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 spec-
tral 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[3,4] (Δt = 23 ps) and a Nd-phosphate glass laser
spectrometer (Δt = 5 ps) has been elaborated[5].

　　In the latter spectrometer (Figure 1) a Nd-phosphate glass
laser with amplifyer supplies the exciting pulse at the harmonic
frequencies (1054, 527, 365, 258 nm) or SRS frequencies generated
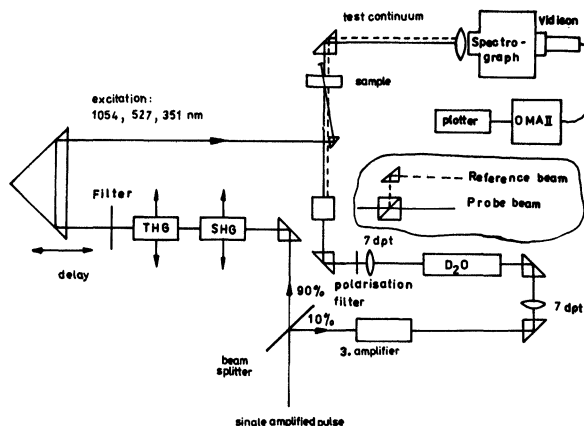
FIGURE 1 Nd-phosphat glass laser spectrometer

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 D_2O. 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 E_{test}/E_{ref} with and without excitation gives trans-
mission like values. The difference of the decadic logarithm of
these values is the difference of the optical density with and
without excitation ΔD.

The quantity ΔD is essential for the further data
processing because it is proportional to the concentration of mo-
lecules in various excited or intermediate states. For systems
with constant total concentration of molecules ΔD is given
quantitatively by

$$\Delta D/z = -\varepsilon_0(\lambda)[c_1(t) + \sum_\alpha c_\alpha(t)] + \varepsilon_1(\lambda)c_1(t) +$$
$$+ \sum_\alpha \varepsilon_\alpha(\lambda)c(t) - \varepsilon_{1e}(\lambda)c_1(t) - \sum_\alpha \varepsilon_{\alpha e}(\lambda)c_\alpha(t) \quad (1)$$

(c_1 is the concentration in the S_1 state, c_α denotes the concen-
tration of an arbitrary intermediate state, $\varepsilon_0, \varepsilon_1, \varepsilon_\alpha$ are absorp-

tion coefficients and ε_{1e}, ε_e gain coefficients). 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 poly-
methine 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 sensi-
tizers of photographic materials. The third point of interest the
ability of the dyes to form aggregates in aqueous solution. Opti-
cal characteristics of such aggregates exhibits analogies to photo-
-biological materials. Therefore we hope to be able to use aggre-
gates and their kinetics as models for description of more compli-
cated systems.

     Here we report on experimental results of investigations of
two polymethine dyes, pseudoisocyanine chloride (PIC) and pina-
cyanol jodide (PC), in their monomer and dimer form in various
solvents and we describe the kinetic behaviour of higher aggre-
gates 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 mo-
des determines the effectivity 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.

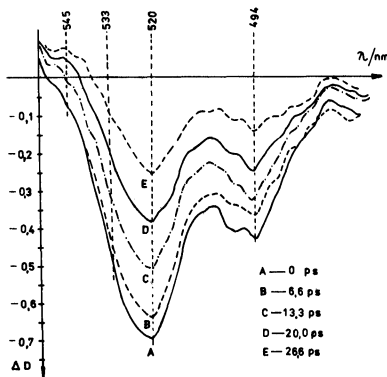   The novelty in our experiments with the ps-excite-and-probe

FIGURE 2 ΔD-spectrum of PIC/butanol

spectroscopy was the detection of short living photoisomers. Sys-
tematic investigation of the kinetics of isomerization has been
performed together with R. Gadonas, R. Danielius, V. Krasauskas
and A. Piskarskas of Vilnius university[6-8].

