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Physical and Chemical Applications of Dyestuffs

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Organic Dyes in Laser Technology

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Reaction of Excited Dye Molecules
at Electrodes

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Semiconductor Properties of Dyes

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Organic Dyestuffs as Catalysts
for Fuel Cells



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**Physical and
Chemical Applications of**

Dyestuffs



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This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

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This book is the first in a new series, REACTIVITY AND STRUCTURE: CONCEPTS IN ORGANIC CHEMISTRY, designed to treat topical themes in organic chemistry in a critical manner. A high standard is assured by the composition of the editorial board, which consists of scientists of international repute. This volume deals with the currently fashionable theme of complexes of transition-metal compounds. Not only are these intermediates becoming increasingly important in the synthesis of substances of scientific appeal, but they have already acquired great significance in large-scale chemical manufacturing. The new potentialities for synthesis are discussed with examples. The 618 references bear witness to the author's extensive coverage of the literature. This book is intended to stimulate organic chemists to undertake further research and to make coordination chemists aware of the unforeseen development of this research field.

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Organic Dyes in Laser Technology

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Introduction

In the years since 1964, when the first passive Q-switching with organic dyes was accomplished, the use of organic dyes in laser technology has become increasingly important. Some of the most important developments in the laser field would not have been possible without organic dyes, and one can foresee even further possibilities for the use of dyes in laser technology which could be realized in the near future.

There are several reasons for the usefulness of organic dyes in the laser field. A physical reason can be seen in the very large cross-sections of dyes for the interaction with light, not only for a few lines but for broad bands in the visible part of the electromagnetic spectrum, including some extensions to the near ultraviolet and infrared. As a chemical reason one can give the almost infinite variety of dyes (with the resultingly large variation of their properties) which can be synthesized using the methods of organic chemistry. Finally, one should not forget to mention the inexpensiveness of organic dyes, an obvious advantage in many applications.

This short review will discuss all of the different applications of organic dyes in the laser field which have been reported up to the present, emphasizing a unified treatment of basic principles and leaving a discussion of the details to special reviews and monographs of the different applications. Within the limited space available it is not possible to give a complete list of references. Therefore, only a selection of the most important literature references will be presented here to enable the interested reader to acquire the complete literature of this field from the secondary references cited in these papers. Two review papers on organic dyes in laser technology appeared in 1970 ^{1,2)}.

Applications making use of the nonlinear absorption of dyes are passive Q-switching in solid-state lasers, pulse shaping, pulse intensity measurements of high-power ultrashort pulses, optical isolation between amplifier stages of high power solid-state lasers, and pulse width measurements of ultrashort pulses by the two-photon-fluorescence (TPF) method.

Dye lasers are presently the most important application of organic dyes in laser technology, making use of the fluorescence of dyes.

Finally, the nonlinear polarizability of dyes is used for frequency tripling the output of high-power lasers.

The nonlinear absorption of dyes will be treated first, followed by a description of the various applications making use of this property. Dye lasers will be examined next, but only briefly, since a monograph on dye lasers has recently been published ³⁾. Finally, frequency tripling in dyes will be considered.

It should be stated here that the term "dye" is used in this context in its broadest meaning, and is meant to include all organic compounds with conjugated double bonds since the mechanism of their interaction with light always involve the excitation or deactivation of π -electrons.

Nonlinear Absorption

A simplified energy level diagram of an organic dye is given in Fig. 1. It shows the singlet levels S_0 , S_1 , S_2 , ... and the triplet levels T_1 , T_2 , ... with some rovibronic sublevels indicated. The absorption (upward) and emission (downward) arrows are drawn as sharp single lines as are the energy levels. Actually, however, the energy levels are smeared out considerably by solvent-solute interactions, and the huge number of possible transitions between the sublevels of the higher and lower levels form a quasi-continuum with a broad envelope, generally several thousand wavenumbers wide. Only at low temperatures (< 20 K), when the environment of the dye molecules cannot change significantly, is it possible to observe sharp, linelike spectra, when the fluorescence is excited with a laser of small spectral width as has been demonstrated only recently ⁴). We will come back to this problem of the superposition of many sharp spectra to form a broad band in the discussion of "spectral hole-burning".

