169. Laser Flash Photolysis of Phthalocyanines in Solution and Microemulsion

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Summary

Triplet state formation (Φ_{isc}) and properties (ε_{T-T}, τ_T) of phthalocyanine (HPC) and zinc phthalocyanine (ZnPC) have been characterized in homogeneous solutions (1-chloronaphthalene, 1-propanol) and in microemulsion by investigating the variation of the transient optical density as a function of the intensity of the exciting laser. Experimental results follow the theoretically predicted dependence only for very low intensities of the exciting pulse. At higher intensities, a more complicated scheme of primary reactions has to be taken into account, implicating qualitative restrictions in the application of saturation experiments. The observed transients at high-intensity excitation are interpreted as being perturbed by aggregational phenomena.

Introduction. – Phthalocyanines revealed to be very interesting, partly as a result of their unique structure which is closely related to chlorophyll, partly because of their high thermal and chemical stability, necessary properties for their application as catalysts [1], dyes [1] and semiconductors [2]. Moreover, phthalocyanines are used as sensitizing pigment dispersions in experiments aiming at a conversion of light into chemical free energy [3–5]. In contrast, there are only few reports on their molecular photophysical parameters such as the triplet-triplet absorption spectra (ε_{T-T}), their triplet energies (E_T) and their quantum yields of intersystem crossing (Φ_{isc}). This is due to their very low solubility in most organic solvents as well as in water. However, evidence for triplet states was gained by conventional flash photolysis [6] [7] and recently by laser flash photolysis [8].

A relatively low triplet energy $E_T \simeq 120 \pm 10$ kJ.M^{-1} and a triplet lifetime $\tau_T \simeq 130 \pm 10 \mu s$ have been reported for the metal-free phthalocyanine in 1-chloronaphthalene [8] indicating a useful and easily detectable triplet counter for our purposes in the research of highly coloured sensitizers [9]. However, a precise value of ε_{T-T} has to be determined; in fact, the *Table* shows the different results reported in

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the literature which apparently depend very much on the experimental method used.

We report in the present paper the values of ε_{T-T} and Φ_{isc} for the metal-free (HPC) and for the zinc (ZnPC) phthalocyanine, respectively.

The results originate from a detailed analysis of the variation of the transient optical density as a function of the intensity of the exciting laser beam. Values obtained in both homogeneous solution and microemulsion are compared.

Table. *ε_{T-T} - and Φ_{isc}-values for HPC in 1-chloronaphtalene*

$\varepsilon_{T-T} \times 10^{-3}$	Method	Reference	Φ_{isc}	Method	Reference
18 ± 2	Equ. 5	This work	0.17 ± 0.03	Equ. 5	This work
37	Extrapolation *(cf. Fig. 2)*	This work	0.14	Comparative technique	[8] [15]
28	Complete conversion	[8]			
38	Singlet depletion	[8]			
36	Energy transfer	[8]			

Fundamentals. – The quantitative analysis of the transient optical density OD. in function of the laser intensity was introduced by *Lachish et al.* [10] [11].

Prior to and after excitation the optical densities of the solution are at a given wavelength λ of analysis:

$$\mathrm{OD.}\,(\lambda) = \varepsilon_g(\lambda)\mathrm{C}_o l \tag{1}$$

$$\mathrm{OD.}^*(\lambda) = [\varepsilon^*(\lambda)\mathrm{C}^* + \varepsilon_g(\lambda)\mathrm{C}_g]l \tag{2}$$

where $\varepsilon_g(\lambda)$ and $\varepsilon^*(\lambda)$ are the molecular extinction coefficients of the ground and the excited state, respectively, at the wavelength of analysis, and where C_g and C^* are the concentrations of the remaining ground state molecules and of the excited molecules; l is the optical path of the sample.

Obviously, $C_o = C^* + C_g$ is constant, but the relative values of C^* and C_g depend on the intensity I of the excitation.

The variation of optical density induced by the light flash is defined as:

$$\Delta\mathrm{OD.}\,(\lambda,\mathrm{I}) = \mathrm{OD.}^* - \mathrm{OD.}_g = [\varepsilon^*(\lambda) - \varepsilon_g(\lambda)]\mathrm{C}^* Il \tag{3}$$

It has been demonstrated [10] that C^* may be written as a function of the excitation energy:

$$\mathrm{C}^*(I) = \mathrm{C}_o\{1 - \exp[-2.3\Phi\varepsilon_g(\lambda')I]\} \tag{4}$$

where Φ = quantum yield of the formation of the excited state analyzed, I = intensity of excitation (einstein/dm^2) and $\varepsilon_g(\lambda')$ = molecular extinction coefficient of the ground state at the wavelength of excitation.

