Determination of Diffusion Parameters of Solved Molecules by Measuring the Relaxation Kinetics on the Picosecond Time Scale

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Picosecond probe beam spectroscopy is used to measure the nonstationary contribution to diffusion controlled excimer formation in dependence on concentration and solvent viscosity. Utilizing a kinetic model, the effective encounter radius and diffusion parameters of pyrene molecules in different solvents have been determined.

Introduction

Energy transfer processes between donor- and acceptor molecules after excitation with short optical pulses can be caused by the Förster-mechanism (long range dipole-dipole interaction) [1] or by direct interaction between neighbouring particles providing, e.g., the formation of encounter complexes and excimers. The energy transfer will be determined by the given initial distribution of the acceptors around the donors as well as by translation (diffusion) of molecules during the excitation.

The influence of diffusion on the electronic excitation energy transfer in solutions has been treated in numerous publications [2–6]. It was found theoretically that diffusion should increase the efficiency of the transfer process. That fact is not in agreement with all experimental results. Whereas some authors report a considerable influence of diffusion on the energy transfer [7–9] only a slight or negligible effect has been observed by others [10, 11].

The methods of picosecond spectroscopy (e.g. time resolved fluorescence, ground state recovery experiments, excited state absorption) allow the direct observation of energy transfer processes on the real time base. Using the probe beam absorption method the influence of diffusion on the photoisomerisation of stilbene [12] and on the formation of encounter complexes of dimethylaminobenzaldehyde [9] could be observed.

This paper presents results of measurements and calculations concerning the kinetics of excimer formation in pyrene solutions.

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Experimental

A probe beam spectrometer with a time resolution of about 20 ps has been used to measure the rise and decay time characteristics of absorption from excited levels of solved pyrene molecules. To excite the sample the second harmonic (SHG) of mode locked ruby laser radiation or the fourth harmonic (FHG) of mode locked Nd-YAG-laser radiation is applied. In order to measure an entire absorption spectrum in a single laser shot a probe pulse with a broad spectral bandwidth is generated by nonlinear interaction of intense picosecond light pulses with H_3PO_4 or D_2O. The parameters of exciting beam and probe continuum are given in Table 1.

The time delay t_D between exciting beam and probe continuum is realized on the path of the exciting beam. After having passed the sample, probe- and reference continuum are analysed with

Table 1. Parameters of exciting beam and probe continuum.

Exciting beam

	SHG of ruby laser	FHG of Nd-YAG-laser
Wavelength	347 nm	265 nm
pulse duration	20 ps	25 ps
pulse energy	3 mJ	1 mJ

Probe beam

	Ruby laser	Nd-YAG-laser
Picosecond continuum generated in	H_3PO_4	D_2O
spectral range	450–620 nm	450–900 nm

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the help of a spectroscope and measured and stored by use of an optical multichannal analyser.

A more detailed description of the experimental arrangement is given in [12, 13].

Results

Kinetic measurements in the picosecond time region were carried out in various pyrene solutions using different nonpolar and polar solvents. As an example the transmission of excited pyrene solutions at two delay times between exciting beam and probe continuum is shown in Figure 1. Within the aviable spectral range of the probe continuum (about 450 nm to 900 nm) one absorption band at λ_1 (540—550 nm) appears immediately after excitation. Changing the delay to longer times an additional absorption band rises at λ_2 (460—470 nm). The absorption bands around λ_1 and λ_2 are connected with the excited monomer state and the excimer state of pyrene, respectively. Figure 2 presents the measured time dependence of depopulation and population of these excited states in different solvents. A fast decrease of the absorption at λ_1 is found corresponding to a fast increase at λ_2 immediately after excitation.

