PICOSECOND RELAXATION PROCESSES IN MONOMERIC AND AGGREGATED DYES UNDER SOLVENT INFLUENCE

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1. INTRODUCTION

The technique of picosecond spectroscopy has been elaborated in the last years to such an extend that spectroscopic measurements in this field become more and more precise. To solve problems in molecular kinetics it is of advantage to employ time resolved fluorescence technique as well as excite-and-probe beam technique. From fluorescence data one gets the time interval in which the relaxation from the $S_1$ state proceeds. For more detailed studies of relaxation or other kinetic processes with non-fluorescing intermediate states the ps-absorption spectroscopy in a wide spectral region is of high advantage.

For time resolved fluorescence measurements we used time correlated single photon counting with deconvolution down to 40 ps \(^1\). For higher time resolution up-conversion technique \(^2\) and the streak camera AGAT are available.

For ps-absorption measurements a Nd-YAG spectrometer with a parametric generator \(^3\) (\(\Delta t = 23\) ps) and a Nd-phosphate glass laser spectrometer (\(\Delta t = 5\) ps) has been elaborated \(^5\).

In the latter spectrometer (Figure 1) a Nd-phosphate glass laser with amplifier supplies the exciting pulse at the harmonic frequencies (1054, 527, 365, 258 nm) or SRS frequencies generated
by the second harmonic (560 and 620 nm). A section of about 10% from the first harmonic was amplified in a separate amplifier, after that a ps continuum was generated in D₂O. The probe light was split in a probe beam, which tested the excited (or nonexcited) sample, and a reference beam. The relation between the probe beam pulse energies \( \frac{E_{\text{test}}}{E_{\text{ref}}} \) with and without excitation gives transmission like values. The difference of the decadic logarithm of these values is the difference of the optical density with and without excitation \( \Delta D \).

The quantity \( \Delta D \) is essential for the further data processing because it is proportional to the concentration of molecules in various excited or intermediate states. For systems with constant total concentration of molecules \( \Delta D \) is given quantitatively by

\[
\frac{\Delta D}{z} = -\epsilon_0(\lambda)c_1(t) + \sum_\alpha \epsilon_\alpha(\lambda)c_\alpha(t) + \sum_\alpha \epsilon_1(\lambda)c_1(t) - \epsilon_{1e}(\lambda)c_1(t) - \sum_\alpha \epsilon_e(\lambda)c_\alpha(t)
\]

(\( c_1 \) is the concentration in the S₁ state, \( c_\alpha \) denotes the concentration of an arbitrary intermediate state, \( \epsilon_0, \epsilon_1, \epsilon_\alpha \) are absorp-
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The first term on the right hand side of (1) describes the ground state bleaching, the second and the third account for intermediate state absorption, the fourth and the fifth result from stimulated emission.

2. PICOSECOND SPECTROSCOPIC STUDIES OF POLYMETHINE DYES

With the described experimental technique we investigated polymethine dyes under various conditions. The interest in polymethine dyes came from their practical application as saturable absorbers in laser oscillators and also from their effectiveness as sensitizers of photographic materials. The third point of interest the ability of the dyes to form aggregates in aqueous solution. Optical characteristics of such aggregates exhibits analogies to photo-biological materials. Therefore we hope to be able to use aggregates and their kinetics as models for description of more complicated systems.

Here we report on experimental results of investigations of two polymethine dyes, pseudoisocyanine chloride (PIC) and pinacyanol jodide (PC), in their monomer and dimer form in various solvents and we describe the kinetic behaviour of higher aggregates of PIC.

These molecules exhibit a high mobility in the polymethine chain. It is assumed that torsional vibrations around a bond within the chain effectively couple to modes of the surrounding solvent molecules.

In the theory of radiationless processes the coupling of modes determines the effectiveness of energy degradation.

It is well-known that polymethine dyes of the described structure are weakly fluorescent dyes in low viscous solvents. The fluorescence quantum yield and lifetime increase with the solvent viscosity.

The novelty in our experiments with the ps-excite-and-probe
spectroscopy was the detection of short living photoisomers. Systematic investigation of the kinetics of isomerization has been performed together with R. Gadonas, R. Danielius, V. Krasauskas and A. Piskarskas of Vilnius university\textsuperscript{6-8}.

