ISOMERIZATION OF DODCI IN THE $S_0$ GROUND STATE

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The long-wavelength absorption spectrum of DODCI indicates the presence of a thermally populated isomer in the electronic ground state. The energy level of this isomer above the normal form is determined by temperature-dependent absorption measurements. The $S_0$–$S_1$ absorption cross section spectrum of the isomer is determined.

1. Introduction

The dye DODCI (3,3'-diethyloxydicarbocyanine iodide) is widely used as a saturable absorber in passively mode-locked dye lasers [1–3]. It may also be applied as a laser dye [4–6]. Conventional flash tube photolysis [7], pulsed laser flash photolysis [7–22], and cw laser excitation spectroscopy [23,24] generate a photoisomer which absorbs and emits at longer wavelength than the normal form. In ref. [14] some evidence is given from rotational diffusion measurements that the normal (N) isomer has a 1,5 cis–cis form or similar coiled up conformation and that the photo (P) isomer has an all-trans or some other elongated form.

In this paper we show that both isomers are present in the electronic ground state ($S_0$) at room temperature. The P isomer is observed in the long-wavelength region of the $S_0$–$S_1$ absorption spectrum. The level energy $E_P$ of the P isomer above the N isomer ground state is determined from temperature-dependent absorption measurements. The $S_0$–$S_1$ absorption cross section spectrum of the P isomer is determined from an analysis of the absorption spectra.

2. Theory

The photoisomerization dynamics of DODCI is explained by a three-well $S_1$ potential curve and a two-well $S_0$ potential curve versus a twisting coordinate [13,18,21]. The $S_0$ potential curve is depicted in fig. 1. Relaxation of the photoexcited $S_1$ state populates both the N and the P state [7–24]. The P state relaxes to the N state across the potential barrier $E_A$ with a rate constant $[13,18,19]$

$$k_{P \rightarrow N}(T) = A_{iso} \exp\left(-E_A/k_B T\right).$$

Fig. 1. $S_0$ ground-state configuration diagram of DODCI.

$A_{iso}$ is the pre-exponential factor of the Arrhenius equation (1), $k_B$ is Boltzmann’s constant and $T$ is the temperature. The potential barrier is $E_A \approx$
The P→N relaxation time constant at room temperature is \( \tau_{P→N} = k_{P→N} \approx 2.53 \text{ ms} \) for DODCI in methanol and \( \tau_{P→N} \approx 2.60 \text{ ms} \) for DODCI in ethylene glycol [16].

The rate of the N→P transition in the electronic ground state is given by

\[
k_{N→P}(T) = A_{iso} \exp\left[ -\frac{(E_p + E_A)}{k_B T} \right].
\]

The fraction of thermally populated P isomers is

\[
\frac{N_{P0}}{N_0} = \frac{N_{P0}}{N_{N0} + N_{P0}} = \frac{\exp\left(-E_p/k_B T\right)}{1 + \exp\left(-E_p/k_B T\right)},
\]

where \( N_{P0} \) and \( N_{N0} \) are the number densities of the P and N isomers, respectively. \( N_0 \) is the total number density.

The apparent absorption cross section \( \sigma' = \alpha/\rho \) is given by

\[
\sigma' = \sigma_N' + \sigma_p' ,
\]

where

\[
\sigma_N' = \frac{\sigma_N}{1 + \exp\left(-E_p/k_B T\right)}
\]

and

\[
\sigma_p' = \frac{\exp\left(-E_p/k_B T\right)}{1 + \exp\left(-E_p/k_B T\right)} \sigma_p.
\]

The frequency dependence of the apparent absorption cross section \( \sigma_N' \) is given by [25,26]

\[
\sigma_N' = \alpha_N'(\nu)/N_{N0}, \quad \text{for} \ \nu > \nu_{01}^N,
\]

\[
= \sigma_{em}^N(\nu) \exp\left[-h(\nu_{01}^N - \nu)/k_B T\right],
\]

\[
\text{for} \ \nu < \nu_{01}^N.
\]

\( \sigma_{em}^N \) is the stimulated emission cross section of the N isomer and \( \nu_{01}^N \) is the frequency difference between the \( S_1 \) and \( S_0 \) electronic level of the N isomer. Its value is determined by the crossing point of the absorption and emission cross section spectra (see figs. 2 and 3).

