

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.

#### REFERENCES

- [1] C. K. N. Patel, "Continuous wave laser action on vibrational rotational transitions of  $\text{CO}_2$ ," *Phys. Rev.*, vol. 136, pp. 1187-1193, Nov. 1964.
- [2] C. A. Fenstermacher, M. J. Nuttér, W. T. Leland, and K. Boyer, "Electron-beam-controlled electrical discharge as a method of pumping large volumes of  $\text{CO}_2$  laser media at high pressure," *Appl. Phys. Lett.*, vol. 20, pp. 56-60, Jan. 1972.

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)

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

TABLE I

*Rate Constants and Absorption Cross Sections of Metal Porphyrins*

	$k_{21} \text{ sec}^{-1}$	$k_{34} \text{ sec}^{-1}$	$k_{31} \text{ sec}^{-1}$	$k_{41} \text{ sec}^{-1}$	$k_{32} \text{ sec}^{-1}$	$\sigma_{13} \text{ cm}^2$
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.

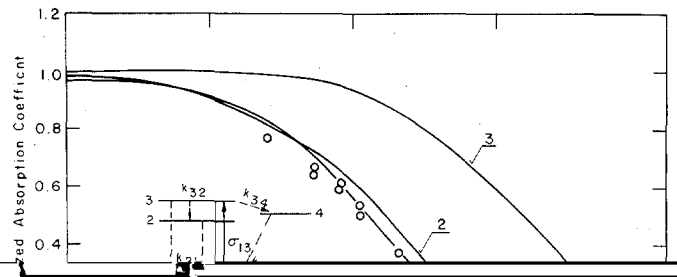
<sup>e</sup> Room temperature.

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

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

$10^7 \text{ cm}^{-1}$  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.



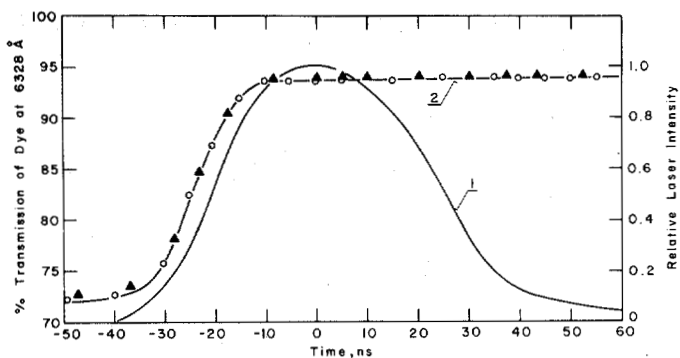
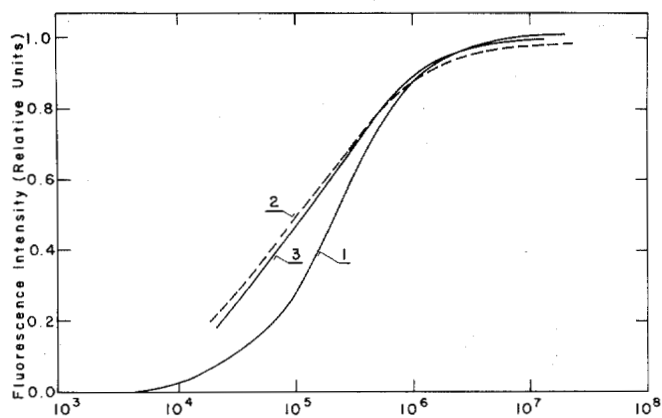


Fig. 5. Transmission of  $H_2Pc$  at 6328 Å versus time. Plot 1—ruby laser pulse shape;  $\circ$ —experimental data of [7];  $\Delta$ —calculated points with proposed model and Table I parameters. Laser peak intensity 2.6

[5], [7], [9] for the triplet decay rate. A value of  $4.05 \times 10^3$

1.0



TABLE II

RATE CONSTANTS AND ABSORPTION CROSS SECTIONS OF CHLOROALUMINUM PHTHALCYANINE ENERGY

color under laser irradiation [4]. This can easily be ex-

[19] P. P. Sorokin, J. J. Luzzi, J. R. Lankard, and G. D. Petit, "Ruby-