The parameters ε_{T-T} and Φ_{isc} may be obtained on combining equ. 3 and 4;

$$\Delta\mathrm{OD.}\,(\lambda,I) = \mathrm{a}(1 - \mathrm{e}^{-bI}) \tag{5}$$

where $a = [\varepsilon_{T-T}(\lambda) - \varepsilon_g(\lambda)]C_o l$ and $b = 2.3\ \Phi_{isc}\varepsilon_g(\lambda')$, and may be determined simultaneously in fitting an experimental set of values $\{\Delta OD., I\}$ to equ. 5.

For convenience in this paper we will deal with energy expressed in mJ per pulse and refer to the following equation:

$$\Delta OD.(\lambda I) = a(1 - e^{-BI}) \tag{6}$$

($b = 5 \times 10^7 B$, for our experimental conditions).

Results and discussion. – *Laser flash photolysis of a 10^{-6}M solution of HPC in 1-chloronaphthalene.* A transient absorption maximum at 480 nm and depletion in the absorption band of the ground state at $\lambda \simeq 650$ nm are observed. The transients analyzed at $\lambda = 480$ and 650 nm follow first-order kinetics with the same rate constants of $5.5 \times 10^3 s^{-1}$ (125 µs) in degassed solution. Moreover, addition of β-carotene leads to the observation of its characteristic triplet (5.5 µs lifetime). These observations are in agreement with those by *McVie et. al.* [8] and confirm the transient of HPC as a triplet.

In *Figures 1* and *2* we report the variations of the optical density at 480 nm as a function of the intensity of the laser pulse. It appears clearly that only for intensities up to nearly 2 mJ are the experimental points satisfactorily fitted by the relation [6] *(Fig. 1).* There is a significant departure from the theoretically expected variation of ΔOD., when more energetic pulses are also taken into account.

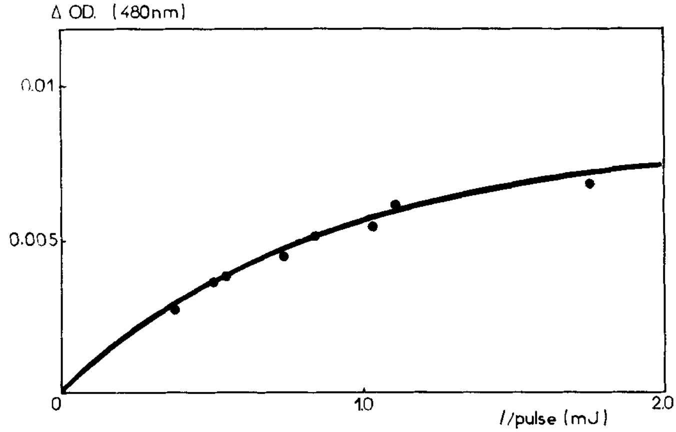

Fig. 1. *Variation of the transient optical density in the case of low excitation intensities for HPC* (10^{-6}M in 1-chloronaphthalene)

The treatment of data reported in *Figure 1* leads to the following values:

$$\left.\begin{array}{l} \varepsilon_{T-T} = 18{,}000 \pm 2{,}000\ M^{-1} \cdot cm^{-1} \\ \Phi_{isc} = 0.17 \pm 0.03 \end{array}\right\}\ I < 2\ mJ$$

It is not possible to compute ε_{T-T} and Φ_{isc} from the results in *Figure 2* since equ. 6 is not satisfied, but a graphical extrapolation of the data would indicate a value of

$\varepsilon_{T-T} \simeq 37{,}000 \pm 4{,}000$ M^{-1}/cm^{-1}. This observation and the results in the *Table* need further discussion.

