Diffusion Coefficients of Aromatic Hydrocarbons in Their Lowest Triplet State: Anthracene in Hexane, Octane, Hexadecane, Perfluorohexane, and Methylcyclohexane; Pyrene and 9,10-Diphenylanthracene in Hexane

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Dedicated to Prof. Dr. Heinz Mauser on the occasion of his 60th birthday

An experimental method is described which allows the determination of the diffusion coefficient D of an aromatic hydrocarbon in its lowest and metastable triplet state T_1 with an absolute accuracy of $\pm 5\%$. D was determined at 25 °C. With anthracene the temperature-dependence of D was measured from 0 °C to 60 °C in hexane and from 20 °C to 89 °C in hexadecane; it was found to be in good but not perfect agreement with the Stokes-Einstein equation. With the investigated systems, D of molecules in T_1 is estimated to be at most 10% smaller than D of molecules in the ground state. No evidence for the formation of triplet excimers was found. Some applications of the method are proposed, and in this connection some questions concerning the kinetics of diffusion-controlled reactions of molecules in T_1 and the existence of triplet excimers are discussed.

1. Introduction

The interpretation of experimental data on photophysical or photochemical processes often requires a knowledge of diffusion coefficients of molecules in electronically excited states (or of excitons) or of short-lived photoproducts. Examples of such processes are: reactions of molecules in electronically excited states, migration of electronic excitation energy in molecular crystals, and reactions of photochemically generated atoms or free radicals. Diffusion coefficients of short-lived molecules or molecules in short-lived excited states cannot be determined with the usual methods [1 − 3] which have been developed for the measurement of diffusion coefficients of stable molecules. In the present paper a method is described which allows the determination of diffusion coefficients of aromatic hydrocarbons in their lowest and metastable triplet state T_1 in liquid solutions.

The principle by which it is possible to determine the diffusion coefficient (DC) of a short-lived and reactive photoproduct A, has been known for a long time [4 − 6]. Let A be produced by monochromatic excitation of M with the quantum yield Φ_A,

$$M + h\nu \to M^* \to A, \tag{1}$$

and let A disappear by a first-order reaction with rate constant β and by a second-order reaction with rate constant γ:

$$A \xrightarrow{\beta} B, \tag{2}$$

$$A + A \xrightarrow{\gamma} C. \tag{3}$$

Let the excitation intensity I_e depend on only one Cartesian space coordinate, x, and on time t, and let the lifetime of M* be very short compared with the lifetime (or half-life in case of second-order decay) of A. The space- and time-dependence $c = c(x, t)$ of the concentration c of A is then determined by the partial differential equation

$$\partial c / \partial t = I_e \varepsilon_n \Phi_A c_M + D \partial^2 c / \partial x^2 - \beta c - \gamma c^2 \tag{4}$$

with $I_e = I_e(x, t)$ the excitation intensity in Einstein cm^{-2} s^{-1}, $\varepsilon_n = (\ln 10) (10^3 \text{ cm}^3 \text{ dm}^{-3}) \varepsilon$ and ε the molar absorptivity at the excitation wavelength λ_0 in dm^3 mol^{-1} cm^{-1} ($= \text{M}^{-1}$ cm^{-1}), $c_M = c_M(x, t)$ the concentration of M, and D the DC of A. Let the reaction volume be bounded by two planes, $x = x_1$ and $x = x_2$. The spatial average v of the rate of reaction

(3) will be

$$v = \gamma \langle c^2(x, t) \rangle_x = (x_2 - x_1)^{-1} \gamma \int_{x_1}^{x_2} c^2(x, t) \, \mathrm{d}x \,. \tag{5}$$

For a given number of molecules A and a given volume V, the average rate v has a minimum $v_{\min}$ when the molecules are statistically distributed over V, i. e. when the concentration of A does not depend on x:

$$v = \gamma \langle c^2(x, t) \rangle_x \geqq \gamma [\langle c(x, t) \rangle_x]^2 = v_{\min} \,. \tag{6}$$

Evidently equilibration of the concentration of A by diffusion has the effect to slow down the average rate of disappearance of A by reaction (3). Therefore, in principle the DC of A can be determined if

(a) $c(x, t)$ at some time t is known, e. g. $(c(x, 0)$;

(b) $c_M(x, t)$ is either known or c_M does not depend on x and t;

(c) $I_e(x, t)$, ε_n, Φ_A, β, γ are known;

(d) the absorption spectrum or some other characteristic of A is known which allows to measure the *absolute* average concentration of A, $\langle c(x, t) \rangle_x$.

Then — apart from D — all quantities are known for the calculation of the spatial average of the concentration of A, and D can be determined by fitting the calculated concentration to the experimental one.

To our knowledge Noyes was the first [7] who tried to determine in this way the DC of a reactive photoproduct. He and his coworkers [8, 9] determined the DC of photochemically generated iodine atoms, with the aim to test the validity of theoretical equations for the rate constant of a diffusion-controlled reaction of type $A + A \to C$ [10]. Noyes recognized the particular advantage of a spatially periodic excitation for which he coined the term "photochemical space intermittency" [7]. He calculated the steady state distribution of a photoproduct A for different one-dimensional and two-dimensional excitation patterns. The DC of iodine atoms was determined by measuring the spatial average of the steady-state concentration of iodine atoms with different excitation patterns and by fitting the calculated dependence of the average steady-state concentration on the excitation pattern to the observed one. The above listing (a) to (d) shows that for the determination of a DC the absolute values of at least eight quantities must be

known. The accuracy of the method is probably mainly limited by the accuracy with which the absolute concentration of A and the second-order rate constant γ can be measured.

The accurate determination of the DC of a photoproduct A is much easier if there is a measurable quantity F which is proportional to $\gamma \langle c^2(x, t) \rangle_x$, i. e. to the spatial average of the rate of the reaction $A + A \to C$. Such a quantity F is the fluorescence of C if C is formed in an excited state:

$$A + A \to C^* \to C + h \nu \,. \tag{7}$$
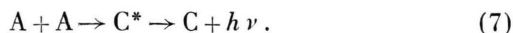
In this case experimental conditions can be chosen in such a way that the second-order term $\gamma c^2(x, t)$ in (4) will be small compared to the first-order term $\beta c(x, t)$. Then for the determination of the DC of A only the excitation pattern and the time-dependence of F must be known (cf. Section 2.3.).

With most aromatic hydrocarbons in their lowest and metastable triplet state T_1 indeed a reaction of type (7) is observed. If the electronic excitation energy of two molecules in T_1 is greater than or equal to the electronic excitation energy of one molecule in its lowest excited singlet State S_1, then the bimolecular reaction

$$T_1 + T_1 \to S_1 + S_0 \tag{8}$$

is energetically possible and indeed takes place. Experimentally the fluorescence $S_1 \to S_0$ is easily detected. Reaction (8) is usually called triplet-triplet annihilation (TTA). If S_1 is populated by TTA the fluorescence $S_1 \to S_0$ is called delayed fluorescence (DF) or according to Parker and Hatchard [11] P-type DF (P stands for pyrene) in order to distinguish it from another type of DF, the so-called E-type DF (E stands for eosin), in which S_1 is populated thermally from T_1. In the present paper DF will always mean P-type DF. The DF of aromatic hydrocarbons is a general phenomenon which was found in the gas-phase [12 – 14], in molecular crystals [15 – 17], in concentrated solid solutions [18, 19], in dilute liquid solutions [20, 21], and in polymers like polyvinylnaphthalene [22]. The first explanation of a DF by TTA was given by Czarnecki [18].

Avakian and Merrifield utilized the DF of anthracene single crystals for the determination of the DC of triplet excitons [23]. They generated triplet excitons by excitation with a helium-neon laser, making use of the spin-forbidden, but in a molecular

crystal sufficiently effective transition $T_1 \leftarrow S_0$. In this case the DF is the only fluorescence. The excitation light fell through a ruling with alternating opaque and transparent strips of equal width $d/2$. By measuring the total steady-state DF as a function of the period d of the ruling, they were able to determine the DC of triplet excitons. Later the method was refined by Ern, Avakian, and Merrifield [14] (the excitation intensity was square-wave-modulated also with respect to time, and the time-dependence of the DF was measured), and by Ern [25] (a $\cos^4(\omega_0 t)$-modulation of the excitation intensity and a phase-angle technique were used).