The radiationless transitions are indicated by wavy lines with the corresponding rate constants or lifetimes. The rates of thermalization of a dye molecule after an absorptive or emissive transition, namely k' in the excited singlet state S_1 and k'' in the ground state S_0 , are so fast that they have not yet been reliably measured. From indirect evidence they are believed to be $k' \approx k'' \approx 10^{12} - 10^{13} \text{ sec}^{-1}$. The rate k_{21} of radiationless internal conversion from S_2 to S_1 has recently been measured for several dyes and was found to be in the range $k_{21} \approx 10^{11} - 10^{12} \text{ sec}^{-1}$ ^{5,6}). While k_{TT} has not yet been measured directly, there is no reason to believe that it should be much different from k_{21} , and indirect evidence seems to

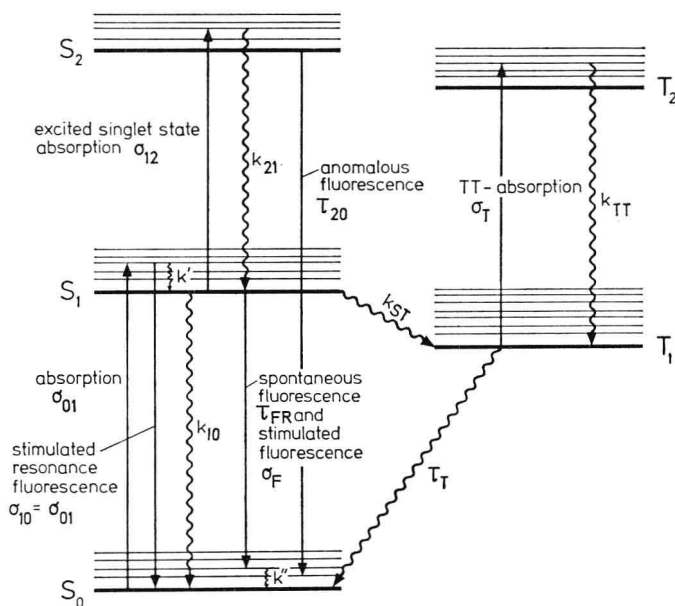


Fig. 1. Generalized energy level scheme of an organic dye molecule. Straight arrows: radiative transitions, wavy arrows: non-radiative transitions. The sigmas, kays, and taus are the corresponding cross-sections, transition rates, and lifetimes, respectively

confirm this assumption. The triplet lifetime τ_T is many orders of magnitude longer than the fluorescent decay time τ_F since the transition $T_1 \rightarrow S_0$ is spin-forbidden. The triplet lifetime approaches the radiative lifetime at very low temperatures and is then found to be several seconds for many dyes ⁷⁾. At room temperature, in liquid solution, τ_T is markedly reduced by spin-orbit coupling with triplet-quenching agents, such as O_2 or solvents with heavy atoms, and can be less than 100 nsec. The sum of $k_{10} + k_{ST}$ can easily be obtained when the fluorescence decay time τ_F is known by comparing with the radiative lifetime τ_{FR} — obtained from the absorption spectrum with the help of the Strickler-Berg formula ⁸⁾ — since $1/\tau_F = 1/\tau_{FR} + k_{10} + k_{ST}$. The two rates can also be distinguished if the quantum yield of triplet production η_T is known, for example from flash-photolysis data, since $\eta_T = k_{ST} \cdot \tau_F$. The relative importance of k_{10} , the internal conversion rate, and k_{ST} , the intersystem crossing rate, on the radiationless deactivation of dye molecules differs greatly for different dyes, even within the same class of dyes, when the structure is slightly changed, and it depends very much on the environment.

The spontaneous fluorescent decay time τ_F is connected with the radiative lifetime τ_{FR} and the quantum yield of fluorescence η_F by $\eta_F = \tau_F / \tau_{FR}$. Since the radiative lifetime is of the order of a few nanoseconds in most dyes, the spontaneous fluorescent decay time is about the same for quantum yields of fluorescence near unity (*i.e.*, $k_{10} \approx k_{ST} \approx 0$) and decreases to a few picoseconds for quantum yields of the order of 10^{-3} .

A large amount of information has been accumulated on T - T -absorption spectra ⁹⁾ although the excited singlet state absorption spectra are much less well known ¹⁰⁾.

With the above facts in mind we can now proceed to discuss the characteristics of light absorption in organic dyes at high light intensities.

