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**ANALYSIS OF PHOTOISOMERIZABLE DYES
USING LASER ABSORPTION
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ABSTRACT

The attention of the present report has been directed mainly to the description of laser-based techniques developed in order to obtain kinetic and spectroscopic properties of polymethine cyanine dyes in solution. Special attention was dedicated to photoisomerizable molecules where the absorption spectra of both isomers are strongly overlapped. As an example, measurements of two different dyes of laser technological interest, DTCI and DODCI were performed. The developed methods provide a complete quantitative description of photophysical processes.

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I. INTRODUCTION

The optical properties of polymethine cyanine dyes (PCD) have attracted great experimental and theoretical interest in the past years, due to its connection with different areas of scientific and technological relevance, mainly in laser technology. These dyes provided tunable laser emission in the 540-1175 nm range [1] used as active material and ultra-short light pulses when they are used as saturable absorbers in mode-locking techniques [2,3].

Among PCD, the existence of steric isomers formed by rotation about a bond in the conjugated chain has long been accepted. As early as 1956 photochemical production of stereo isomers in PCD was reported at first time [4]. In further works of the same group was recognized that transient species are formed by trans-cis photo conversions followed by subsequent dark reversion. Trans-cis isomerization has been studied among other compounds than PCD, including stilbens, indigo dyes, azo compounds, anils, conjugated nitriles and other molecules. Irradiation with light resonant with the first excited state or higher of the singlet manifold of most PCD normally produces an unstable species, the photoisomer, P. This transient species relax in almost reversible way to the normal form, N. The measured life-times of P (ground state) span several orders of magnitude. Short-lived P with nanoseconds lifetimes and long-lived P with microseconds and milliseconds lifetimes have been reported [see data of ref.5]. For each compound the lifetime and other kinetics and spectroscopic parameters depend strongly on temperature and solvent properties.

The formation of P species has been demonstrated through extensive experimental studies. Flash photolysis [6], fluorescence [7], transient absorption [8] and picosecond-time resolved spectroscopy [9] have been used among other experimental techniques. The photophysics of PCD has been studied extensively by absorption and emission spectroscopy,

particularly DODCI (3,3'-diethyloxadicarbocyanine iodide) [10,11,12]. For dyes with relatively long-lived P ground state, like DODCI, CW lasers can be used. Dyes with short-lived transient species can not be studied by CW excitation and high power pulsed lasers are needed.

Despite this great amount of work the information available to model the system is reduced to the normal species parameters and the P_0 lifetime. Few information exist about the quantum yield of photo-isomerization for most of the PCD. The properties of S_1^P , the first excited state of P, and its participation in the backward photoisomerization process is still less studied. By high fluence irradiation using pulsed or CW lasers, high relative population of P can be obtained and its optical properties can be inferred. The saturated population of P ground state (P_0) was used recently to study the optical properties of P and its kinetics connections with photoisomerization of DODCI [13].

The attention of the present report has been directed mainly to the description of laser-based techniques developed by the authors in order to obtain kinetic and spectroscopic properties of PCD and more specially to those molecules with isomeric-absorption spectra strongly overlapped. As an example, measurements of two different PCD of laser technological interest, DTCI and DODCI through these techniques was performed.

THEORY AND METHODS

Notation used in the text is as follow (see scheme of fig. 1):

N_0 , N_1 and P_0 , P_1 are the ground and excited state populations of the normal and photoisomer species, respectively.

$N = N_0 + N_1 + P_0 + P_1$, concentration of the sample,

$B = \sigma_P / \sigma_N$, with σ_P , σ_N the absorption cross sections

of the P and N species at a given wavelength,
 $a = I \cdot \sigma_N$, rate of light absorption, where I is the excitation fluence.

w is the rate of sample renewal within the irradiated volume by circulation of the solution.

k, k' are rate constants of the $P_0 \rightarrow N_0$ and $N_0 \rightarrow P_0$ processes.

τ_N, τ_P are lifetimes of excited states for the normal and photoisomeric species, and

ϕ_{NP}, ϕ_{PN} are quantum yields of $S_1^N \rightarrow S_0^P$ and $S_1^P \rightarrow S_0^N$ isomerization processes.