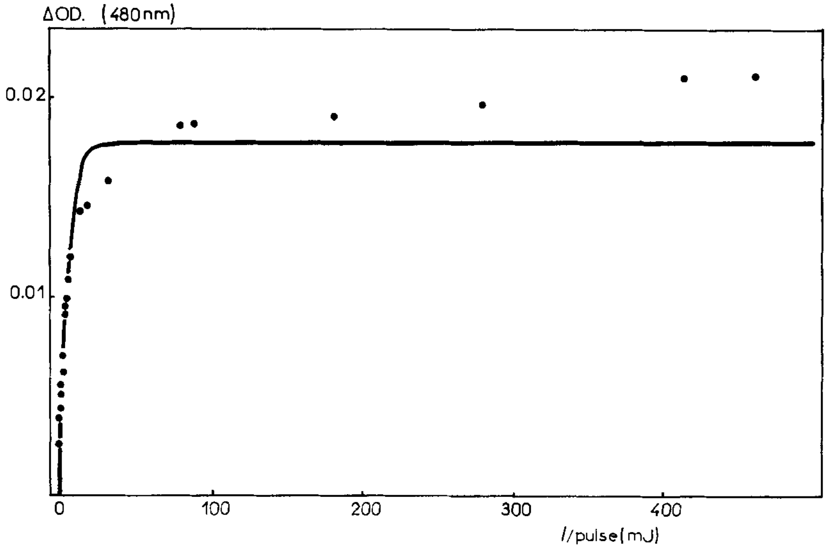

Fig. 2. *Variation of transient optical density* (whole range of available excitation energies) *for HPC* (10^{-6}M in 1-chloronaphthalene)

It should be noted that the method of complete conversion, the most reliable as claimed by *McVie et al.* [8], deals with high-power excitation. Since the photophysical properties of the phthalcyanines investigated satisfy the fundamentals of the *Lachish* equation [10], and since there is no *a priori* indication that this equation is restricted to low levels of excitation, we conclude that the primary processes upon high-intensity excitation are not fully understood and bias the determination of ε_{T-T} based on saturation experiments. This conclusion is indeed substantiated by the fact that the Φ_{isc} value determined according to equ. 6 is in good agreement with a previous evaluation ($\Phi_{isc} = 0.14 \pm 0.02$) [8] based on the comparative technique of *Amand & Bensasson* [15] for which the use of low laser intensities is necessary.

In order to verify the validity of the above conclusions we equally investigated ZnPC. We observed the same kinetic behaviour as in the case of HPC. Indeed, we found the same dependence on the intensity of excitation as described in *Figures 1* and *2*.

For low laser intensities, experimental data are quite well-fitted by equ. 6 ($\varepsilon_{T-T} = 16{,}000 \pm 3{,}000$ M^{-1}cm^{-1} and $\Phi_{isc} = 0.65 \pm 0.04$). The graphical extrapolation, however, yields $\varepsilon_{T-T} = 34{,}000 \pm 4{,}000$ M^{-1}cm^{-1} at high excitation intensities. The results seem like those we obtained for HPC, but no published data are available for comparison in this case.

We find i) no significant dependence of ε_{T-T} on the central atom, and ii) an enhanced Φ_{isc} due to the heavy-atom effect. Very recently, Φ_{isc} of three other metal-phthalocyanines were determined by picosecond laser photolysis [16]. It seems important to us that, in an empirical plot of the available values for Φ_{isc} [8] [16] *vs.* the atomic number of the metal atom *(Fig. 3)*, our data fit very well the apparent curve.

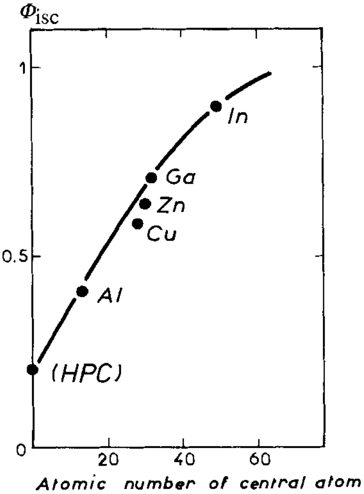

Fig. 3. *Empirical dependence of Φ_{isc} on the atomic number of the central metal ion*

We have been curious as to whether the unexpected dependence of ΔOD. on the light intensity would be related to the nature of the solvent. We repeated, therefore, the same investigation in 1-propanol, one of the rare solvents for phthalocyanines, quite different in polarity and chemical reactivity from 1-chloronaphthalene. In fact, we obtain qualitatively the same variations of ΔOD. in functions of *I*. Quantitatively, Φ_{isc} remains solvent independent, and ε_{T-T} is only slightly increased.

Laser flash photolysis of a microemulsion of HPC in oil/water (for preparation see exper. part). In order to gain evidence for aggregational effects being responsible for the observed deviation from the theoretical curve, we tried to isolate the phthalocyanine molecules within the aggregates of a surfactant [17]. To our knowledge, the photophysics of this chromophore has not yet been investigated in microheterogeneous phase and turned out to be very intriguing. As in the case of homogeneous solutions, we observed the same transient characteristics and the calculated parameters (ε_{T-T}, Φ_{isc}) do not differ significantly from those in homogeneous solution. However, the oscillograms reveal a distinct additional absorption as the laser intensity is increased. The examination at a fast time scale shows that no simple kinetics is involved.