The absorption cross section ratio, \( \sigma_p/\sigma_N' \), at \( \nu_{P,max} \) (\( \nu_{P,max} < \nu_{01}^N \)) is

\[
\frac{\sigma_p}{\sigma_N'} = \frac{\sigma_p \exp\left(-E_p/k_B T\right)}{\sigma_N' \exp\left(-E_p/k_B T\right)}
\]

\[
= \frac{\sigma_p}{\sigma_{em}^N} \exp\left[ -\frac{(E_p - E_N)/k_B T} \right],
\]

where \( E_N = \hbar (\nu_{01}^N - \nu_{p,\text{max}}) \). \( E_p \) is determined by measuring the ratio \( \sigma_p/\sigma_N' \) at two different temperatures \( T_1 \) and \( T_2 \). Application of eq. (8) gives

\[
E_p = E_N + \frac{k_B T_1 T_2}{T_1 - T_2} \left[ \ln\left( \frac{\sigma_p(v_{P,\text{max}}, T_1)}{\sigma_N'(v_{N,\text{max}}, T_1)} \right) \right. \]

\[
- \ln\left( \frac{\sigma_N'(v_{P,\text{max}}, T_2)}{\sigma_N'(v_{P,\text{max}}, T_2)} \right). \]

After determining \( E_p \) and \( E_N \) the apparent \( S_0-S_1 \) P isomer absorption cross section spectrum may be determined from eq. (8):

\[
\sigma_p(\nu, T) = \frac{\sigma_p(\nu, T)}{\sigma_N'(v_{P,\text{max}}, T)} \sigma_{em}^N(v_{P,\text{max}}, T)
\]

\[
\times \exp\left[ (E_p - E_N)/k_B T \right].
\]

The stimulated emission cross section \( \sigma_{em}^N(\nu) \) is determined from fluorescence quantum distribution measurements \( \tilde{E}(\lambda) \) \[\int \tilde{E}(\lambda) \lambda \, d\lambda = 1\] [27]. It is

\[
\sigma_{em}^N = [1 + \exp\left[-(E_p/k_B T)\right] \sigma_{em}^N \]

and [28–30]

\[
\sigma_{em}^N = \frac{\lambda^2 n_F \tilde{E}(\lambda)}{n_A} \int \tilde{E}(\lambda) \lambda^2 \, d\lambda \int \frac{\sigma_N(\lambda)}{\lambda} \, d\lambda.
\]

\( n_F \) and \( n_A \) are the average refractive indices of the solution in the \( S_1-S_0 \) emission and the \( S_0-S_1 \) absorption band, respectively. The integrations extend over the \( S_1-S_0 \) emission band (em) and the \( S_0-S_1 \) absorption band (abs).

3. Experimental

10–4 molar solutions of DODCI in ethylene glycol and in methanol are investigated. The absorption cross section spectra were measured with a conventional spectrophotometer (Beckman model ACTA M4). The temperature was varied with a thermostat. The fluorescence quantum distribution measure-
ments were carried out with a home-made fluorimeter [27] applying the front-face collection technique. The excitation wavelength for the fluorescence detection was set to $\lambda_{\text{exc}}=570$ nm. The excitation light was vertically polarized and the fluorescence signal was detected at the magic angle of 54.7° to the excitation polarization.