In photoequilibrium of both isomeric species several photophysical parameters can be evaluated using the isomerization model and the corresponding rate equations [12]. Under these conditions and exciting with cw radiation, the fraction of P-ground state level population can be expressed by:

$$x_P = P_0/N = [(1+p.B) \cdot (1+a_0/a)]^{-1}, \quad (1)$$

where:

$$p = \phi_{PN}/\phi_{NP}, \quad (2)$$

$$a_0 = (k+w)/[\phi_{NP} \cdot (1+p.B)], \quad (3)$$

and B is taken at the excitation wavelength λ^* . Saturation intensity I_s can be defined by the fluence $a_s = I_s \cdot \sigma_N$ necessary to obtain one half of the maximum photoisomer population, i.e. $x_P(a_s) = 1/2 \cdot (1+p.B)$. For high intensity, ($a \gg a_0$), eq. 1 can be reduced to:

$$x_P = (1+p.B)^{-1} \quad (4)$$

Under the last condition, called saturation, the population of S_0^P depends on the excitation wavelength, as a result of the dependence of B on λ , but it is independent of the laser fluence. In this case, the analysis of the results is greatly simplified and more reliable. In some

cases, near total population can be transferred to S_0^P by using a CW high fluence dye laser [13].

Absorption methods

Laser Absorption Spectroscopy provides a sensitive technique for monitoring kinetic mechanisms and to characterize unknown species. Basically, we studied changes in the absorbance of the sample depending on the excitation fluence in a differential configuration. Synchronic detection can be used and high sampling rates improved the reproducibility of experimental results. With a pump and probe method using a second low power CW laser, it was possible to determine p and B(λ) at different excitation wavelengths (eq. 4).

Figure 2 shows the experimental set-up employed. A chopped pump beam of wavelength λ^* and intensity I^* produces a modulated stationary population of S_0^P . Absorption variation is monitored by a CW probe beam of intensity I ($I \ll I^*$) and wavelength λ . Because the beams are perpendicularly polarized one to the other and due to the polarizers arrangement, only the probe beam is detected in D_x , while the D_z signal is related to I^* . Absorption coefficients are obtained by measuring the transmitted intensity:

$$\alpha_0 = (1/l) \cdot \ln(I/I_0), \quad \text{when pump off,}$$

$$\alpha_s = (1/l) \cdot \ln(I/I_s), \quad \text{when pump on.}$$

I is the intensity of the incident beam and I_0, I_s are the transmitted intensities in both cases.

Absorption coefficients can be calculated from:

$$\alpha_0 = N \cdot \sigma_N, \quad (5a)$$

$$\alpha_s = N_0 \cdot \sigma_N + P_0 \cdot \sigma_P \quad (5b)$$

where σ_N and σ_P are the absorption cross sections of N and P species at wavelength λ . Combining these equations, we get:

$$(\alpha_0 - \alpha_s) / \alpha_0 = (B-1) \cdot \phi^P \quad (6)$$

and the use of eqs. 1 - 3 leads to :

$$\frac{\alpha_0}{\alpha_0 - \alpha_s} = \frac{(1+p \cdot B^0)}{(B-1)} + \frac{(k+w)}{(B-1) \cdot \phi_{NP}} \cdot \frac{1}{a} \quad (7)$$

The straight line dependence obtained when eq.7 is plotted as a function of $1/a$ represents the basis of the method, developed specially for the case of overlapping absorption spectra. Excitation at different wavelengths can be used to obtain the values of p, B and ϕ_{NP} taking $(k+w)$, the rate of deactivation of S_0^P , from the time dependant part of the absorption signals.

Fluorescence methods.

Measurements of the fluorescence properties of PCD are particularly important to understand the photophysics behavior of singlet excited state of the molecules.

Photoisomeric emission appears in the favorable cases, as a distribution change of the normal species emission spectrum, when appropriated excitation fluence are used. But in the general case, the presence of the photoisomer only can be detected through the overall fluorescence intensity change. Reliable measurements of fluorescence spectrum, quantum yield and lifetime of excited state of photoisomeric species required very sensitive techniques and a carefully analysis of the system.

When the emission spectra of isomeric species are strongly overlapped, the determination of kinetic and spectroscopic parameters is more difficult. In this case the fluorescence (at any wavelength) is coming from both species and the total intensity must be written:

$$I_f = \phi_f^N \cdot a \cdot N_0 + \phi_f^P \cdot a \cdot B \cdot P_0, \quad (8)$$

replacing N_0 and P_0 by using the condition $N = N_0 + P_0$ and eq. 1, the following eq. can be obtained:

$$\frac{I_f}{a} = K \cdot \frac{(1+G \cdot a/a^*)}{(1 + a/a^*)} \quad (9)$$

where K is an instrumental constant, $G = (p+f)/(p+1/B)$, with $f = \phi_f^P / \phi_f^N$, and p and a^* as were defined before.