Let $m_0, m_1, m_2, m_{T1}, m_{T2}$ be the populations of the lowest rovibronic sublevels of S_0, S_1, S_2, T_1 , and T_2 , respectively, with $m = m_0 + m_1 + m_2 + m_{T1}$ the total dye population [molecules/cm³]. For simplicity the populations of higher rovibronic states are assumed to be negligibly small, which means that k' and k'' are assumed to be much greater than all other rates involved and that the temperature is low enough so that the Boltzmann distribution leaves higher sublevels empty.

Let us first consider the simplest case of a dye which has no excited singlet state absorption in the spectral region of the longest wavelength absorption band corresponding to the transition $S_0 \rightarrow S_1$, and has a time of irradiation that is long compared to τ_F and short compared to $1/k_{ST}$. The latter condition means that we can forget about the triplet state in this simple case. A dye fulfilling these conditions would, for instance, be a xanthene dye with a quantum yield near unity and an irradiation time of around 20 nsec. This could be produced using a giant-pulse laser, such as a frequency-doubled neodymium laser, which would irradiate the dye at a wavelength of 532 nm and which should be absorbed by the particular dye. Now the rate equations for the populations in this simple case are the following:

$$\frac{\partial m_0}{\partial t} = -m_0 \sigma_{01} n c + m_1 / \tau_F, \quad (1)$$

$$\frac{\partial m_1}{\partial t} = m_0 \sigma_{01} nc - m_1 / \tau_F, \quad (2)$$

$$m_1 + m_0 = m. \quad (3)$$

Here n is the photon density [photons/cm³] and c is the velocity of light in the medium, so that nc is the intensity of the laser light expressed in photons/cm²·sec.

For an optically thin sample we can neglect the variation of nc over the distance x traveled by the light in the dye solution. Then, combining (1), (2), and (3) results in

$$T_N = 1 - \frac{A}{A_0} = 1 - \frac{m_0}{m} = \frac{nc \sigma_{01} \tau_F}{1 + nc \sigma_{01} \tau_F}, \quad (4)$$

where T_N is the normalized transmission, A the absorption of the sample at a laser intensity nc , and A_0 the transmission of the sample at low light levels, since the absorption of the sample is proportional to the population density m_0 of the ground state S_0 . If we call the laser intensity at which the normalized transmission equals 1/2 the saturation intensity $(nc)_s$, then

$$(nc)_s = 1/(\sigma_{01} \tau_F), \quad (5)$$

and (4) becomes

$$T_N = \frac{nc/(nc)_s}{1 + nc/(nc)_s}. \quad (6)$$

A plot of the relative transmission T_N of the dye sample versus the normalized laser intensity $nc/(nc)_s$, according to (6), is shown in Fig. 2. It is seen that the absorption is completely bleached at very high light levels.

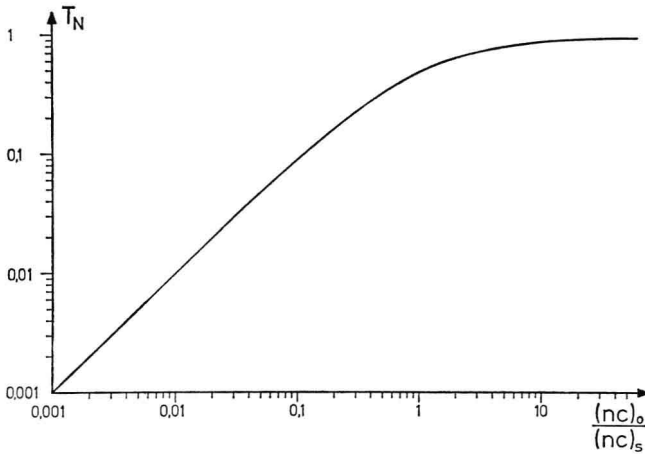


Fig. 2. Normalized transmission T_N versus the normalized laser intensity $nc/(nc)_s$, according to Eq. (6)

For optically thick samples, which is the more interesting case applicable to the majority of experiments, Eqs. (1) – (3) have to be combined with the photon-transport equation:

$$\frac{\partial n}{\partial t} + c \frac{\partial n}{\partial x} = -m_0 \sigma_{01} n c . \quad (7)$$

Since τ_F is assumed to be much smaller than the width of the laser pulse we may treat this problem as a stationary one and set all partial time derivatives equal to zero so that one differential equation remains:

$$c \frac{\partial n}{\partial x} = -n c \sigma_{01} m \frac{1}{1 + n c \sigma_{01} \tau_F} . \quad (8)$$