4. Results

The absorption cross section spectra, $\sigma'(\lambda)$, and the stimulated emission cross section spectra $\sigma'_{\text{em}}(\lambda)$ of DODCI in ethylene glycol and in methanol are plotted in figs. 2 and 3, respectively. These spectra were measured at room temperature ($T=294.5$ K). $\sigma'_{\text{em}}(\lambda)$ is approximately equal to $\sigma'_{\text{em}}(\lambda)$. The shoulders in the long-wavelength region of the $S_0$-$S_1$ absorption band indicates the $P$ isomer contribution.

In figs. 4 and 5 the long-wavelength absorption spectra are shown in more detail. In fig. 4a the absorption spectra $\sigma'(\lambda)$ (solid curves) at $T_1=294.5$ K (1) and $T_2=368$ K (2) are depicted for DODCI in ethylene glycol. At elevated temperatures DODCI gradually decomposes and the $S_0$-$S_1$ absorption coefficient decreases. Therefore the spectra are adjusted such that $\sigma'(\lambda_{01}^N, T_1)$ is equal to $\sigma'(\lambda_{01}^N, T_1)$. The broken curves represent $\sigma'_{\text{N}}$ (eqs. (5) and (7)). The differences $\sigma'_{\text{P}}=\sigma'_{\text{N}}$ (eq. (7)) are shown in fig. 4b by the broken curves. The absorption peak of the $P$ isomer occurs at $\lambda_{\text{P, max}}=620$ nm. At this wavelength the $S_0$-$S_1$ absorption of the $N$ isomer starts at $E_s^N=\hbar(\nu_{01}^N-\nu_{\text{P, max}})=\hbar c[0.119-1.0\times10^{-20} J=593 \text{ cm}^{-1}$ above the $S_0$ ground level ($\lambda_{01}^N=598$ nm). The level position of the ground state of the $P$ isomer is calculated from eq. (9). Its value is $E_P=1.45\times10^{-20}$ J=727 cm$^{-1}$. This energy value gives a fraction of $N_{\text{P}}/N_0\approx2.7\%$ of molecules in the $P$ isomer state at 294.5 K (eq. (3)). The apparent $S_0$-$S_1$ absorption

![Fig. 2. Apparent absorption and emission spectra of $10^{-4}$ molar DODCI in ethylene glycol. $T=21.5^\circ$C. Structural formula of DODCI is included.](image-url)
Fig. 4. Long-wavelength $S_0$–$S_1$ absorption spectra of DODCI in ethylene glycol. (1) $T=294.5$ K; (2) $T=368$ K. (a) Solid curves, apparent absorption cross sections $\sigma^* = \sigma_e + \sigma_p$. Broken curves, apparent absorption cross sections $\sigma_e$. (b) Broken curves, apparent absorption cross sections $\sigma_p$. Solid curve, $\sigma_p(\lambda)$ at $T=294.5$ K.
cross section spectrum $\sigma_P(\lambda)$ is depicted by the solid curve in fig. 4b. It is calculated from eq. (10). The peak absorption cross section is found to be $\sigma_P(620 \text{ nm}) = 5.7 \times 10^{-16} \text{ cm}^2$. This value is not considered to be very accurate because of its exponential dependence on $E_P - E_N$. (The standard deviation of $\sigma_P(620 \text{ nm})$ is $\approx 2 \times 10^{-16} \text{ cm}^2$.)

The long-wavelength $S_0-S_1$ absorption spectrum of DODCI in methanol is shown in fig. 5a. The temperature is $T = 294.5 \text{ K}$. The solid curve presents $\sigma' (\lambda)$, the broken curve gives $\sigma_N (\lambda)$ (eqs. (5) and (7)). $\sigma_P (\lambda) = \sigma' (\lambda) - \sigma_N (\lambda)$ (eq. (6)) is shown by the broken curve in fig. 5b. The P isomer $S_0-S_1$ absorption peak is at $\lambda_P_{\text{max}} = 615 \text{ nm}$. The value of $E_N$ is $h\nu_0 [ (\lambda_{\text{P, max}}^N)^{-1} - \lambda_{\text{P, max}}^1 ] = 1.31 \times 10^{-20} \text{ J} = 660 \text{ cm}^{-1}$ ($\lambda_{\text{P, max}}^N = 591 \text{ nm}$). The P isomer absorption cross section spectrum $\sigma_P (\lambda)$ (solid curve in fig. 5b) is taken from ref. [7] where it was determined from absorption changes in flash photolysis experiments for DODCI in ethanol. $E_P$ is determined from the broken and solid curve in fig. 5b by application of eq. (6). The value $E_P = 1.51 \times 10^{-20} \text{ J} = 760 \text{ cm}^{-1}$ is ob-