McVie et al. [8] reported the possible participation of excitons formed by electronic excitation within and on the surface of micro-crystalline aggregates when dealing with $\sim 2 \times 10^{-5}$M solutions, but the disappearance followed a first-order kinetics.

The fact that the *Lachish* equation is not verified at high laser intensities in homogeneous solution prompted us to relate this failure to those observations in the microheterogeneous phase. Oscillograms as those observed in this investigation are in fact frequently found when working with colloidal systems. At the beginning of this study, we had expected that solubilization of phthalocyanine in microemulsions would preclude the formation of aggregates. In fact, the contrary effect was observed: inclusion of phthalocyanines in microemulsions results in a pronounced modification of the UV. spectra where two new broad absorption bands appear at 740 nm and 860 nm. This observation was particularly significant with CuPC even at such low concentrations as 4×10^{-7} M. The additional absorption bands are located at wavelengths corresponding to a thin film state [18]. These results are of considerable interest since they show that it is not possible to isolate those chromophores: apparently the strong aggregation forces cannot be compensated by the differences of potentials at the interface of microheterogeneous systems[3]).

We attempted to overcome this drawback by using pure sodium lauryl sulfate micelles and similar micelles containing 1-chloronaphthalene, where in both systems the concentration of the solubilized phthalocyanine has been as low as the mean occupancy $\bar{n}$ was close to 0.3 based on the *Poisson*'s statistics. The UV. spectra of these systems resemble those of the microemulsions. Moreover, the UV. spectra change with time, the absorption due to the monomer decreasing continuously.

We are pursuing this investigation by testing other detergents and microemulsions[4]).

No significant differences between homogeneous and microheterogeneous phases have been obtained with regard to the molecular absorption coefficient, the quantum yield and the lifetime of the triplet states. This is in accordance with the fact that the UV. maxima are practically the same in the two phases. This indicates a similar microenvironment for the chromophore in both systems. Thus, we explain our results with the presence of aggregates in both homogeneous solution and microheterogeneous phase.

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Experimental. – HPC *(Bauer and Pfalz)* and ZnPC *(K & K)* were sublimated at 400° under reduced pressure. Phthalocyanines are highly insoluble, even in 1-chloronaphthalene, the most suitable organic solvent, aggregation occurs at 10^{-5}M [8] [12]. Thus, the solutions were heated during 12 h up to 160° for 1-chloronaphthalene and 80° for 1-propanol.

UV. spectra were checked before and after flashing in order to detect the presence of aggregated particles [13] [14] to rule out degradation processes.

The light intensity from a ruby laser (*J. K. Lasers*, series 2000) could be readily controlled by using a 'black glass' calorimeter *(Laser Instrumentation)* and filters of known optical density at 694 nm. Homogeneity of the laser beam was carefully tested thoughout all the experiments by checking its impact at four to five different intensities on photographic paper before and after each series of experiments, since

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[3]) Aggregational effects are also oberved in homogeneous systems ($\sim 10^{-6}$M) when solutions have not been prepared carefully.

[4]) According to a very recent publication [19], it should be possible to prevent aggregation by incorporating ZnPC in *CTAC* and in *IGEPAL CO 630* micelles. Nevertheless, a broad band at 740 nm is clearly seen in the published spectrum which does not exist in the monomer spectra of this phthalocyanine.

the reliability of the determinations of coefficient B in equ. 6 depends on this condition. The laser cell had 0.6 cm path length. The oscillograms were first recorded on a memory oscilloscope (*Tektronix* 7834), then taken on photographs.

The fitting of the experimental points to the theoretical curve expressed by equ. 6 was performed by using a non-linear least-squares program written by Dr. *P. P. Infelta* for an *H. P.* 9820 A desk calculator and an *H. P.* 9862 A calculator-plotter.

The oil/water (o/w) microemulsion was prepared by mixing 1.8 g of sodium lauryl sulfate with 4 ml of cyclohexanol, 2 ml of an adequate solution of phthalocyanine in 1-chloronaphthalene and completing to 20 ml by tri-distilled water. Solutions and microemulsion were degassed by purging solvents and solutions with high purity argon.

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