Fig. 6 the experimental transmission data of Gibbs [12] and those of Armstrong [13] are shown together with the calculated points, computed with the decay rates and cross section that yielded the best fit given in Table II. Fig. 6 shows complete bleaching at intensities of  $1.0 \text{ MW/cm}^2$  and a decrease in the transmission at still higher intensities. This is easily understood: once the first absorption is saturated, the second absorption with lower cross section is effective and results in a decrease of the transmission.

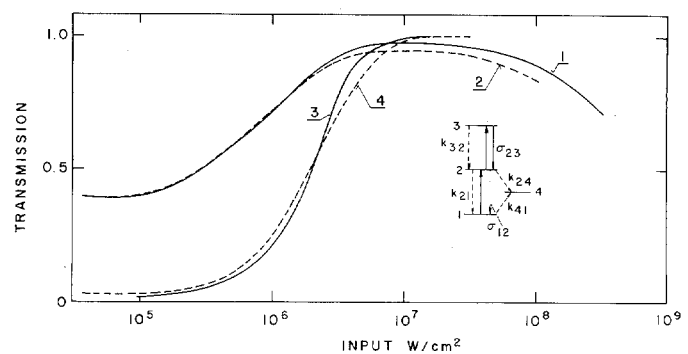


Fig. 6. Transmission of CAP versus laser intensity. Plot 1—experimental data of [12]—laser pulsewidth 20 ns; plot 2—exact calculation for experiment of [12] according to model in insert and parameters of Table II; plot 3—experimental data of [13] (original data were replotted in order to match the same coordinate system as the previous graph), laser pulsewidth 30 ns; plot 4—exact calculation for experiment of [13].

Similar behavior was observed by Gires [8]; however, he also observed residual absorption that he attributes to undissolved dye particles that may cause local heating and dissociation [31], [38]. Also, the calculated results for the transmission experiment of Hercher *et al.* [7] match his experimental data within 2 percent, namely, transmission of 70, 30, 25, and 20 percent for intensities of 10, 0.5, 0.3, and 0.2 MW/cm<sup>2</sup>, respectively. The transmitted pulse is delayed compared to the arrival time of the pulse, which does not pass the dye. This delay was measured by Hercher *et al.* [7] and found to be 2 ns, depending on intensity. Calculation with rates of Table II yields a similar result. A more detailed calculation on the delay intensity dependence, which turns out to be sensitive towards  $k_{21}$ , seems unjustified at this stage in view of the scarce experimental data.

##### B. Blue Fluorescence

The results of Gibbs [12] together with the calculated data are depicted in Fig. 7: the intensity of the blue ( $\lambda = 400 \text{ nm}$ ) fluorescence versus the laser intensity. It is seen that the fluorescence depends on the square of the intensity at low intensities and on the first power at high intensities. An increase of the slope is seen at still higher laser irradiation intensities. This is not borne out by the calculation, and it is very difficult to construct a model that will give an increase (instead of saturation) of this blue fluorescence when the transmission already decreases. It seems that local heating may lead to dissociation products that fluoresce more effectively in this region. Phthalocyanine dyes are known to dissociate under these conditions [38].

##### C. Red Fluorescence

Fig. 7 shows the red ( $\lambda = 700 \text{ nm}$ ) fluorescence versus laser intensity. The experimental results are of Gires [8], the calculated plot is ours. Again, a very good agreement is obtained. Bowe *et al.* [17] measured the delay between fluorescence and laser pulse and obtained 5 ns, which con-

TABLE II  
RATE CONSTANTS AND ABSORPTION CROSS SECTIONS OF CHLOROALUMINUM PHTHALOCYANINE; ENERGY LEVEL DIAGRAM IN INSERT TO FIG. 6

	$\sigma_{12}$ (cm <sup>2</sup> )	$\sigma_{23}$ (cm <sup>2</sup> )	$k_{21}$ (sec <sup>-1</sup> )	$k_{32}$ (sec <sup>-1</sup> )	$k_{24}$ (sec <sup>-1</sup> )	$k_{41}$ (sec <sup>-1</sup> )
This work	$3 \times 10^{-16}$	$5 \times 10^{-17}$	$6 \times 10^8$	$10^{12}$	$10^9$	$10^8$
Literature values	$4 \times 10^{-16}$ (8) $2.68 \times 10^{-16}$ (35) $2 \times 10^{-16}$ (36) <sup>a</sup>		$10^8$ (36) <sup>a</sup> $2 \times 10^8$ (17) <sup>b</sup> $10^8$ (33) <sup>c</sup> $> 5 \times 10^7$ (8) <sup>d</sup> $1.7 \times 10^7$ (18) <sup>d</sup> $1.7 \times 10^8$ (29) <sup>g</sup>	$> 2 \times 10^8$ (12) <sup>f</sup> $> 10^{13}$ (37) <sup>h</sup>	$> 10^7$ (37) <sup>e</sup>	$10^3$ (33) <sup>i</sup>

<sup>a</sup> Estimate by fitting results of [7] to two-level model.