Integrating (8) from $x = 0$ to $x = L$, the depth of the sample, we get

$$\ln \frac{(nc)_E}{(nc)_0} + \sigma_{01} \tau_F [(nc)_E - (nc)_0] = -\sigma_{01} m L , \quad (9)$$

where $(nc)_0$ is the laser intensity entering the sample and $(nc)_E$ the intensity at the exit. For small light intensities this relation reduces to Beer's law,

$$\ln T_0 = \ln \frac{(nc)_E}{(nc)_0} = -\sigma_{01} m L , \quad (10)$$

with T_0 being the low-intensity transmission. Using the intensity dependent transmission $T = (nc)_E / (nc)_0$, (9) can be rewritten as

$$T = T_0 \exp [\sigma_{01} \tau_F (nc)_0 (1 - T)] \quad (11)$$

or

$$\frac{\ln T / T_0}{1 - T} = \frac{(nc)_0}{(nc)_S} . \quad (12)$$

This relation ¹¹⁾ gives the sample transmission T as a function of the normalized intensity $(nc)_0 / (nc)_S$. Figure 3 shows the saturation characteristics, according to (12), for several values of T_0 . These curves approach complete bleaching of the sample at very high light levels, as in Fig. 2., but the point where the absorption of the sample is half of the initial value $A_0 = 1 - T_0$ is not reached at $(nc)_0 / (nc)_S = 1$, but rather at higher light levels: the greater is A_0 , the higher is the light level at half-absorption.

Unfortunately there are no experimental results which could be compared with these theoretical curves. All experiments reported in the literature are either made with cyanine dyes showing some excited state absorption or with phthalocyanine dyes which have an extremely high intersystem crossing rate so that triplet populations cannot be neglected.

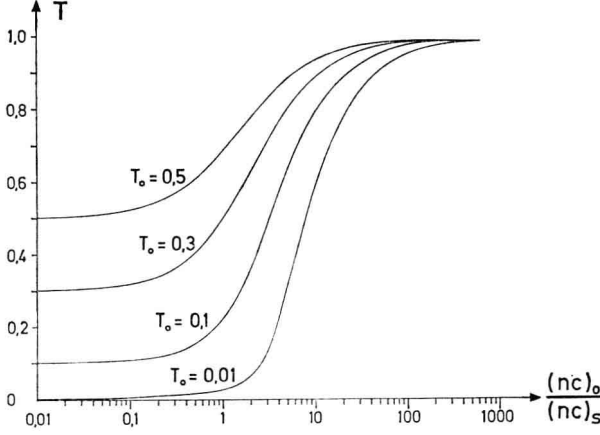


Fig. 3. Transmission T versus normalized laser intensity $nc/(nc)_s$ with low-level transmission T_0 as a parameter

To include excited-state absorption into the above model, Eqs. (1)–(3), and (7) have to be rewritten and another rate equation for the population m_2 of the singlet level S_2 has to be included:

$$\frac{\partial m_0}{\partial t} = -m_0 \sigma_{01} nc + m_1 / \tau_F \quad (1a)$$

$$\frac{\partial m_1}{\partial t} = (m_0 \sigma_{01} - m_1 \sigma_{12}) nc + m_2 k_{21} - m_1 / \tau_F \quad (2a)$$

$$\frac{\partial m_2}{\partial t} = m_1 \sigma_{12} nc - m_2 k_{21} \quad (13)$$

$$m_0 + m_1 + m_2 = m \quad (3a)$$

$$c \frac{\partial n}{\partial t} + c \frac{\partial n}{\partial x} = -(\sigma_{01} m_0 + \sigma_{12} m_2) nc \quad (7a)$$

reducing again to a single differential equation,

$$c \frac{\partial n}{\partial x} = -nc \sigma_{01} m \frac{1 + \sigma_{12} \tau_F nc}{1 + \sigma_{01} \tau_F nc (1 + \sigma_{12} nc / k_{21})}$$

with the solution ¹²⁾,

$$\ln\left(\frac{T}{T_0}\right) + \sigma_{01} \tau_F (nc)_0 (T - 1) + \left(\frac{\sigma_{01}}{\sigma_{12}} - 1 - \frac{\sigma_{01}}{\sigma_{12} \tau_F k_{21}} \ln\left[\frac{1 + \sigma_{12} \tau_F T (nc)_0}{1 + \sigma_{12} \tau_F (nc)_0}\right]\right) = 0 \quad (11a)$$

For low intensities ($(nc)_0 < (nc)_s$) this reduces to (11); for high light intensities ($(nc)_0 > k_{21}/\sigma_{12}$), however, to

$$T \approx T_0 \left[(\sigma_{12}/\sigma_{01})^{(1+(nc)_0 \cdot \sigma_{12}/k_{21})} \right], \quad (14)$$

which shows that for very large values of k_{21} there should be a residual absorption at high light intensities:

$$T \approx T_0^{(\sigma_{12}/\sigma_{01})}. \quad (15)$$

This latter result has already been derived by Hercher ¹¹⁾.