The corresponding rate parameters depend on solvent viscosity, but they are nearly constant for solvents of comparable viscosity and of different

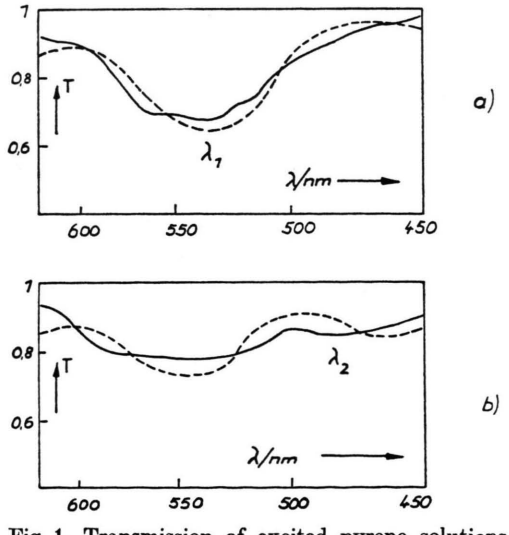

Fig. 1. Transmission of excited pyrene solutions at two delay times (t_D) between exciting beam and probe continuum; a) $t_D = 30$ ps, b) $t_D = 250$ ps. —— pyrene in n-heptane; ---- pyrene in cyclohexane.

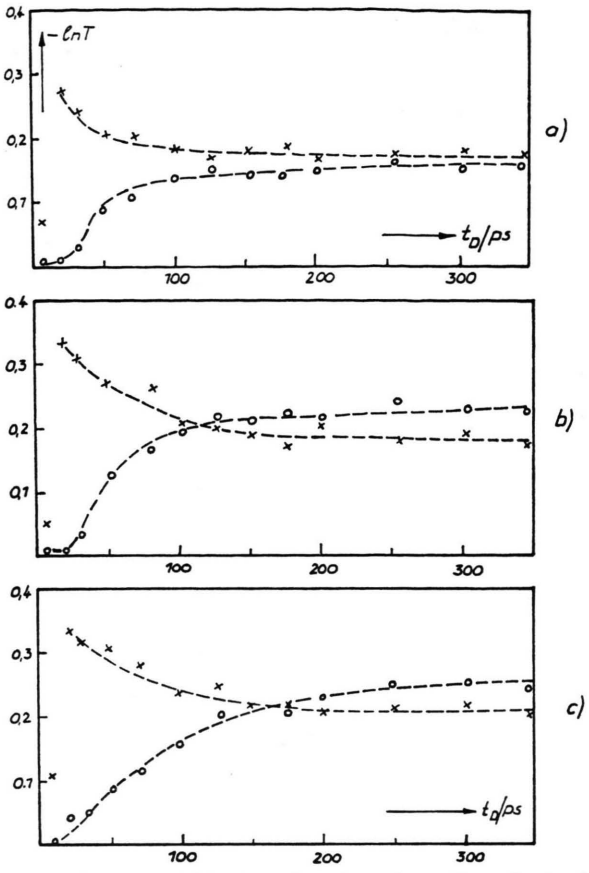

Fig. 2. Picosecond kinetics of excimer formation of solved pyrene molecules; a) in n-heptane, b) in cyclohexane, c) in ethanol; × depopulation of the excited monomer state, ○ population of the excimer state.

polarity. The influence of this fast process on the kinetics of excited pyrene molecules strongly depends on concentration and vanishes at concentrations less than 10^{-3} mol l^{-1}.

Discussion

The experimental results are discussed on the base of a simple reaction scheme of excimer formation.

$$\begin{array}{ccc} A^* + A & \underset{k_{EA^*}}{\overset{k_{A^*E}\, c_A}{\rightleftharpoons}} & (AA)^* \\ \downarrow k_A & & \downarrow k_E \\ A & & A + A \end{array}$$

A general description of the process is possible on the base of the equation of diffusion and was given by Smoluchowski [14] and Weller [2]. This theory yields the following expression for the

second order rate parameter.

$$k_{A^*E}\, c_A = [\gamma k_s + \gamma^2 k_{ns}(t) F(\beta t)]\, c_A\,, \quad (1)$$

$$k_s = 4\pi D' N R_0,$$

stationary contribution, (2)

$$k_{ns}(t) = 4\sqrt{\pi} N R_0^2 (D'/t)^{1/2},$$
$$= k_{ns} t^{-1/2},$$

nonstationary contribution. (3)

c_A, molar concentration of A-molecules, N, number of particles per millimole, R_0, encounter radius, $D' = D_A + D_{A^*} \approx 2D$; D, diffusion parameter, γ, probability of reaction between A*- and A-molecules.

$$F(\beta t) = \sqrt{\pi \beta t}\, e^{\beta t} \operatorname{erfc}(\beta t), \quad \beta = \frac{D'}{(1-\gamma) R_0}.$$

The time dependend part of the rate parameter is caused by a nonstationary initial distribution of the A-molecules around the A*-molecules. Very quickly a stationary distribution is attained.