The method of Avakian, Merrifield, and Ern allows the determination of the DC of the triplet energy. It is independent of the way in which the triplet energy is transported (by pure energy migration in molecular crystals, or by diffusion of molecules in the triplet state T_1 in the gas-phase and in dilute liquid solutions). It is mainly limited by diffraction of the excitation light at the ruling. Nickel proposed a modification of the method in which a spatially periodic excitation of a sample is achieved by interference of two coherent laser beams [26]. Nickel, Nickel, and Meyer demonstrated the feasibility of the modified method and its large range of application by measuring the temperature-dependence of the DC of ^{3}pyrene* in glycerol [27] (population of T_1 by $S_1 \leftarrow S_0$ and intersystem crossing (ISC) $S_1 \rightsquigarrow T_1$, excitation with a standing light wave) and of ^{3}anthracene* in hexadecane [27, 28] (population of T_1 by $S_1 \leftarrow S_0$ and ISC $S_1 \rightsquigarrow T_1$, excitation with two coherent laser beams, a definite angle between the beam directions being obtained either with a Mach-Zehnder interferometer [28] or with a biprism [29]). Independently from us Burkhart tried to measure diffusion coefficients of molecules in T_1 [30 – 32]. His method directly went on from the method of Ern, Avakian, and Merrifield [24].

The aim of the present paper is threefold. First, we want to communicate and to discuss the results obtained with our method [33]. Second, the method for the determination of the DC of molecules in T_1 is rather indirect. Its reliability strongly depends on the degree to which the assumptions of the theory can be realized experimentally. Therefore we want to present a careful analysis of the simplifying assumptions of the theory and to communicate all experimental details which to our knowledge are

essential in order to obtain reproducible results. Third, we want to propose some applications of the method. In this connection some questions concerning the kinetics of diffusion-controlled reactions and the existence of triplet excimers will be discussed.

2. Time-Dependence of the Delayed Fluorescence

2.1. Kinetics of disappearance of triplets

If the triplet state T_1 is populated by $S_0 \rightarrow S_1 \rightsquigarrow T_1$ then during excitation a selective measurement of the DF is not possible. Only the decay of the DF can be measured, and (4) is reduced to

$$\partial c/\partial t = D \, \partial^2 c/\partial x^2 - \beta c - \gamma c^2. \qquad (9)$$

The assumption that the disappearance of molecules in T_1, ^{3}M*, can be described by (9) means:

(a) The concentration c of ^{3}M* depends on time t and on one space coordinate only. For the present purpose (cf. Section 2.4.) this assumption has to be valid only for small regions with a diameter of the order of magnitude of the diffusion length $(2 D/ \beta)^{1/2}$.

(b) D does not depend on c. This assumption is certainly correct because the concentration c of ^{3}M* is very low ($< 10^{-7}$ M).

(c) There is either only one molecular species ^{3}M*, or, if there are different molecular species $(^3M^*)_i$ $(i = 1, 2, \ldots)$, then these are in equilibrium with respect to one another. For molecules in T_1 this assumption is not trivial. First, it is well known that the three substates of T_1 (e. g. T_{1x}, T_{1y}, and T_{1z} for molecules with D_{2h} symmetry in zero magnetic field) are not populated with equal probability by ISC $S_1 \rightsquigarrow T_1$ (optical spin polarization [34]). In general, all decay processes of triplets will depend on the particular substate of T_1 [34]; in particular also the result of TTA may depend on the annihilated triplet substates (i. e. whether an excited singlet state or an excited triplet state is formed by TTA). With respect to the experimental realization of our method it is necessary that spin-lattice relaxation (SLR) $T_{1i} \longleftrightarrow T_{1j}$ $(i \neq j; \, i, j = x, y, z)$ is sufficiently fast, $\tau_{SLR} < 100 \, \mu s$. Second, apart from triplet monomers ^{3}M* also triplet excimers $^3(MM)^*$ or even higher associates may be present. Then the application of (9) implies that either the fraction of triplets which are present in the form of excimers

is very small, or the establishment of the equilibrium $^3M^* + {}^1M \longleftrightarrow {}^3(MM)^*$ is very fast compared to the decay processes and to diffusion-relaxation (cf. Sect. 2.3.) of triplets.

(d) The second-order rate constant γ is assumed to be independent of time t. This is not strictly correct. According to v. Smoluchowski [35] the rate constant for a diffusion-controlled reaction of type (3) is (for spherical particles, which are statistically distributed at time $t = 0$, and for a continuous solvent)

$$\gamma = 8 \pi R_0 D N_L (10^{-3} \, \mathrm{dm^3 \, cm^{-3}}) [1 \qquad (10)$$
$$+ R_0 / \sqrt{2 \pi D t}]$$

with R_0 the encounter distance at which the reaction takes place, and N_L Loschmidt's number. For solutions of low or moderate viscosity the neglect of the transient term in (10) is justified. Example: With $R_0 = 10^{-7}$ cm, $D = 10^{-6} \, \mathrm{cm^2 \, s^{-1}}$, and a minimum dead-time $t = 10^{-4}$ s between excitation and measurement of the DF, follows $R_0 / \sqrt{2 \pi D t} \lesssim 0.004 \ll 1$.

(e) The first-order rate constant β does not depend on x and t. If a sample contains traces of oxygen and of other adventitious quenchers of $^3M^*$, which reduce the lifetime $1/\beta$ of $^3M^*$, then their concentrations must not depend on x and t. For practical purposes it is sufficient if the variation of β with respect to space and during a single experiment does not exceed a few percent; in case of pure first-order decay an observable decrease of the average concentration of $^3M^*$ by two orders of magnitude then still can be described by a single exponential function with high accuracy.

2.2. Time-dependence of DF with homogeneous excitation

In this case the partial differential equation (9) is simplified to the ordinary differential equation

$$dc/dt = -\beta c - \gamma c^2 . \qquad (11)$$

With the boundary condition $c(0) = c_0$ the solution of (11) is:

$$c(t) = c_0 e^{-\beta t} \{1 + (\gamma c_0/\beta)(1 - e^{-\beta t})\}^{-1} . \quad (12)$$

When the second-order term in (11) is very small or small compared to the first-order term, two useful approximate solution of (11) can be obtained. With

$$p = \gamma c_0/\beta \ll 1 : \qquad (13)$$
$$c(t) \cong c_0 e^{-\beta t} ; \qquad (14)$$

and with the less restrictive condition

$$p^2 = (\gamma c_0/\beta)^2 \ll 1 : \qquad (15)$$
$$c(t) \cong c_0 \{(1-p) e^{-\beta t} + p e^{-2\beta t}\} . \qquad (16)$$

The intensity I_{DF} of the DF is proportional to the concentration of molecules in S_1. Since S_1 is populated by TTA, and since the lifetime of S_1 is at least 10^{-4} times shorter than the lifetime of T_1, the steady-state treatment of the concentration of molecules in S_1 is allowed, and the following proportionality holds with high accuracy:

$$I_{DF} \propto [S_1] \propto [T_1]^2 \equiv c^2(t).$$

The expressions for I_{DF}, corresponding to (12), (14), and (16), then are:

$$I_{DF} \propto c^2(t) = c_0^2 e^{-2\beta t} \{1 + (\gamma c_0/\beta)(1 - e^{-\beta t})\}^{-2} , (17)$$
$$I_{DF} \propto c^2(t) \cong c_0^2 e^{-2\beta t} \qquad \text{with} \quad p \ll 1, \quad (18)$$
$$I_{DF} \propto c^2(t) \cong c_0^2 \{(1 - 2p) e^{-2\beta t}$$
$$+ 2 p e^{-3\beta t}\} \qquad \text{with} \quad p^2 \ll 1 . \quad (19)$$

2.3. Time-dependence of DF with excitation by two interfering plane light waves

The simplest spatially periodic excitation is achieved by interference of two coherent and linearly polarized plane light waves of equal intensity $I_{e0}/2$ [26]. Let λ_0 be the wavelength and $2 \varphi_0$ be the angle between the wave vectors k_{10} and k_{20} of the two light waves in vacuo. If k_{10} and k_{20} lie both in the x, y-plane of a Cartesian coordinate system and form an angle φ_0 with the y-axis (cf. Fig. 1), and if the electric vectors of both light waves are parallel to the z-axis, then the light intensity (or excitation intensity) is a periodic function of x, $I_e(x)$, with the period d determined by the wavelength λ_0 and the angle of interference, $2 \varphi_0$:

$$I_e(x) = I_{e0} \{1 + \cos(2 \pi x/d)\} , \qquad (20)$$
$$d = \lambda_0/(2 \sin \varphi_0) . \qquad (21)$$