To test this model, the nonlinear absorption of cryptocyanine solutions has been investigated by several authors ¹³⁻¹⁵⁾. The most conclusive results were obtained by Schüller and Puell ¹²⁾ who used a ruby laser which, when focussed, produced an intensity of nearly 10^{10} W/cm² during a pulse width of 8 nsec. Their results for cryptocyanine dissolved in glycerol or alternatively in methanol are shown in Fig. 4. The solid lines in this figure, drawn through the experimental points, show the best fit to the relation (11a). The fitted parameters for glycerol solutions were σ_{12} , τ_F , and k_{21} which were fitted at the points indicated by arrows and resulted in the following values: $\sigma_{12} = 10^{-16}$ cm², $\tau_F = 0,83$ nsec, and $k_{21} = 0,83 \cdot 10^{12}$ sec⁻¹. The value of $\sigma_{01} = 5 \cdot 10^{-16}$ cm² was taken from the recorded absorption spectrum. For methanol it is known that τ_F is much shorter ¹⁶⁾, while

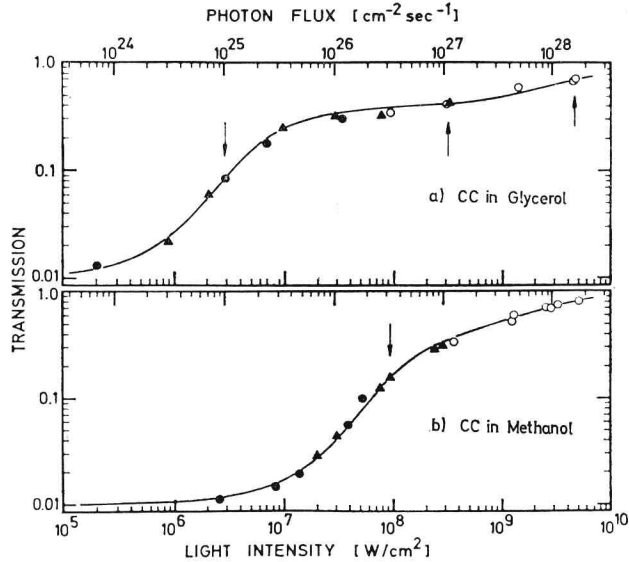


Fig. 4. Measured transmission versus incident light intensity for solutions of cryptocyanine in glycerol and methanol at room temperature. Initial dye transmission $T_0 = 1\%$. Theoretical curves (—) according to Eq. (11a) were obtained from matching theory and experiment at points indicated by arrows. (From Ref. ¹²⁾)

one should expect the ratio σ_{12}/σ_{01} and the value of k_{21} should remain unaffected. Hence the only parameter that had to be readjusted was τ_F . This was done at the point indicated by the arrow resulting in $\tau_F = 25$ psec for this solvent. The agreement between the theoretical curve and the experimental data is seen to be excellent. The molecular data obtained by the curve-fitting must be regarded with some reservations, however, because of the neglect of stimulated emission which acts in two ways. First, the stimulated emission at the ruby laser wavelength would become noticeable at the highest pump powers, affecting the value of σ_{12} and/or k_{21} . Second, spontaneous emission is amplified at the wavelength of the peak of the fluorescence spectrum when it passes through the excited parts of the sample, thus effectively shortening the fluorescence decay time τ_F at high intensities. The values of τ_F found in these experiments are already shortened by stimulated emission and can only be considered a lower bound for the true spontaneous fluorescence decay time τ_F as measured at low light levels. The excitation of the second excited singlet state S_2 in these experiments is also substantiated by similar experiments by Müller and Pflüger ¹⁷⁾ who found an anomalous blue fluorescence in ruby-laser-excited solutions of cryptocyanine, the kinetics of which also confirmed it as a two-step population of S_2 by the ruby laser excitation.