During the decay of the nonstationary distribution an excess contribution to the diffusion controlled process of excimer formation results. Especially a higher velocity of excimer formation is caused immediately after excitation.

On the conditions k_A, k_E, $k_{EA^*} \ll k_{A^*E} c_A$ (fulfilled in the case of solved pyrene molecules [15, 16]) the value of γ is nearly 1. Hence it follows that $\lim_{\gamma \to 1} F(\beta t) = 1$ and (1) is simplified to

$$k_{A^*E}\, c_A = [k_s + k_{ns}(t)]\, c_A\,. \quad (1')$$

Therefore the time dependence of the population density of the monomer and excimer state on the picosecond time scale can be described in a simple manner (δ-pulse excitation at $t = 0$):

$$\varrho_{A^*}(t) = \varrho_0 \exp[-k_s - 2k_{ns}(t)]\, c_A t\,, \quad (4)$$

$$\varrho_{(AA)^*}(t) = \varrho_0 \{1 - \exp[-k_s - 2k_{ns}(t)]\, c_A t\}\,. \quad (5)$$

Fitting the calculated curves to the measured values at small delay times the parameters k_s and k_{ns} have been determined (Table 2).

The values of k_s are in agreement with results of other authors who have used pulse fluorimetry [15], phase fluorimetry [16] and excited state absorption [17] to investigate the kinetics of solved pyrene molecules in the nanosecond region. Using the parameters of Table 2 as well as the definition of D' previously mentioned it is possible to obtain the diffusion coefficient and encounter radius of solved pyrene molecules from the (2) and (3):

$$D^3 = \frac{1}{128\pi^3 N^2} \frac{k_s^4}{k_{ns}^2}, \quad (6)$$

$$R_0 = k_s / 8\pi N D; \quad (7)$$

The parameters D and R_0 together with the viscosities η of the used solvents at room temperature are shown in Table 3. The diffusion coefficient of pyrene solved in benzene has been found by Othmer and Thaker [18] and is given here for comparison with the values determined in this work.

A linear dependence of the diffusion parameters on the reciprocals of the corresponding solvent viscosities has been found to be a good approach (Figure 3).

Table 2. Nonstationary and stationary contribution to the diffusion controlled process of excimer formation.

Pyrene solved in	k_{ns} / 10^6 l mol^{-1} s$^{-1/2}$	k_s / 10^9 l mol^{-1} s^{-1}
n-heptane	2.6	8.5
cyclohexane	1.7	7.6
methanol	2.0	6.6
ethanol	1.4	5.2

Table 3. Encounter radius and diffusion parameter of pyrene in various solvents.

Pyrene $c_A = 5 \cdot 10^{-3}$ mol l^{-1} solved in	R_0 / 10^{-10} m	D / 10^{-9} m^2 s^{-1}	η / 10^{-3} Pa · s
n-heptane	7.5	1.4	0.41
cyclohexane	8.0	0.6	0.98
methanol	7.0	0.9	0.61
ethanol	9.0	0.5	1.21
benzene	7.0	0.8 *	0.62

* This value is given in [18].

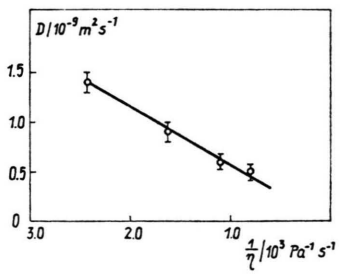

Fig. 3. Dependence of the measured diffusion parameters on the reciprocals of the corresponding solvent viscosities.

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