In order to use eq. 9 the fluorescence intensity divided by the excitation intensity was plotted in terms of this last value. The fitting contains three adjustable parameters K, a^* and G. No useful information can be extracted from K, which depends on many factors such photomultiplier sensitivity, geometry, wavelength, and dye concentration. Measurements of a^* from fluorescence have less precision that those obtained from absorption. The most useful information, regarding photo- isomerization quantum yields of N and P, is contained in G, the limit value for $I_f/K \cdot a$ when $a \rightarrow a^*$. If p and B are known from absorption measurement, $f = \phi_f^P / \phi_f^N$ can be obtained.

RESULTS

Fig 3 shows experimental values obtained from a low concentration solution ($2 \cdot 10^{-6} M$ in ethanol) of 3,3'-diethylthiacarbocyanine iodide (DTCI), which has been studied at several wavelengths under absorption at $\lambda^* = \lambda$. Different sign and slope when eq. 7 is plotted come from the $(B-1)$ factor. Special caution was taken to control the temperature and the flow speed because of the strong dependence of some photophysical constants on these parameters. The best fit of experimental points was obtained by using eq. 7 with $\phi_{NP} = 0.8$, $p = 0.8$ ($\phi_{PN} = 0.64$), $B(514 \text{ nm}) = 1.15$ and $B(557 \text{ nm}) = 0.6$.

Fluorescence quantum yield of the photoisomeric species was obtained for DTCI using the fluorescence technique mentioned above. Fig. 4 shows a typical normalized fluorescence intensity in terms of the excitation fluence at 550 nm. Fit of the experimental points by using eq. 9 and the results above mentioned, allow us to obtain $f < 0.1$ at room temperature ($\phi^F < 0.007$, taking into account that $\phi^N = 0.07$ for DTCI at 25°C). This result is in agreement with the fact that no spectral distribution change was observed varying the temperature, or the excitation fluence from low values where only the normal species emission contribute, to saturation values, where both species are present (fig. 5a).

For some PCD, the emission spectra of both species present regions where they do not overlap, as the case of DODCI [14]. Fig. 5b. shows a fluorescence distribution at two excitation fluence, where the emission from both species can be observed.

Photoisomer emission can be more easily analyzed by superimposing to the continuous excitation that produces a stationary photoisomeric population, a pulsed beam that probe this population in a region where only the photoisomer absorbs. Pulsed fluorescence emission obtained in this way and shown in curve (b) of fig. 6, corresponds to the photoisomeric species emission. Curve (a) corresponds to the cw emission spectrum achieved when only the continuous excitation beam is present and $B \ll 1$. In this case, normal species emission is basically present. Using this experimental arrangement, both species can be separately analyzed to obtain the photophysical properties of excited states.

CONCLUSION

In this paper a description of laser absorption and fluorescence techniques as a very sensitive tools applied to the study of photoisomerizable dyes was performed. The developed methods provide a complete quantitative description of photophysical processes, even when the spectrum of both species are strongly overlapped, as is the case for DTCI. On the other hand, when the spectra are not completely overlapped (DODCI) a modified technique allows us to have a separate description of both species.

The energy difference ΔE between the ground states of both species can not be obtained by these methods and photoacoustic or thermal lens techniques should be used to establish a quantitative energy level scheme.

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FIGURE CAPTIONS

Fig. 1 : Four level scheme used for the interpretation of the photochromic system. The activation-deactivation channel are indicated by rate constants (a , $B.a$, k) or quantum yields (ϕ_f , ϕ_{NP} , ϕ_{PN}).

Fig. 2 : Experimental set-up of the absorption technique. The pump beam is shown by the dashed line and its power is detected by D_2 . Probe beam is shown by the continuous line and monitored by D_1 . L: lens ; P: polarized; E: mirror; CH: chopper; R: polarization rotator; O: calibrated pinhole; C: cell; DH: beam splitter; D_1 , D_2 : photodiode.

Fig. 3 : Absorption coefficient measurements for DTCl in terms of pump fluence. Eq. (7) is plotted for best fitting with: $\phi_{NP}=0.8$; $p=0.8$ ($\phi_{PN}=0.64$); $B(514 \text{ nm})=1.15$ and $B(557\text{nm})=0.6$. $\Delta = 557 \text{ nm}$ $\square = 514 \text{ nm}$.

Fig. 4 : Plot of fluorescence intensity (I_f) normalized to excitation intensity ($I_{exc.}$), in arbitrary units as a function of $\log. I_{exc.}$.