The situation is quite different with dyes like the phthalocyanines which have very high intersystem crossing rates k_{ST} (e.g. vanadiumphthalocyanine, $k_{ST} > 6 \cdot 10^9$ ¹⁴⁾). In addition, the triplet lifetime τ_T is usually in the microsecond region ⁷⁾ for air-equilibrated samples and even longer in degassed solutions. This means that a laser pulse of a few nsec duration will increase the transmission of the sample by bringing many molecules into the triplet state T_1 via the excited singlet state S_1 . How much the transmission is increased no longer depends on the peak intensity but rather on the energy density of the laser pulse $J = c \int_0^t n(t) dt$.

We therefore define an energy transmission ¹¹⁾

$$T_J = \frac{(\text{transmitted energy density})}{(\text{incident energy density})} = \frac{J}{J_0}$$

with J_0 being the energy density of the incident laser pulse. Neglecting excited singlet and/or triplet state absorption, which is justified in the case of the phthalocyanines, and assuming that the internal conversion rate k_{10} can be neglected in comparison with k_{ST} , which means that $\eta_F = \frac{1/\tau_{FR}}{1/\tau_{FR} + k_{ST}}$, we obtain the following rate equation for m_0 in an optically thin sample:

$$dm_0/dt = -m_0 \sigma_{01} (1 - \eta_F) n c . \quad (16)$$

For every molecule which absorbs, η_F molecules return directly to the ground state, while $1 - \eta_F$ are transferred into the long-lived triplet state. Integrating (16) gives

$$\frac{m_0(t)}{m_0(t=0)} = e^{-\sigma_{01}(1-\eta_F)nc t} \quad (17)$$

or a normalized energy transmission T_{NJ} of

$$T_{\text{NJ}} = 1 - e^{-\sigma_0(1-\eta_F)J} . \quad (18)$$

which becomes with $J_S = 1/[\sigma_0(1-\eta_F)]$,

$$T_{\text{NJ}} = 1 - e^{J/J_S} . \quad (18a)$$

This result shows that J_S is the energy density that is needed to reduce the sample absorption by a factor of $1/e$. Similarly, for an optically thick sample one finds¹⁴⁾

$$T_J = (J_S/J_0) \ln[1 + T_0 (e^{J_0/J_S} - 1)] . \quad (19)$$

Plotted curves illustrating this relation, Fig. 5, resemble very much the curves of Fig. 3. Consequently, one cannot infer from a measured intensity or energy saturation curve reliable values of molecular data without additional information, as for instance an independent measurement of k_{ST} . Another possibility is a measurement of the temporal characteristics of the bleaching as demonstrated in an experiment by Hercher *et al.*¹⁴⁾. These authors bleached a thoroughly degassed solution of metal-free phthalocyanine in 1-chloronaphthalene by a ruby laser pulse (694.3 nm) of about 59 nsec pulse width. At the same time they measured the absorption at 632.8 nm using a He-Ne-laser, and the result of this measurement is shown in Fig. 6. It clearly demonstrates that the sample was almost completely bleached even before the laser pulse reached its maximum intensity, and that almost all of the molecules were stored in the triplet state because the transmission did not decrease with the fall of the laser intensity for at least 100 nsec. A small residual absorption indicates triplet-triplet absorption.

For the general case, when neither the steady state approximation nor approximations regarding relaxation rates are valid, one has to use computer solutions of a set of rate equations, analogous to those above, including the triplet population.

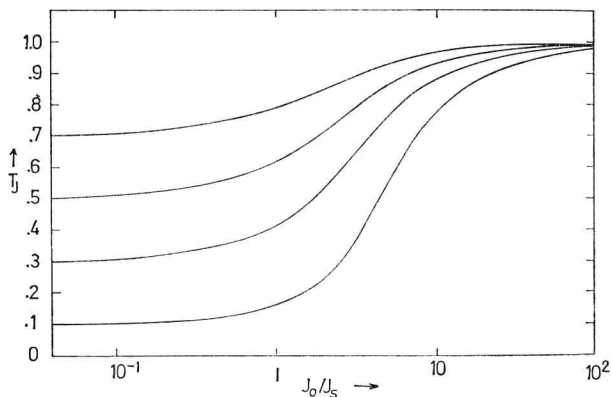


Fig. 5. Energy transmission T_J versus normalized energy density J_0/J_S . (From Ref. 14)