The latest investigation was carried out by our Nd-Phosphate glass laser spectrometer with 5 ps time resolution for dyes exhibiting very fast relaxation processes. In Figure 2 the $\Delta D$-spectrum PIC/butanol after excitation is shown. The solvent butanol was used because the first study in methanol showed that the time resolution of 5 ps was too small for the observation of photoisomerization in this dye. In Figure 2 a strong bleaching of the $S_0 - S_1$-absorption was observed, which decrease with a time constant of $\tau = 22$ ps. On the long wavelength side there emerges a new spectrum, the maximum of which lies at (559 ± 5) nm. In the case of photoisomer formation the $\Delta D$-spectrum consist in a superposition of the bleaching - negative $\Delta D$-values, proportional to the concentration of all molecules absent in the ground state - and of positive $\Delta D$ values which are proportional to the concentration of photoisomers.
\[ \Delta D(\lambda, t) = -\varepsilon_{01}(\lambda)[c_1(t) + c_{pi}(t)] + \varepsilon_{pi}(\lambda)c_{pi}(t) \]

\[ c_0(t) + c_1(t) + c_p(t) = c_{\text{total}} \]

(\varepsilon_{pi} and c_{pi} are photoisomer absorption coefficient and concentration). A value \(\Delta D(t) = 0\) at a fixed wavelength (isosbestic point) cannot be expected.

Photoisomerization on the dye PC was observed in a series of n-alcohols. There a dependence of the \(S_1\)-lifetime measured by the nearly \(\tau \sim \eta^{9,27}\). The determination of the isomerization quantum yield from the \(\Delta D(\lambda, t)\) values is not so simple as we thought in our first studies. This is demonstrated in Figure 3. At the maximum bleaching \((t = 0)\) it can be assumed that there exist only exited molecules in the \(S_1\) state but not in other intermediate states, so that \(\Delta D(0) = \varepsilon_{01}(0)c_1(0).\) In an ideal case, if no other absorption exists at the probe wavelength the \(\Delta D\)-values at delay times greater than the \(S_1\) lifetime, \((\text{the values } D(t \gg \tau))\) is due to that part of excited molecules which undergo photoisomerization or other chemical conversion. For the quantum yield of isomerization than holds \(\Delta D(t \gg \tau) / \Delta D(0) = c_{pi}/c_1(0) = \Phi_{iso}.\)

![Figure 3](image-url)  
FIGURE 3 \(\Delta D\)-spectrum of PC/butanol
But the $\Delta D$-spectra of PC (FIGURE 3) show that the photoisomer absorb in a broad spectral region, therefore holds

$$\frac{\Delta D(\text{t} \gg \tau)}{\Delta D(0)} = \frac{(E_{01} - E_{\text{PI}})}{E_{01}} \frac{c_{\text{PI}}}{c_{1}(0)} < \Phi_{\text{ISO}}$$

The quantum yield of isomerization can be determined only with a systematic error, because $E_{\text{PI}}$ is unknown. By comparison of measurements in various solvents the systematic error is constant, if the spectra of the stable form and the photoisomer are non shifted in wavelengths.

The short living species which we called a photoisomer can be characterized by the following spectroscopic data (Table I).

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>Spectroscopic and kinetic data of isomers of polymethine dyes in butanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dyes</td>
<td>$\lambda_{0}(\text{nm})$</td>
</tr>
<tr>
<td>$N_{1}$</td>
<td>605</td>
</tr>
<tr>
<td>$N_{2}$</td>
<td>523</td>
</tr>
<tr>
<td>$N_{3}$</td>
<td>510</td>
</tr>
</tbody>
</table>

Further efforts are necessary to determine the stability and the geometry of this species.

From ns-laser flash experiments the reformation of the unstable to the stable form could be measured by testing the decrease of the photoisomer absorption. In PC the reformation time is also viscosity dependent and amounts in methanol to $\tau_{\text{r}} = 25 \pm 5$ ns and in butanol to $\tau_{\text{r}} = 55 \pm 15$ ns $^{10}$. In PIC no isomer absorption could be detected, that means the reversion to the normal form proceeds in times shorter than the resolution of the excitation pulse of 15 ns.

Results on the geometry of the photoisomer have been obtained by Lau, Werncke et al $^{11}$ by means of resonance CARS with nanosecond
time resolution. They detected the CARS-spectrum of PC without and with strong excitation. Thereby intensity alteration of lines and new Raman lines indicate a species of other geometry.