If a sample is bounded by a plane surface (the x, z-plane in Fig. 1) and if the angle of incidence, φ_0, is the same for both light waves then from the law of refraction follows that inside the sample (with refractive index n) the spatial period of excitation is the same as in vacuo. Throughout this paper an excitation geometry like that in Fig. 1 will be assumed. The obvious advantage of this excita-
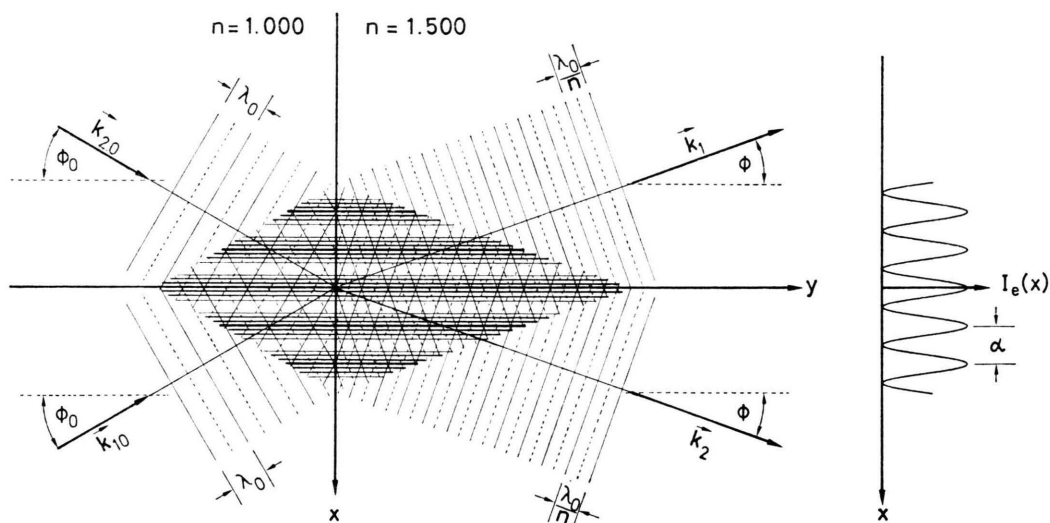
Fig. 1. Generation of non-localized interference fringes by interference of two plane light waves (electric vector in direction of z-axis). The fringe distance d is not changed by refraction at the x, z-plane when both waves have the same angle of incidence, φ_0.

tion geometry is that the refractive index of the sample need not be known.

After short excitation $S_1 \leftarrow S_0$ of a solution of an aromatic hydrocarbon M with light of the intensity distribution (20), at time $t = 0$, the initial space-dependence of the concentration of $^3M^*$, $c(x, 0)$, is

$$c(x, 0) = c_0 \{1 + \cos(2\pi x/d)\}, \qquad (22)$$

provided, that only a small fraction of the molecules in the ground-state has been excited, so that during excitation the concentration of molecules in the ground-state has been virtually constant. Short excitation means that the duration of excitation is very short compared to the lifetime of $^3M^*$ and to the time needed for equilibration of the concentration by diffusion.

To our knowledge, with the boundary condition (22) a solution of the partial differential equation (9) in the form of known functions does not exist. However, for the present purpose approximate solutions, which correspond to (14) and (16) in the case of spatially homogeneous excitation, are sufficient. It is convenient to consider first the case $\beta = 0$, $\gamma = 0$. (9) is then reduced to the one-dimensional form of Fick's second law, and with the boundary condition (22) the solution is

$$c(x, t) = c_0 \{1 + e^{-\delta t} \cos(2\pi x/d)\} \qquad (23)$$

with

$$\delta = (2\pi/d)^2 D. \qquad (24)$$

(23) means, the spatially periodic deviation of $c(x, t)$ from the average value c_0, $c_0 e^{-\delta t} \cos(2\pi x/d)$, decays exponentially. δ will be called diffusion-relaxation constant, and $1/\delta$ diffusion-relaxation time. The approximate solution of (9), corresponding to (13), is simply obtained by replacing the constant average concentration c_0 in (23) by the time-dependent average concentration (14):

$$c(x, t) \cong c_0 e^{-\beta t} \{1 + e^{-\delta t} \cos(2\pi x/d)\}. \qquad (25)$$

The approximate solution of (9), corresponding to (15), is

$$\begin{aligned}
c(x, t) \cong c_0 \Big\{ &\Big(1 - p\,\frac{3\beta + 4\delta}{2\beta + 4\delta}\Big) e^{-\beta t} + p\, e^{-2\beta t} \\
&+ p\,\frac{\beta}{2\beta + 4\delta}\, e^{-(2\beta + 2\delta)t} \qquad (26) \\
&+ [(1 - 2p)\, e^{-(\beta + \delta)t} \\
&+ 2p\, e^{-(2\beta + \delta)t}]\cos(2\pi x/d) \Big\}
\end{aligned}$$

with p given by (15). The reason why an approximate solution of the form (26) can be found, is given in the appendix.

The time-dependence of the DF corresponding to (25) and (26) is obtained by integration of $c^2(x, t)$ over one period:

$$I_{DF} \propto \langle c^2(x, t)\rangle_x = \frac{1}{d}\int_0^d c^2(x, t)\,dx, \qquad (27)$$

$$I_{DF} \propto c_0^2 \left\{ e^{-2\beta t} + \frac{1}{2} e^{-(2\beta + 2\delta)t} \right\} \quad \text{for} \quad p = \gamma c_0/\beta \ll 1;$$
(28)

$$I_{DF} \propto c_0^2 \left\{ (1 - 2 p q) e^{-2\beta t} + \left(\frac{1}{2} - 2 p \right) e^{-(2\beta + 2\delta)t} \right.$$
$$\left. + 2 p [e^{-3\beta t} + q e^{-(3\beta + 2\delta)t}] \right\}$$
(29)

with $q = (3 \beta + 4 \delta)/(2 \beta + 4 \delta)$ and for $p^2 = (\gamma c_0/\beta)^2 \ll 1$.

2.4. Time-dependence of DF with laser excitation

A laser beam is not a plane light wave. With respect to the present application two differences are important: a laser beam has a certain divergence and a certain diameter. Because of the divergence the non-localized interference fringes of two interfering laser beams do not form planes but curved surfaces [36]. Because of the limited diameter of a laser beam radial diffusion of the molecules in T_1 may be important, and, with interference angles $2 \varphi_0 > 0$, the intensities of the two interfering laser beams can no longer be equal at every point in space. Nevertheless, under the experimental conditions of the present investigation (cf. Sect. 3.1.), excitation by one or two laser beams is a very good approximation to excitation by one or two plane light waves. A detailed explanation of this fact has been given in the original version of this paper which can be supplied on special request. Here we communicate only some of the conclusions.

With a Gaussian radial intensity distribution of the laser beam, $I_e(r) = I_{e0} \exp(-2 r^2/r_0^2)$, a laser beam diameter $2 r_0 \geq 3$ mm is always sufficient for complete neglect of radial diffusion. With excitation by two beams the DF has to be measured in the range of maximal intersection of the two beams in order that the average interference fringe distance will be equal to d in (21). The application range of (19) and (29) is restricted by the requirement $p^2 = (\gamma c_0/\beta)^2 \ll 1$. With excitation by one beam, for c_0 the maximum has to be taken. If the parameters in (4) are known, then for given values of p^2 and of the excitation duration in turn c_0, I_{e0}, and, by integration over the beam cross-section, the laser power P_e can be calculated. With excitation by two interfering beams, because of (22), $P_e' \leq \frac{1}{4} P_e$ has to taken as save upper limit of the excitation power P_e' of each one of the beams.