<sup>b</sup> Estimate from fluorescence delay.

<sup>c</sup> Radiative part only from oscillator strength.

<sup>d</sup> Recovery of initial absorbance.

<sup>e</sup> Estimate for intersystem crossing.

<sup>f</sup> Decay of blue fluorescence.

<sup>g</sup> Decay of red fluorescence.

<sup>h</sup> Estimate for internal conversion.

<sup>i</sup> An estimate.

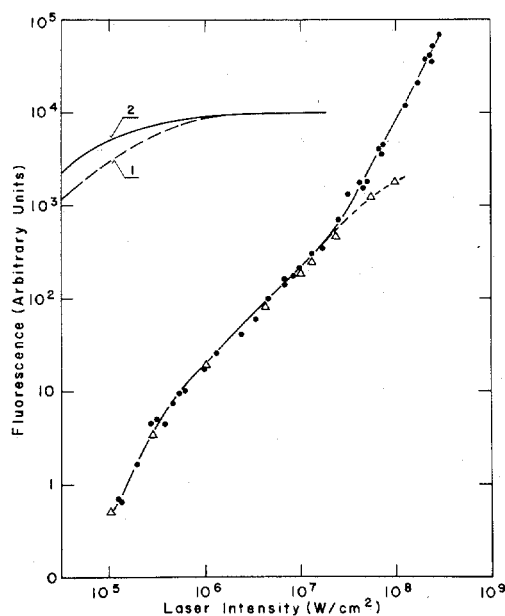


Fig. 7. Fluorescence intensity of CAP versus laser intensity. Plot 1—red fluorescence: exact calculation; plot 2—red fluorescence: data of [8]; laser width 30 ns,  $OD_0 = 1.22$ ;  $\Delta$ —blue fluorescence: exact calculation;  $\bullet$ —blue fluorescence: data of [12], laser width 20 ns,  $OD_0 = 0.5$ . Both by model of insert of Fig. 6 and parameters of Table II.

forms very well with 6 ns of our computations. This value should also be compared with 8 ns as calculated for the delay of the fluorescence of  $H_2Pc$  [11].

#### D. Laser Pulse Shaping

Hercher *et al.* [7] measured the change of laser pulse shape during its passage through CAP solution at various light intensities. It turns out that appreciable (2–3 ns) narrowing occurs in this process at intermediate inten-

sities, while small changes take place at low and high intensities. This familiar behavior [2], [18] is reproduced by our model calculation and is found to be sensitive to the excited-state absorption, in the sense that for  $\sigma_{23} > \sigma_{12}$ , broadening of the laser pulse occurs instead of narrowing. It is unfortunate that such interesting experimental data are not available with more details, since they could be used as a sensitive criterion for more precise determination of the parameters involved.

#### E. Discussion

Table II summarizes the results of this work together with literature values. The higher value of the triplet-singlet decay rate compared to that found in the case of the metal-free phthalocyanine is caused by the increase of spin-orbit coupling because of the existence of metal in the compound; still higher values are estimated for phthalocyanines of other metals (with higher atomic numbers) [10]. From the spectrum, one obtains values for  $k_{21}^R = 10^8 \text{ s}^{-1}$  [33]; therefore, the quantum yield for the red fluorescence will be  $k_{21}^R / (k_{21} + k_{24}) = 0.062$  as compared to 0.6 of the metal-free compound [28], again in accord with the presence of the metal. The value of the second absorption cross section is very reasonable; however, no direct experimental evidence is known for it in the literature. The assumption of this absorption is a must in order to explain the decrease in transmission at very high intensities. The magnitude of the cross section is determined both from the transmission data and from the pulse shape. Higher values of the second cross section would cause pulse broadening instead of the experimental narrowing [7].

Finally, the dimeric form of CAP [39] was shown to

color under laser irradiation [4]. This can easily be explained by assuming that dissociation to the monomer occurs with high cross section at the ruby wavelength.

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