Fig. 5 : Fluorescence emission (a) of DTCl; (b) of DODCl at two excitation fluence.

Fig. 6 : Uncorrected fluorescence emission spectrum of DODCl in ethanol obtained by cw (520 nm, 20 mW) and pulsed (645 nm, 200 μ J), 1 μ s) excitation : (a) cw, (b) cw and pulsed.

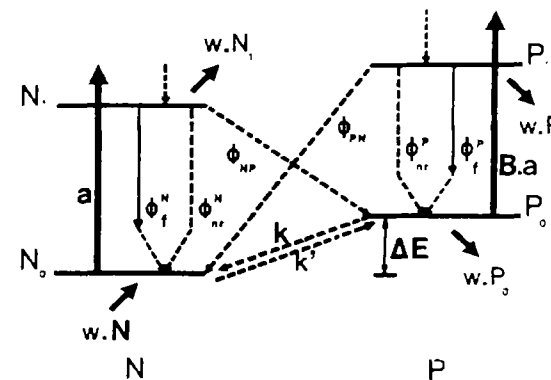


FIGURA 1

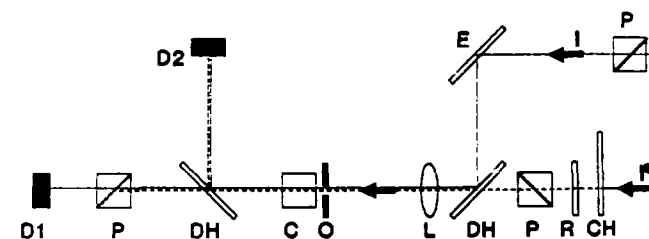


FIGURA 2

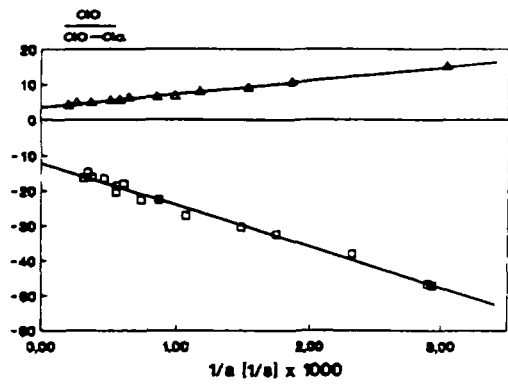


FIGURA 3

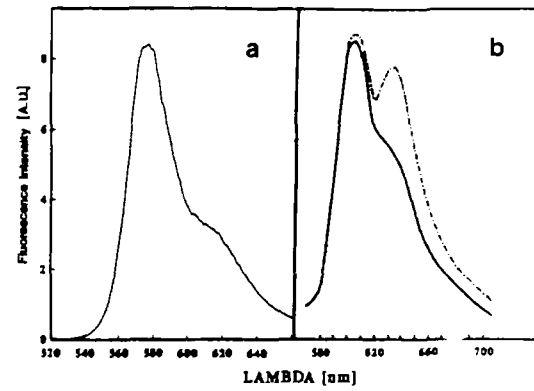


FIGURA 5

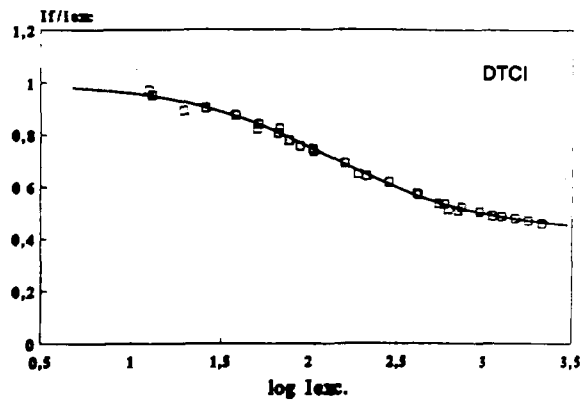


FIGURA 4

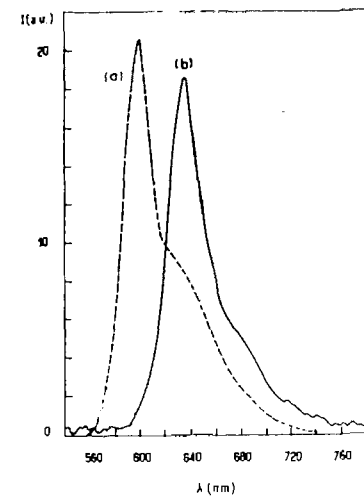


FIGURA 6