   The latest investigation was carried out by our Nd-Phosphate
glass laser spectrometer with 5 ps time resolution for dyes exhib-
iting very fast relaxation processes. In Figure 2 the ΔD-spectrum
PIC/butanol after excitation is shown. The solvent bytanol was
used because the first study in methanol showed that the time re-
solution of 5 ps was too small for the observation of photoisomer-
ization in this dye. In Figure 2 a strong bleaching of the $S_o - S_1$-
-absorption was observed, which decrease with a time constant of
τ = 22 ps. On the long wavelength side there emerges a new spec-
trum, the maximum of which lies at (559 $\pm$ 5) nm. In the case of
photoisomer formation the ΔD-spectrum consist ih a superposition
of the bleaching - negative ΔD-values, proportional to the concen-
tration of all molecules absent in the ground state - and of posi-
tive ΔD values which are proportional to the concentration of
photoisomers.

$$\Delta D(\lambda, t) = -\varepsilon_{01}(\lambda) [c_1(t) + c_{PI}(t)] + \varepsilon_{PI}(\lambda) c_{PI}(t)$$

$$c_o(t) + c_1(t) + c_p(t) = c_{total}$$

(ε_{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-liretime 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[6]. 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 $\Delta D(0) = \varepsilon_{01}(t) c_1(0) z$. In an ideal case, if no other absorption exists at the probe wavelength the ΔD-values at delay times greater than the S_1 lifetime, (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 $\Delta D(t \gg \tau)/\Delta D(0) = c_{PI}/c_1(0) = \Phi_{iso}$.

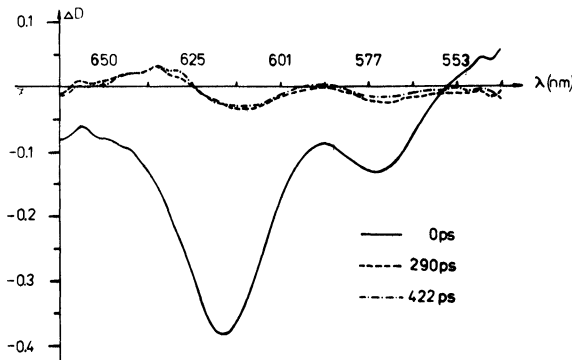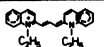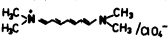FIGURE 3 ΔD-spectrum of PC/butanol

But the ΔD-spectra of PC (FIGURE 3) show that the photoisomer absorb in a broad spectral region, therefore holds

$$\frac{\Delta D(t \gg \tau)}{\Delta D(0)} = \frac{(\varepsilon_{01} - \varepsilon_{PI})}{\varepsilon_{01}} \frac{c_{PI}}{c_1(0)} < \Phi_{iso}$$

The quantum yield of isomerization can be determined only with a systematic error, because ε_{PI} is unknown. By comparison of measuremets 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 I   Spectroscopic and kinetic data of isomers
            of polymethine dyes in butanol

Dyes	λ_N(nm)	λ_{PI}(nm)	$\Delta \nu$(cm^1)	τ(ps)	Φ_{ISO}
(structure) /J$^-$	605	635	781	35	0.09
(structure) /Cl$^-$	523	545	772	22	0.33
(structure) /ClO$_4^-$	510	545	1260	36	0.35

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

From ns-laser flash experiments the reformation of the instable 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 τ_r = 25 ± 5 ns and in butanol to τ_r = 55 ± 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 photo-isomer 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[12]. The solvent viscosity is proportional to the drag coefficient of the equation of motion.

Detailed stulies[13] of the relaxation process in a wide range of viscosity showed a complicate relationship between τ and η which contains not only that part where the lifetime τ decrease with de-creasing solvent viscosities, but a region of middle viscosity, where τ is nearly independent on solvent viscosity and a low vis-cosity region,where even an increase of τ with decreasing η is expected.

For the dye PC $\tau(\eta)$ has been measured in a wide range of about three orders of magnitude of viscosity[15]. These results are suit-able to prove theoretical results. The theoretical analysis of the experimental data of PC[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[16]. The solutions of the rate equation can be proved

experimentally[17]. A distinction between the models is possible
measuring the formation kinetics in the time range t ⩽ τ 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 chemi-
cal 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 transi-
tion to the higher level is allowed, but to the lower one forbid-
den. 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[18]. The known monomer spectrum multiplied by a factor
was subtracted from the experimental spectra under various condi-
tions. In this way a dimer spectrum was obtained. Picosecond inves-
tigation of such a monomer-dimer system implicitly contains the
task to measure two superposed ΔD-spectra and their kinetics. Using
of special excitation wavelength for selective excitation of only
monomers or dimers we obtained ΔD-spectra of both components, be-
cause at strong excitation the selectivity is low.

     Another way to separate both components is the kinetics. In
Figure 4 the ΔD-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.