3. Experimental Realization of the Method and Evaluation of Experimental Data

3.1. Excitation of a sample with two interfering laser beams

In the experiments, described in this paper, the 351.1-nm-line (TEM$_{00}$) of an argon ion laser (Spectra-Physics, model 171-03) was used for excitation. The 351.1-nm-line was separated from the other uv-lines with the aid of two 60° quartz glass dispersion prisms P_1 and P_2 (cf. Figure 2). The dispersed laser beam was focused by lens L_1 (plano-convex, focal length 40 nm) onto the pinhole PH (diameter 20 μm) and again collimated by lens L_2 (double-convex, designed for minimum spherical aberration, focal length 120 mm). The diameter of the expanded beam was 5 to 6 mm. Because of the space-filtering the expanded beam had a smooth intensity profile without any interference patterns. By reflection at the mirror M_3 the direction of the electric vector was changed from vertical to horizontal. By reflection at the semitransparent mirror M_5 and at the mirror M_6 respectively the mirrors M_7 and M_8 two parallel coherent beams of approximately the same intensity were obtained. Different and reproducible interference angles $2 \varphi_0$ were obtained with a set of Fresnel bi-prisms P_3 (cf. Fig. 3 and Table 1). The connection between the angle α of the bi-prism and the interference angle $2 \varphi_0$ is

$$\varphi_0 = \arcsin(n \sin \alpha) - \alpha,$$
(30)

where n is the refractive index of the bi-prism at the respective wavelength λ_0. For $\lambda_0 = 351.1$ nm the
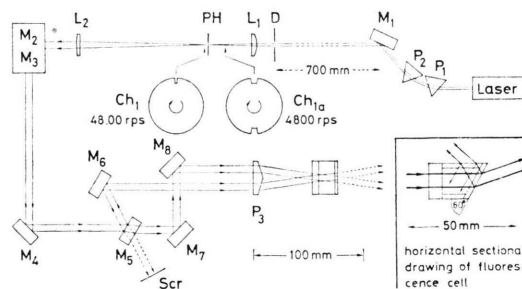
Fig. 2. Excitation with two interfering laser beams. P_1, P_2, P_3: prisms; M_1 to M_4, M_6 to M_8: mirrors with high reflectivity; M_5: semitransparent mirror; D: diaphragm; L_1, L_2: lenses; PH: pinhole; Scr: fluorescent screen; Ch_1, Ch_{1a}: mechanical choppers (about 1/4 of the correct relative size). The electric vector is vertical between laser and M_3, and horizontal between M_3 and the sample.
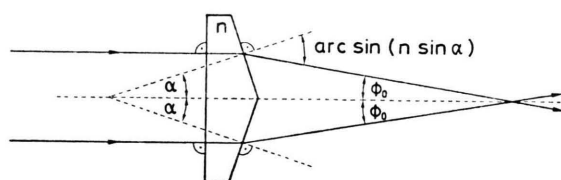
Fig. 3. Connection between angle α and refractive index n of Fresnel biprism and interference angle φ_0.

refractive index of quartz glass (Suprasil I) is 1.47671 ± 0.00003 (value interpolated from data in [37]). In Table 1 calculated values of φ_0, $\sin \varphi_0$, and the period $d = \lambda_0/(2 \sin \varphi_0)$ are listed for later reference. The choice of the bi-prism was determined by the requirement $\delta \geq 3 \beta$.

The uncertainty of φ_0 is mainly due to in-complete parallelism of the two beams to the left of prism P_3 (Fig. 2) and to the uncertainty with which the angle 2α of prism P_3 is known. The parallelism of the two beams on the left of P_3 is easily checked with the aid of the interference pattern, produced on the fluorescent screen Scr by the beams which are reflected at the left surface of P_3. The adjustment of the two beams was considered as satisfactory when the fringe distance on the screen was not less than 4 mm (with a beam diameter of about 6 mm). According to (21) this corresponds to a maximum angle between the two beams of about $10''$. The angle 2α was known with an accuracy of $\pm 12''$. According to (21) and (24) the diffusion coefficient D is inversely proportional to $\sin^2 \varphi_0$. The un-certainty of $\sin^2 \varphi_0$ is given in Table 1. All optical surfaces were accurate to at least $1/5$ of a wave-length, and wedge angles of mirrors and windows were less than $10''$.

3.2. Measurement of time dependence of DF

The DF was separated from the prompt fluores-cence (PF) in the usual way with mechanical chop-

pers (cf. Figures 2 and 4). The excitation light was chopped by two choppers: one fast chopper Ch_1 (48.00 rps) with a single slit of variable width, and one slow chopper Ch_{1a} (4.800 rps) with one or more (2 or 5) slits. The excitation time was about 100 µs. The diameter of the laser beam was less than 0.2 mm in the plane of Ch_1. Diffraction at the chopper edges caused at most a weak and nearly homogene-ous background excitation of the sample (with a moving edge a spatially stable diffraction pattern cannot develop). The use of the fast chopper secured that the dead-time between excitation and measure-ment of DF was short. The use of the slow chopper secured that the time between successive excitations was sufficiently long so that at the beginning of a new excitation the triplet concentration would be virtually zero. The fluorescence light beam was chopped by a single fast chopper Ch_2 (48.00 rps) with two narrow segments (Figure 4). The relative phase of the choppers Ch_1 and Ch_2 was adjusted mechanically by rotation of the motor base of one of the two synchromotors (Dunker). The short-term
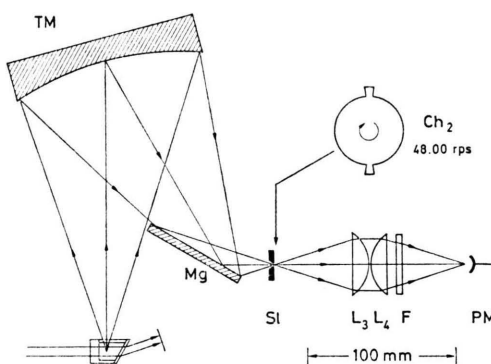

Fig. 4. Measurement of DF. TM: toroidal mirror; M_9: plane mirror; Sl: slit; Ch_2: mechanical chopper (about $1/3$ of the correct relative size); L_3, L_4: lenses; F: glass filter; PM: photomultiplier.

Table 1. Data for calculation of the spatial excitation period d: the angle α is defined in Fig. 3; φ_0 was calculated with (30) for $n = 1.47671$ ($\lambda_0 = 351.1$ nm); d was calculated with (21); for the uncertainty of $\sin^2 \varphi_0$ see Section 3.1.

Prism No.	α	φ_0	$\sin \varphi_0$	$d/\mu m$	Uncertainty of $\sin^2 \varphi_0$
1	$58' 37''$	$27' 57''$	0.00813	21.59	$\pm 0.95\%$
2	$1° 40' 54''$	$48' 8''$	0.01400	12.54	$\pm 0.55\%$
3	$2° 56' 42''$	$1° 24' 22''$	0.02454	7.154	$\pm 0.31\%$
4	$5° 0' 0''$	$2° 23' 41''$	0.04178	4.202	$\pm 0.19\%$
5	$7° 59' 51''$	$3° 51' 31''$	0.06729	2.609	$\pm 0.12\%$
6	$13° 3' 0''$	$6° 25' 40''$	0.11195	1.568	$\pm 0.05\%$

and the long-term stability of the relative phase were very good (better than $\pm 20'$) because of frequency and voltage stabilization of the power supply (Elgar model 251). The choppers were vibrationally isolated against the table which supported the laser and the experimental set-up. The slit in front of chopper Ch_2 and the lenses L_3 and L_4 (Fig. 4) were fixed to the table (and not to the chopper housing). The demands to be put to vibrational isolation of the experimental set-up were not very severe because the interference pattern had to be stable in space only for the excitation time, i. e. for about $100\,\mu s$. A constancy of room temperature of $\pm 1\,°C$ was sufficient for long-term stability of optical adjustments.

The sample was a fluorescence cell with a carefully degassed solution of an aromatic hydrocarbon (cf. Section 3.3.). A non-rectangular horizontal cross-section of the fluorescence cell was chosen in order to minimize the disturbing interference between the incident beams and the internally reflected beams. The cell angle of $60°$ secures that with small interference angles 99% or more of the excitation light can leave the fluorescence cell (at an angle close to the Brewster angle), and that the spatial period, resulting from interference of the incident beams with the beams, twice internally reflected, is very small because of the large interference angle of about $120°$ (with $\lambda_0 = 351.1\ nm$ and a refractive index $n = 1.5$ of the solution, $120°$ corresponds to a period $d = 135\ nm$, and with (24) and $D = 5 \cdot 10^{-6}\ cm^2\ s^{-1}$ to $\delta = 1.08 \cdot 10^6\ s^{-1}$; that means, equilibration of concentration by diffusion over this short period d is very fast and cannot cause any trouble in the determination of D). The DF of the region of maximum intersection of the two interfering beams was imaged by a toroidal mirror TM and a plane mirror M_9 onto the slit Sl (Fig. 4) in front of chopper Ch_2. The slit Sl was imaged onto a blue-sensitive cooled photomultiplier (EMI 9789 QA). The phosphorescence $T_1 \rightarrow S_0$ of the sample was absorbed by suitable glass filters F (Schott UG or BG filters). The sample was placed in an optical cryostat (Fig. 5) which in principle allowed measurements between liquid nitrogen temperature and $150\,°C$. The temperature was kept constant within $\pm 0.1\,°C$. The sample space was filled with helium. The windows through which the excitation light entered the sample space had anti-reflection coatings. The fluorescence cell, the win-
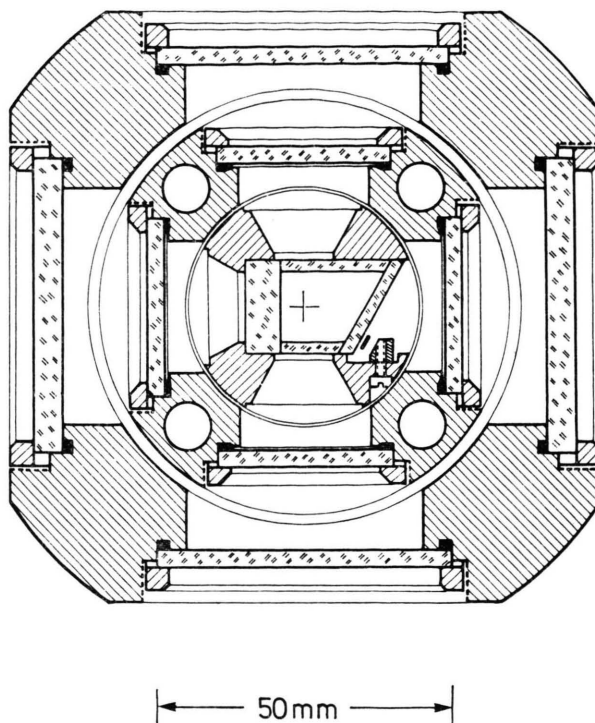