All the together confirm the idea of the formation of a photoisomer in the picosecond time scale in its ground state with altered geometry and a lifetime of a few nanoseconds.

Theoretical concepts have been elaborated to describe the well-known dependence of the lifetime on solvents viscosity. One approach starts from the assumption that the relaxation proceed during the motion of part of a molecule along a configurational co-ordinate in a nearly parabolic potential with a barrier under influence of fluctuational forces\(^\text{12}\). The solvent viscosity is proportional to the drag coefficient of the equation of motion.

Detailed studies\(^\text{13}\) of the relaxation process in a wide range of viscosity showed a complicate relationship between \(\mathcal{T}\) and \(\eta\) which contains not only that part where the lifetime \(\mathcal{T}\) decrease with decreasing solvent viscosities, but a region of middle viscosity, where \(\mathcal{T}\) is nearly independent on solvent viscosity and a low viscosity region, where even an increase of \(\mathcal{T}\) with decreasing \(\eta\) is expected.

For the dye PC \(\mathcal{T}(\eta)\) has been measured in a wide range of about three orders of magnitude of viscosity\(^\text{15}\). These results are suitable to prove theoretical results. The theoretical analysis of the experimental data of PC\(^\text{14}\) showed that besides the barrier crossing an additional relaxation channel (Franck-Condon transition) has to be taken in consideration, which is domenant at high viscosity.

By picosecond spectroscopy not only lifetime measurements can be performed precisely, but moreover the formation kinetics and the quantum yield of the photoisomer can be determined. These data allow to prove models for the photoisomerization process.

We described three models, used in the literature, with rate equations\(^\text{16}\). The solutions of the rate equation can be proved
A distinction between the models is possible measuring the formation kinetics in the time range $t \leq \tau$ with high accuracy.

3. PICOSECOND STUDIES OF MONOMER-DIMER-SYSTEMS

Both dyes, PC and PIC, which we studied as monomer in several alcohols, form dimers in aqueous solution, which exist in a chemical equilibrium with monomers.

From the quantum theoretical description we know that the excited dimer levels originate from monomer levels, split owing to molecular interaction. For so called sandwich-dimers the transition to the higher level is allowed, but to the lower one forbidden. The vibronic coupling yield a broad dimer absorption band with a maximum at shorter wavelength than the monomer maximum and weak shoulder on the long wavelength side.

The dimer spectrum is always superposed with that of the monomers. The pure dimer spectrum is not known for the dyes under study. Recently a dimer spectrum of PIC was calculated by computer simulation\(^1\). The known monomer spectrum multiplied by a factor was subtracted from the experimental spectra under various conditions. In this way a dimer spectrum was obtained. Picosecond investigation of such a monomer-dimer system implicitly contains the task to measure two superposed $\Delta D$-spectra and their kinetics. Using of special excitation wavelength for selective excitation of only monomers or dimers we obtained $\Delta D$-spectra of both components, because at strong excitation the selectivity is low.

Another way to separate both components is the kinetics. In Figure 4 the $\Delta D$-spectrum at different times after excitation is shown. Both the maxima of monomers and dimers are bleached, but the monomer maximum decays faster than the dimer one. The time constants are different in nearly one order of magnitude.

The monomer component of PC decays with $\tau = 16 \pm 8$ ps whereas
The dimer decays with $\tau = 100 \pm 20$ ps along the whole bleached band. The kinetics opened a new way to isolate a dimer spectrum experimentally.

The $\Delta D$-spectrum of the system some time after excitation must be a pure dimer spectrum. In PC we find that the monomers undergo photoisomerization and so a little remainder $\Delta D$-value of monomer bleaching superposed the dimer spectrum at a longer delay time.

Analogous studies of the kinetics of PIC at room temperature showed no difference in the relaxation times of monomers and dimers. The reason is the extremely short monomer relaxation time and the strong superposition of both spectra in which only the dimer relaxation could be observed. We performed the study at a temperature of 10°C, where the relaxation processes proceed more slowly. In Figure 5 it can be clearly seen that the $\Delta D$-curve consists of two components, which must be assigned to the monomer and dimer relaxation.

The main result in studying monomer-dimer systems of polymethine dyes consists in the detection of different relaxation kinetics of both components. Dimers always exhibit a longer relaxation time.
FIGURE 5 Kinetics of the PIC monomer-dimer system

than monomers. The reason is the strong intermolecular coupling of the molecules in the dimer which prevent the molecular torsion around the polymethine chain. In this way the system was rigidized and therefore the radiationless relaxation is less effective in the dimers than in the monomers.