### Table 1

Spectroscopic parameters of DODCI. $T = 21.5^\circ \text{C}$. Concentration $10^{-4} \text{ mol/dm}^3$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Solvent</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>ethylene glycol</td>
<td>methanol</td>
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<tr>
<td>$\lambda_{\text{P, max}}$ (nm)</td>
<td>620</td>
<td>615</td>
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</tr>
<tr>
<td>$\sigma_{P, \text{max}}$ (cm$^2$)</td>
<td>$(5.7 \pm 2) \times 10^{-16}$</td>
<td>$(7 \pm 0.7) \times 10^{-16}$ [7]</td>
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<tr>
<td>$N_{\text{P}}/N_0$</td>
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<td>0.024</td>
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<tr>
<td>$N_{\text{N}}/N_0a)$</td>
<td>0.054</td>
<td>0.039</td>
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</tr>
<tr>
<td>$E_P$ (cm$^{-1}$)</td>
<td>727</td>
<td>760</td>
<td></td>
</tr>
<tr>
<td>$E_N$ (cm$^{-1}$)</td>
<td>593</td>
<td>660</td>
<td></td>
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</tbody>
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$^a$ Fraction of N isomers absorbing effectively at $\lambda_{\text{P, max}}$. 

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Fig. 5. Long-wavelength $S_0-S_1$ absorption spectra of DODCI in methanol. Temperature $T = 21.5^\circ \text{C}$. (a) Solid curve, apparent absorption cross section spectrum $\sigma'$. Broken curve, apparent absorption cross section spectrum $\sigma_N$. (b) Broken curve, apparent absorption cross section spectrum $\sigma_P (\lambda)$. Solid curve, apparent absorption cross section spectrum $\sigma_P(\lambda)$, taken from ref. [7]. Dash-dotted curve, $\sigma_P (\lambda)$ curve calculated from eq. (10).
tained. Eq. (10) gives the dash-dotted curve in fig. 5b for \( \sigma_r(\lambda) \). The fraction of molecules in the P isomer state at \( T = 294.5 \text{ K} \) is \( N_{P0}/N_0 \approx 2.4\% \) (eq. (3)).

The spectroscopic data obtained for DODCI in ethylene glycol and methanol are collected in table 1.

5. Discussion

Analysis of the \( S_0-S_1 \) absorption spectra of DODCI in the long-wavelength absorption region enables us to determine the P isomer absorption cross section spectrum, the energy level position of the ground state of the P isomer, and the fraction of P isomers in thermal equilibrium with the N isomers. The potential energy curve of the \( S_0 \) state of DODCI versus the twisting coordinate between the isomer configurations [14] is shown in fig. 1. The activation energy \( E_A \approx 9.95 \times 10^{-20} \text{ J} = 5005 \text{ cm}^{-1} \) is taken from ref. [13]. The time constant for P isomer formation is estimated to be

\[
\tau_{N \rightarrow P} = k_{N \rightarrow P} = k_{P \rightarrow N} \exp(E_p/k_BT) = 0.092 \text{ s}
\]

for DODCI in ethylene glycol and 0.10 is for DODCI in methanol at \( T = 294.5 \text{ K} \).

6. Conclusions

The technique of long-wavelength absorption analysis described here may be applied to study the thermal formation of ground-state isomers in molecules which form isomers by photo-excitation.

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References