|←   50 mm   →|

Fig. 5. Horizontal sectional drawing of optical cryostat.

dows of the cryostat, and the lenses L_3 and L_4 were made of quartz glass Suprasil I (Heraeus).

The intensity of the DF was measured with the photon-counting technique. Decay curves of the DF were measured with a multichannel analyzer (MCA) (Canberra 8100) in its multichannel scaling mode. A sweep of the MCA was triggered by a pulse derived from the excitation light. Usually the dwell-time per channel was $100\,\mu s$, and 512 channels were used. The dwell-time was known with an accuracy better than $\pm 0.1\%$. In a single experiment, usually about 10^4 decay curves of the DF were accumulated. The data, stored in the MCA, were directly transferred to a computer (DEC, PDP 11).

3.3. Preparation of samples

All aromatic hydrocarbons were purified by column chromatography, sublimation in vacuo, and zone melting. All solvents were purified by column chromatography with active aluminum oxide and (with the exception of hexadecane) by rectification over a column. The minimum purity of the solvents was 99%. Oxygen-free solutions of aromatic

hydrocarbons were prepared with the usual freeze-pump-thaw technique.

A sample was suitable for the determination of the DC of molecules in T_1 if with weak excitation by a single laser beam the decay of the DF could be described by (18) or (19) and if the triplet lifetime $1/\beta$ was not shorter than about 10 ms. It turned out to be difficult to prepare samples with these properties. Only about 20% of all prepared samples were suitable. The procedure of sample preparation was modified several times during the course of this work. Here we mention only a few points which we regard as important:

(a) The solvent was chromatographed a second time immediately before use. This turned out to be essential for getting long triplet lifetimes ($\gtrsim$ 10 ms) and dry solutions. Storage of the purified dry and degassed solvent in sealed ampules with a breakseal should be equivalent. See, however point (c) below.

(b) During equilibration of liquid phase and vapour phase the connection to the high vacuum line was closed by a glass needle valve (cf. Fig. 6) so that liquid and vapour would be in contact with glass only.

(c) Perhaps the most critical step in sample preparation is the final sealing off. The heating of glass to the softening point is always accompanied by the evolution of volatile substances the nature of which will depend on the glass, on pretreatment of the glass surface, and on substances adsorbed at the surface. With the usual technique about half of the amount of volatile substances is condensed in the sample. The amount of condensed substances can be greatly reduced by use of a magnetic value (MV in Fig. 6) which is closed during the sealing off. In this connection we only mention that pretreatment of the glass with nitric acid gave short triplet lifetimes (~ 1 ms), possibly because of evolution of nitric oxide (NO) which acts as a triplet quencher. Pretreatment with chromosulfuric acid in general did not cause trouble in this respect. However, a consequence of the treatment with chromosulfuric acid might be evolution of sulfur dioxide during sealing off; sulfur dioxide forms ground-state complexes with aromatic hydrocarbons [38], and possibly it was responsible in some cases for non-exponential decay of the DF.

3.4. Evaluation of experimental data

Measured decay curves of the DF were corrected for the limited maximum counting rate f_{max} of the
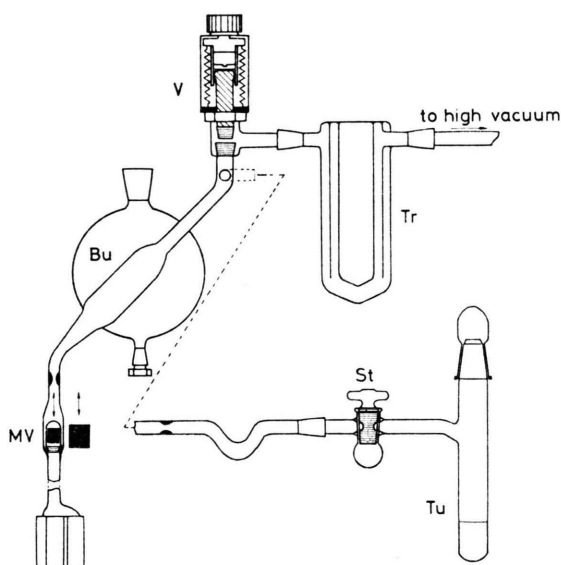
Fig. 6. Sample preparation. MV: magnetic ground-glass valve; Bu: bulb for cooling the inner tube with liquid nitrogen or a methanol/dry ice mixture; V: ground-glass valve with stainless-steel-bellow-sealed shaft; Tr: liquid nitrogen cooling trap; St: stopcock; Tu: tube containing the chromatographed and degassed solvent.

Fig. 7. (a) Decay of DF after excitation with two interfering laser beams at time $t = 0$. The dashed curve represents the decay which would be observed after excitation with two incoherent laser beams. (b) Deviation of the experimental decay curve from the calculated decay curve in units of the standard deviation. (System: see Table 2, last line.)

multichannel analyzer (MCA) and for the dark pulse rate f_d of the photomultiplier. f_{max} was determined experimentally with equidistant pulses and was found to be 10 to 12 MHz with the Canberra MCA 8100 (depen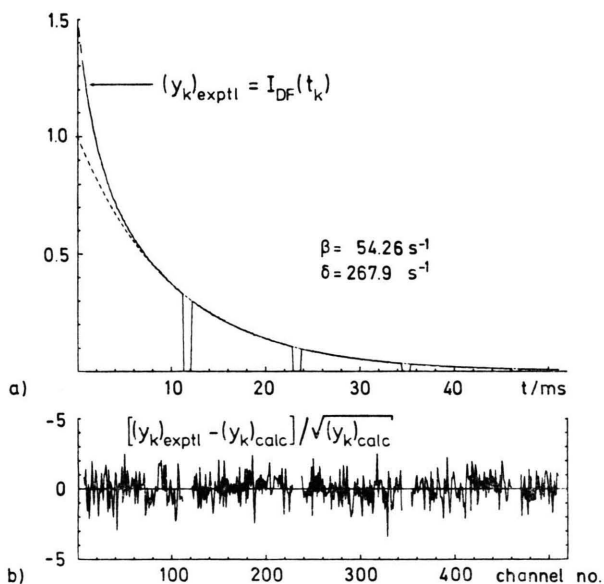ding on the specimen). f_d was about 1 Hz; it was obtained from those parts of the decay curve of the DF during which the fluorescence light path was closed by the chopper (cf. Figure 7). If f_c is the number of counted pulses per second, and f_t is the true number of pulses per second, proportional to the intensity of the DF, then

$$f_t \cong f_c (1 + f_c/f_{max}) - f_d . \qquad (31)$$

Relation (31) yields f_t with an accuracy better than $\pm 0.1\%$ if $f_c/f_{max} \leqq 0.01$. (31) follows from statistical considerations; the validity of (31) was verified experimentally in the intensity range of interest. Three minor sources of error were not taken into account: First, the finite channel dead-time of 1.0 µs or 3.5 µs (depending on the type of memory of the MCA) was neglected because the channel dwell time was always $\geqq 100$ µs. Second, the slight decrease of the DF intensity during the channel dwell time was neglected. Third, the instability of the laser power was neglected. These three neglects and the use of (31) itself caused a small undercorrection which, however, even at the beginning of a decay curve caused an error of at most -0.1%.