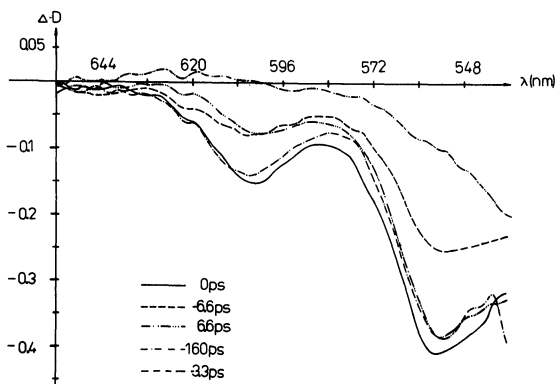   The monomer component of PC decays with τ = 16 ± 8 ps whereas

FIGURE 4 ΔD- spectrum of the PC monomer-dimer system in
water/methanol

the dimer decays with $\mathcal{T}$ = 100 ± 20 ps along the whole bleached
band. The kinetics opened a new way to isolate a dimer spectrum
experimentally.

The ΔD-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 ΔD-value of monomer
bleaching superposed the dimer spectrum at a longer delay time.

Analogous studies of the kinetics of PIC at room temperature
[7,26] showed no difference in the relaxation times of monomers and
dimers.'The reason is the extremly 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 ΔD-curve con-
sists of two components, which must be assigned to the monomer and
dimer relaxation.

The main result in studing monmer-dimer systems of polymethi-
ne dyes consists in the detection of different relaxation kinetics
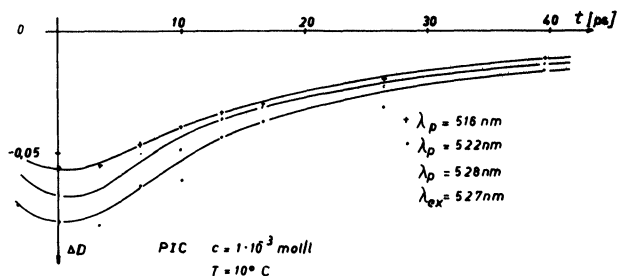of both components. Dimers always exhibit a longer relaxation time

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 (λ = 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 π-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, ..., 100 interact with the radiation dield 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 fluores-
cence measurements by Dähne and coworkers[22,23]. We have carried
out such work together with the group of A. Piskarskas from Vilni-
us university[24,25] with the help of excite-and-probe-spectro-
meters.

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 conponent vanishes more and more, as the excitation
pulse energy decreases, but the slow component seems to vary be-
tween 300 and 600 ps. The difficulty of aggregate studies consist
in the measuring of a thin layer (10 μm) of highly viscous aggre-
gated solution, in which the absorbed photons may cause local tem-
perature increase or even destruction of molecules.

Recently Stiel et al[22] reported a strong temperature depen-
dence of the aggregate fluorescence lifetime and quantum yield,
measured by weak excitation and single photon counting. The life-
time and the quantum yield decrease strongly with increasing tem-
perature. 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 compo-
nents of different polarization[9]. Moreover a superposition of
transient absorption bands with the aggregate band has been
observed[19].

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 ($\lambda < 573$ nm) is of a factor of about 10^{-3} lower than J-band absorption coefficient. This result agrees with measurements of intensity dependent bleaching[26].

In this experiment[26] bleaching occurs at an excitation intensity of $\lambda = 530$ 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 of by energy transfer from excited monomers to aggregates. If such an energy transfer does
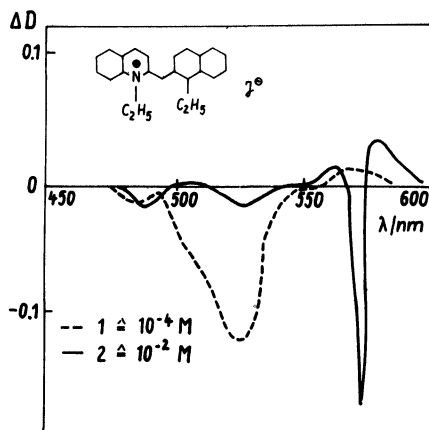

FIGURE 6 ΔD-spectrum of PIC monomers, dimers and aggregates, excited with $\lambda = 530$ nm

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 al-

ready observed at dimers. The aggregate is a rigidized system in

which the excited state lives longer.

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