4. PICOSECOND STUDIES OF AGGREGATES

The dye PIC forms aggregates in aqueous solution at a concentration of $C \sim 10^{-3}$ mol/l. The aggregation is accompanied by an alteration of the optical spectrum, which exhibits now the strong and narrow J-band, shifted to longer wavelengths ($\lambda = 573$ nm, $\Delta \tilde{\nu} = 163$ cm$^{-1}$), but the monomer and dimer spectra decrease in the aggregated solution. The J-band polarization is perpendicular to that of the monomer and dimer bands. By comparison with an investigation of PIC crystals the axis of the J-band polarization was determined to be the b-axis, the direction in which the overlap of the $\pi$-electron system of the neighbouring molecules is maximal$^{19}$. The excitonic character of the J-band was recently supported by density matrix descriptions of finite molecular systems$^{20}$. The lineshape of the PIC aggregates was calculated in detail in$^{21}$. Aslangul$^{20}$ showed that an aggregate of a number of molecules of $N = 3, \ldots, 100$ interact with the radiation field as a unit. Excitation of a part or a molecule within the aggregate does not exist,
so that it is not necessary to speak about energy transfer within the aggregates. In a real system there may exist monomers, dimers and aggregates in a chemical equilibrium so that energy exchange between the components may be possible.

Kinetic studies of aggregates were carried out by fluorescence measurements by Dähne and coworkers. We have carried out such work together with the group of A. Piskarskas from Vilnius university with the help of excite-and-probe-spectrometers.

The recovery kinetics measured after excitation with $\lambda = 527$ nm at probe wavelengths within the monomer and dimer band result in a two exponential decay. The aggregate bleaching first decays fast with 16 ps and than slowly with about 500 ps.

The fast component vanishes more and more, as the excitation pulse energy decreases, but the slow component seems to vary between 300 and 600 ps. The difficulty of aggregate studies consist in the measuring of a thin layer (10 $\mu$m) of highly viscous aggregated solution, in which the absorbed photons may cause local temperature increase or even destruction of molecules.

Recently Stiel et al reported a strong temperature dependence of the aggregate fluorescence lifetime and quantum yield, measured by weak excitation and single photon counting. The lifetime and the quantum yield decrease strongly with increasing temperature. So it seems to be possible that at strong excitation with ps-pulses local heating causes lifetime shortening of excited aggregates.

Detailed spectral measurements in the range of the J-band after excitation showed that the band itself contains two components of different polarization. Moreover a superposition of transient absorption bands with the aggregate band has been observed.
In order to clarify the nature of the aggregate band we used various excitation wavelengths for excitation within the monomer and dimer bands as well as within the aggregate band. Exciting the monomer-dimer band results in the bleaching of the whole absorption band, whereas direct excitation of the J-band results only in the bleaching of the J-band. In this experiment $\Delta D = 10^{-3}$ really could be measured, the absence of bleaching at shorter wavelengths means that the absorption coefficient of the J-band in this spectral range ($\lambda < 573 \text{ nm}$) is of a factor of about $10^{-3}$ lower than J-band absorption coefficient. This result agrees with measurements of intensity dependent bleaching.

In this experiment bleaching occurs at an excitation intensity of $\lambda = 530 \text{ nm}$ (monomer band) which is more than $10^3$ times higher than the J-band (at 573 nm). The aggregate bleaching upon excitation at 530 nm may be caused either by a small absorption cross section of the aggregates itself or by energy transfer from excited monomers to aggregates. If such an energy transfer does

![FIGURE 6 ΔD-spectrum of PIC monomers, dimers and aggregates, excited with $\lambda = 530 \text{ nm}$](image)
exist, one must proceed within a time of about one ps, because no delayed bleaching of the aggregate band was observed.

Summarizing the kinetic data about the PIC aggregate system we found, that monomers and dimers at room temperature exist and relax with their own relaxation time. The J-band relaxation is strongly influenced by temperature and excitation energy. The nature of the extremely short decay at high excitation is not quite clear up to know, superluminescence could not be detected. The recovery time at low excitation energy shows the tendency already observed at dimers. The aggregate is a rigidized system in which the excited state lives longer.

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