A measured decay curve of the DF consisted of a sequence of integrals of the DF intensity I_{DF} over the channel dwell time Δt. If I_{DF} decreased during Δt by not more than a few percent, the measured decay of I_{DF} could be regarded as a sequence of intensities $I_{DF}(t_1)$, $I_{DF}(t_2)$, ..., $I_{DF}(t_k)$, $I_{DF}(t_{k+1})$, ... with $t_{k+1} - t_k = \Delta t$. Moreover, as long as a decay curve of the DF could be represented by a sum of exponential functions, a finite dwell time did only change the pre-exponential factors but not the exponential functions. Theoretical equations were fitted to experimental decay curves by a Simplex procedure. With $y_k \equiv I_{DF}(t_k)$ the criterium for the optimal fit was

$$\sum_k \{ [(y_k)_{exptl} - (y_k)_{calc}] / \sqrt{(y_k)_{calc}} \}^2$$
$$= F = \text{minimum} . \qquad (32)$$

The weighting factor $1/\sqrt{(y_k)_{calc}}$ in the least-square fit (32) was found to be essential for the most reliable calculation of β and δ. The fitting procedure was stopped when

$$F(\beta, \delta) \leqq F(\beta \pm 0.001\,\beta, \ \delta \pm 0.001\,\delta) . \qquad (33)$$

A sample was considered as suitable for determination of diffusion coefficients when, with excitation by a single laser beam at low excitation intensity, I_{DF} was described by (19), i. e. by

$$I_{DF} = A_1\, e^{-2\beta t} + A_2\, e^{-3\beta t} \qquad (34)$$

with $A_2/A_1 \leqq 0.1$. With excitation by two interfering laser beams I_{DF} was described by (29), i. e. by

$$I_{DF} = B_1\, e^{-2\beta t} + B_2\, e^{-(2\beta + 2\delta)t} + B_3\, (e^{-3\beta t} \qquad (35)$$
$$+ q\, e^{-(3\beta + 2\delta)t}) .$$

Only two of the three quantities B_1, B_2, B_3 are linearly independent. In the fitting procedure all three quantities B_1, B_2, B_3 were treated as independent parameters. In order to decide whether a measured decay curve of the DF should be used for the determination of the diffusion coefficient or not, the following criteria were applied: First, the deviations of the measured decay curve of the DF from the calculated one had to be random. In Fig. 7 as an example the decay curve of the DF, belonging to the last line of Table 2, is shown. The dashed curve in Fig. 7 a represents the decay of the DF which would be observed with excitation by two incoherent laser beams. In Fig. 7 b the deviation of the measured decay curve from the calculated one is plotted in units of the standard deviation. No systematic deviation is found. Second, by comparison of (35) with (29) several relations can be obtained, which should be satisfied by the values of B_1, B_2, and B_3, yielded by the fitting procedure. However, one must not expect that these relations will hold exactly, for several reasons: The intensities of the interfering laser beams are not equal at every point in the region, the DF of which is measured; the time $t = 0$ is not exactly known; the DF is integrated over the dwell time of each channel; finally and most important, because of the noise of a decay curve the relative values of the fitting parameters B_1, B_2, and B_3 will vary from experiment to experiment. Taking into account these sources of error in the appropriate way, and also the limited application range of (29), we obtained the following criteria for a reliable experiment:

$$B_1/B_2 \geqq 1.79 , \qquad (36)$$

$$1 + (B_2 + B_3) / (B_1 + q\, B_3) \leqq 1.55 , \qquad (37)$$

$$0 \leqq B_3/(B_1 + q\, B_3) \leqq 0.08 . \qquad (38)$$

4. Results

4.1. Self-consistency of the method

The diffusion coefficient (DC) D of the triplet energy must be independent of the interference angle $2\varphi_0$ of the two interfering laser beams. This was checked in two cases:

(a) Anthracene $(1.5 \cdot 10^{-5} \text{ M})$ in octane at 25.0 °C, prisms no. 1 and no. 2 of Table 1:

$$\sin^2 \varphi_0 = 0.661 \cdot 10^{-4},$$
$$D = (1.97 \pm 0.02) \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ (3 values)};$$

$$\sin^2 \varphi_0 = 1.960 \cdot 10^{-4},$$
$$D = (2.04 \pm 0.04) \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1} \text{ (5 values)}.$$

The agreement of the two values of D is satisfactory in view of the fact that a difference of $\pm 1.5\%$ can be caused by the uncertainty of $\sin^2 \varphi_0$ (cf. Table 1).

(b) Anthracene $(2.5 \cdot 10^{-5} \text{ M})$ in hexadecane at 25.0 °C, prisms no. 2 and no. 3 of Table 1:

$$\sin^2 \varphi_0 = 1.960 \cdot 10^{-4},$$
$$D = (5.45 \pm 0.07) \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ (11 values)};$$

$$\sin^2 \varphi_0 = 6.022 \cdot 10^{-4},$$
$$D = (5.36 \pm 0.12) \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1} \text{ (5 values)}.$$

Another test for the self-consistency of the method is the dependence of the DC on the concentration of the molecules in the ground state. At low concentration of the aromatic hydrocarbon and at room-temperature, transport of triplet energy should be due nearly exclusively to diffusion of monomer molecules in the triplet state T_1. In Table 2 the results of two series of measurements of the DC D of the triplet energy of anthracene in hexane, with the concentration of anthracene $2.5 \cdot 10^{-5}$ and $1.0 \cdot 10^{-5}$ M, are shown. The agreement of the two values of D_{av} is very satisfactory. Table 2 illustrates also a point which is important for the accurate determination of the DC. The constancy of the first-oder rate constant β depended on the quality of a sample and on the time over which the experiments extended. With the first sample the experiments extended over several days, with the second sample the experiments extended over one day only. The variation of β with the first sample is typical; evidently it would not make sense to determine β by an independent experiment with excitation by a single laser beam. Another example for the independence of the DC on the concentration of molecules in the ground-state is anthracene in hexadecane (cf. Table 5).

4.2. Diffusion coefficient of ³anthracene* in different solvents

The diffusion coefficient D of ³anthracene* was measured in hexane, octane, hexadecane, perfluorohexane, and methylcyclohexane at 25.0 °C (Table 3). The temperature-dependence of D was measured for ³anthracene* in hexane (Table 4), and — with a simpler experimental set-up and with evaluation of data by (18) and (28) — for ³anthracene* in hexadecane (Table 5). In Tables 4 and 5 the observed temperature-dependence of D is compared with the calculated one, obtained from the Stokes-Einstein equation

$$D_{SE} = k \, T / (6 \pi \eta \, r), \tag{39}$$

where k is Boltzmann's constant, η is the viscosity of a continuous solvent, and r is the radius of a spherical particle. For non-spherical solute molecules, and for solute molecules and solvent molecules being of about the same size, (39) still gives the correct value of D within a factor of $2^{\pm 1}$ if for r in (39) a suitable average radius of the solute molecules is taken. From the fact that (39) predicts the right order of magnitude for arbitrary viscosities and temperatures follows that in general (39) should describe the temperature-dependence of D rather accurately. In Table 4

Table 2. Diffusion coefficient D of ³anthracene* in hexane at (25.0 ± 0.1) °C: c_M = concentration of anthracene in the ground state; prism 1 in Table 1 was used.

c_M	β	δ	D	D_{av}
10^{-5} M	s^{-1}	s^{-1}	10^{-5} cm^2 s^{-1}	10^{-5} cm^2 s^{-1}
2.5	74.03	267.7	3.161	
2.5	74.84	271.4	3.205	
2.5	73.42	266.6	3.148	
2.5	75.09	271.0	3.200	
2.5	74.61	266.0	3.140	
2.5	74.69	265.0	3.129	3.15 ± 0.05
2.5	74.61	263.1	3.106	
2.5	72.92	272.8	3.220	
2.5	74.25	262.0	3.093	
2.5	72.81	269.6	3.183	
2.5	75.86	268.4	3.169	
2.5	74.58	261.0	3.082	
1.0	54.33	269.7	3.185	
1.0	54.28	271.9	3.210	3.18 ± 0.03
1.0	54.34	266.7	3.149	
1.0	54.26	267.9	3.163	

Table 3. Diffusion coefficient D of ^{3}anthracene* in different solvents at $(25.0 \pm 0.1)\,°C$: c_M = concentration of anthracene in the ground-state; n = number of measurements; No. = number of prism in Table 1; viscosities η [a, b] are taken from [39, 40].

Solvent	$\eta/10^{-2}$ P	$c_M/10^{-5}$ M	β/s^{-1}	No.	n	δ/s^{-1}	$D/10^{-5}$ cm^2 s^{-1}
Hexane	0.2985[a]	2.5	74.31 $\pm$ 0.89	1	12	267.1 $\pm$ 3.8	3.15 $\pm$ 0.05
		1.0	54.30 $\pm$ 0.04	1	4	269.1 $\pm$ 2.3	3.18 $\pm$ 0.03
Octane	0.5151[a]	1.0	53.41 $\pm$ 0.36	1	3	167.1 $\pm$ 1.0	1.97 $\pm$ 0.02
				2	5	512.8 $\pm$ 9.8	2.04 $\pm$ 0.04
Hexadecane	3.095[a]	2.5	52.50 $\pm$ 0.65	2	11	136.9 $\pm$ 2.9	0.545 $\pm$ 0.007
				3	5	416.4 $\pm$ 6.9	0.536 $\pm$ 0.012
Perfluorohexane	0.67[b]	1.0	114.8 $\pm$ 1.0	2	10	450.7 $\pm$ 7.8	1.80 $\pm$ 0.03
Methylcyclo-hexane	0.685[a]	2.5	76.53 $\pm$ 0.57	2	6	404.1 $\pm$ 9.5	1.61 $\pm$ 0.04

Table 4. Temperature-dependence of diffusion coefficient D of ^{3}anthracene* in hexane: c_M = concentration of anthracene in the ground-state; n = number of measurements; in all experiments prism no. 1 of Table 1 was used; values of D_{SE} were obtained with (39), with $k = 1.38054 \cdot 10^{-16}$ erg K^{-1} and $r = 2.315 \cdot 10^{-8}$ cm; viscosities are taken from [39].

T/K	$\eta/10^{-2}$ P	Sample	$c_M/10^{-5}$ M	n	β/s^{-1}	$D/10^{-5}$ cm^2 s^{-1}	D/D_{SE}
273.16 $\pm$ 0.1	0.3810	a	1.0	5	51.10 $\pm$ 0.90	2.16 $\pm$ 0.06	0.952 $\pm$ 0.026
283.16 $\pm$ 0.1	0.3436	a	1.0	4	53.22 $\pm$ 0.74	2.48 $\pm$ 0.05	0.951 $\pm$ 0.020
298.16 $\pm$ 0.1	0.2985	b	2.5	12	74.31 $\pm$ 0.89 }	3.16 $\pm$ 0.04	1.000 $\pm$ 0.013
		c	1.0	4	54.30 $\pm$ 0.04 }		
303.16 $\pm$ 0.1	0.2854	a	1.0	4	60.91 $\pm$ 0.62	3.43 $\pm$ 0.05	1.021 $\pm$ 0.015
313.16 $\pm$ 0.1	0.2619	a	1.0	3	65.16 $\pm$ 0.48	3.94 $\pm$ 0.12	1.042 $\pm$ 0.031
323.16 $\pm$ 0.1	0.2411	a	1.0	3	70.95 $\pm$ 1.28	4.35 $\pm$ 0.02	1.026 $\pm$ 0.005
333.16 $\pm$ 0.1	0.2223	a	1.0	4	77.02 $\pm$ 0.72	4.82 $\pm$ 0.07	1.017 $\pm$ 0.014

Table 5. Temperature-dependence of diffusion coefficient D of ^{3}anthracene* in hexadecane: c_M = concentration of anthracene in the ground state; n = number of measurements; excitation at 350.7 nm (krypton ion laser), interference angle $2\varphi_0 = 2°3'17''$; values of D_{SE} were obtained with (39), with $k = 1.38054 \cdot 10^{-16}$ erg K^{-1} and $r = 1.284 \cdot 10^{-8}$ cm; viscosities from [39] were interpolated by $\log \eta = A + B/T$.

T/K	$\eta/10^{-2}$ P	$c_M/10^{-5}$ M	n	β/s^{-1}	$D/10^{-6}$ cm^2 s^{-1}	D/D_{SE}
293.76 $\pm$ 0.1	3.434	5.3	2	67.95 $\pm$ 0.02	4.88 $\pm$ 0.07	1.000 $\pm$ 0.014
293.76 $\pm$ 0.1	3.434	0.95	3	48.29 $\pm$ 0.14	4.88 $\pm$ 0.05	1.000 $\pm$ 0.010
308.46 $\pm$ 0.1	2.474	5.3	1	81.60	6.91	0.971
323.16 $\pm$ 0.1	1.866	0.95	3	58.94 $\pm$ 0.12	9.07 $\pm$ 0.17	0.917 $\pm$ 0.017
334.46 $\pm$ 0.1	1.541	0.95	2	68.70 $\pm$ 0.28	11.37 $\pm$ 0.18	0.918 $\pm$ 0.014
346.96 $\pm$ 0.1	1.273	0.95	2	76.04 $\pm$ 0.44	14.52 $\pm$ 0.36	0.934 $\pm$ 0.023
362.16 $\pm$ 0.1	1.034	0.95	2	79.62 $\pm$ 0.17	18.02 $\pm$ 0.32	0.911 $\pm$ 0.016

and 5 the ratio D/D_{SE} of the experimental value D and the calculated value D_{SE} is listed. In both solvents a small systematic deviation of D/D_{SE} from constancy is found. On the basis of the present data it cannot be decided whether this deviation is caused by a systematic error of the method or by a failure of (39). With anthracene in hexane we were not able to determine D at temperatures below $-10\,°C$, because with excitation by a single laser beam the time-dependence of the DF could no longer be described by (34). Since the choice of the lowest

temperature $(0.0\,°C)$, at which the method still worked, was somewhat arbitrary, it is conceivable that the first two values of D in Table 4 contain a systematic error of a few percent. For the remaining 5 values of D in Table 4 the constancy of D/D_{SE} is very satisfactory.

The temperature-dependence of D of ^{3}anthracene* in hexadecane (Table 5) is represented with a standard deviation of $\pm 1.5\%$ by

$$\log_{10}(D/(\text{cm}^2\,\text{s}^{-1})) = -2.2945 - 885.7\,\text{K}/T . \quad (40)$$

Table 6. Diffusion coefficient D of ^{3}pyrene*, ^{3}9,10-diphenylanthracene* (DPA), and (for comparison) ^{3}anthracene* in hexane at (25.0 ± 0.1) °C: c_M = concentration of the aromatic hydrocarbon in the ground-state; n = number of measurements; No. = number of prism in Table 1.

Solute	$c_M/10^{-5}$ M	n	No.	β/s^{-1}	δ/s^{-1}	$D/10^{-5}$ cm^2 s^{-1}
Pyrene	2.5	12	1	35.81 ± 0.76	247.7 ± 2.9	2.93 ± 0.04
DPA	1.0	4	2	48.79 ± 0.08	453.0 ± 4.2	1.80 ± 0.02
Anthracene	1.0	4	1	54.30 ± 0.04	269.1 ± 2.3	3.18 ± 0.03

For 25.0 °C (298.16 K) the interpolated value of D, $5.43 \cdot 10^{-6}$ cm^2 s^{-1}, is in excellent agreement with the corresponding value of Table 3. Since the data of Table 5 were obtained with an experimental set-up [41], completely different from that described in the present paper, one may conclude that the reliability of D does not critically depend on a particular realization of the method.

4.3. Diffusion coefficient of ^{3}pyrene* and ^{3}9,10-diphenylanthracene* in hexane at 25.0 °C

The diffusion coefficient D of ^{3}pyrene* and ^{3}9,10-diphenylanthracene* (DPA) in hexane at 25.0 °C was determined. Results are shown in Table 6 and compared with D of ^{3}anthracene*. The pyrene data show that occasionally the reproducibility of δ may even be better than that of β. The quantum yield of the ISC $S_1 \rightsquigarrow T_1$ of DPA is very low, but still sufficient for the measurement of the DF. The spectra of the DF and the PF of DPA were found to be identical.

5. Discussion

5.1. Reliability of the method and possible improvements

The data in Tables 2 – 6 show that the reproducibility of the measured value of a diffusion coefficient D was typically about $\pm 2\%$. The uncertainty of the value of D, due to the uncertainty of the interference angle $2\varphi_0$, did not exceed $\pm 1\%$ (see Table 1). The check of the self-consistency of the method (see Section 4.1.) suggests, that the uncertainty of D, caused by any systematic errors, does not exceed $\pm 2\%$. So we conclude that the absolute accuracy of the obtained values of D is not worse than $\pm 5\%$. This accuracy is about the same as that of known values of D of aromatic hydrocarbons in the electronic ground-state (see Section 5.2.). For some purpose (see Section 5.3., (III)) it would be desirable to know diffusion coefficients of aromatic hydrocarbons with an absolute or at least relative accuracy of about $\pm 1\%$. We believe that with the present method such an accuracy can be achieved, and we want to briefly indicate possible improvements:

(a) A substantial increase of the reproducibility of D can only be achieved by an increase of the number ob counts per channel (typically about 10^5 in the first channel, in this investigation); in practice that means an extension of the duration of a single experiment by a factor of 4 or more. At the time when the present data were obtained, the duration of a single experiment was limited to about 1 hour because of insufficient constancy of the uv-power of the argon ion laser. Since now argon ion lasers are available with constant uv-power (within $\pm 1\%$) for many hours, it should be possible to attain a reproducibility of D of $\pm 1\%$ or better. An additional small increase of the reproducibility of D can be achieved by shorter excitation (e. g. with a pulsed laser) and by reduction of the phosphoroscope dead-time (cf., however, points (c) and (d) in Section 2.1.).

(b) It should be possible to reduce the maximum error of D, caused by the uncertainty of the interference angle $2\varphi_0$, to about $\pm 0.5\%$.

(c) By use of a faster photon-counting system (e. g. with a pulse-pair resolution of 10 ns) and by a more sophisticated correction of the measured decay curve of the DF, it should be possible to reduce any systematic error, caused by the photomultiplier and the photon-counting system, by one order of magnitude.

(d) The use of the approximate expression (29) instead of an exact expression for the time-dependence of the DF will cause a small systematic error of the value of D. This error can be estimated for given values of c_0, β, γ, and δ by approximation of

the exact time-dependence of the DF (obtained by numerical solution of the partial differential equation (9) with boundary condition (22) and by numerical integration (27)) with the approximate expression (29).

(e) Finally, the technique of sample preparation can be improved. In this respect perhaps much can be learned from the work of Tsai and Robinson [42].

5.2. Comparison with other data

Burkhart has tried to determine the diffusion coefficient D of ^{3}anthracene* in methylcyclohexane (MCH) and cyclooctane at 25 °C [32]. With a $1.0 \cdot 10^{-5}$ M solution of anthracene in MCH he obtained for D $(2.67 \pm 0.27) \cdot 10^{-5}$ cm^2 s^{-1}, and his value of D strongly decreased with increasing concentration c_M of anthracene. He interpreted this concentration-dependence of his value of D as evidence for triplet-excimer formation. In our opinion this interpretation cannot be true for two reasons: First, it is hard to understand why the probability for triplet-excimer formation should strongly depend on the particular alkane which is chosen as solvent. Second, if one assumes equilibrium between triplet-monomers $(D = D_1$, $[^3M^*] = c_1)$ and triplet-excimers $(D = D_2$, $[^3(MM)^*] = c_2)$, one would expect the average diffusion coefficient $\bar{D}$ to be

$$\bar{D} = \frac{c_1}{c_1 + c_2} D_1 + \frac{c_2}{c_1 + c_2} D_2 , \qquad (41)$$

with the ratio c_2/c_1 being determined by c_M and the equilibrium constant (association constant) K,

$$c_2/c_1 = K c_M . \qquad (42)$$

The effective Stokes-radius r_2 of the triplet-excimer should be less than twice the effective Stokes-radius r_1 of the triplet-monomer, and therefore

$$0.5 < D_2/D_1 < 1.0 . \qquad (43)$$

With (41), (42), and (43) the maximum relative change of $\bar{D}$, which can be effected by an increase of c_M by a factor of 5, is estimated to be less than -25%. Burkhart found with an increase of c_M from $1.0 \cdot 10^{-5}$ M to $4.9 \cdot 10^{-5}$ M a decrease of $\bar{D}$ from $2.67 \cdot 10^{-5}$ cm^2 s^{-1} to $1.24 \cdot 10^{-5}$ cm^2 s^{-1}, i. e. relative change of $\bar{D}$ by about -50%. We conclude that his values are distorted by a large systematic error.

With aromatic hydrocarbons in alkanes one does not expect that the DC D of molecules in T_1 will be very different from the DC D_0 of molecules in S_0. Unfortunately for none of the systems, investigated by us, D_0 is known. Nevertheless, two sets of measurements of diffusion coefficients are known which allow a comparison of D and D_0. Miller, Prater, Lee, and Adams [43] measured D_0 of anthracene in a dioxane-water mixture, in acetonitrile, and in dimethylformamide at 25 °C with a tracer technique. Gorrell and Dubois [44] measured D_0 of naphthalene, phenanthrene, and chrysene in hexadecane at temperatures close to 25 °C with a diaphragm cell method. With both sets of data the Stokes-Einstein equation (39) can be used in order to obtain approximate values of D_0 of anthracene in hexane (from the data in [43] by making use of the constancy of $D \eta$ for a given solute at constant temperature) and in hexadecane (from the data in [44] by making use of the constancy of $D r$ for a given solvent at constant temperature). The estimates of D_0, obtained in this way, $(3.35 \pm 0.23) \cdot 10^{-5}$ cm^2 s^{-1} for anthracene in hexane and $(6.2 \pm 0.6) \cdot 10^{-6}$ cm^2 s^{-1} for anthracene in hexadecane, agree reasonably well with the corresponding values of D in Table 3. In conclusion one may state: For aromatic hydrocarbons, and on the basis of the present data, no significant difference between D and D_0 is found; if there is a difference between D and D_0, we would expect $0.9 < D/D_0 < 1.0$.

Finally, in consideration of the preceding conclusion, the data of Tables 3 and 6 allow to test the validity of various formulae for the prediction of diffusion coefficients. We refer the reader to a recent discussion of such formulae by Schuh and Fischer [45].

5.3. Conceivable applications of the method

The particular advantages of the present method are rather obvious: First, the accuracy of the method is about as good as or even better than that of conventional methods. Second, the concentration of the aromatic hydrocarbon can be very low; hence no extrapolation of the measured DC to infinite dilution is necessary. Third, with a single sample the DC can be measured in the whole temperature range between the freezing point and the boiling point of the solvent, and the number of measurements is in practice unlimited with a sufficiently photostable compound. Fourth, with some problems indeed the DC of molecules in T_1 or, more generally, the DC of the triplet energy has to be known. In the

present section and in the following one we want to mention or briefly discuss three problems to the solution of which the present method may contribute essentially.

(I) The existence of triplet excimers or triplet exciplexes in liquid solution − see Section 5.4.

(II) The question, whether TTA in liquid solutions is a diffusion-controlled reaction or not, has not yet been answered satisfactorily. The answer to this question is of interest with regard to the possible spin-statistical limitation of TTA: if the energy of two triplets is less than the energy of the lowest quintet state Q_1 then pair quintet states $^5(T_1 \ldots T_1)$ do not contribute directly to TTA because the TTA $^5(T_1 \ldots T_1) \rightarrow {}^5(Q_1 \ldots S_0)$ cannot take place [46]. A comparison of experimental values γ_{exptl} of the rate constant of TTA of ^{3}anthracene* in cyclohexane at 25 °C [47, 48] with the theoretical value γ_{theor}, obtained with (10), yields $\gamma_{exptl} \cong 0.5 \, \gamma_{theor}$. However, this result can not yet be regarded as conclusive evidence for a spin-statistical rate-limiting factor in TTA for two reasons: First, the derivation of (10) is based on the simplest conceivable model, and, according to Noyes [10], "it is unwise to assume that the absolute predictions of such models are valid to better than a factor of two, although the models may predict ratios of quantities more accurately than this". Second, the choice of the encounter distance R_0 in (10) is somewhat arbitrary for non-spherical molecules; it was assumed to be twice the average radius of the anthracene molecule $(2 \cdot 0.35 \text{ nm})$. We believe that a solution of the problem can be found, in the sense of the second part of Noyes' statement, by a comparative study of TTA and a reaction like triplet energy transfer (TET) [49 − 52] in a wide range of viscosity. With suitably chosen reactants, e. g. with the TTA of ^{3}anthracene* or ^{3}phenanthrene* and the TET ^{3}phenanthrene* + ^{1}anthracene → ^{1}phenanthrene + ^{3}anthracene*, the present method would allow to determine the diffusion coefficients of ^{3}anthracene* and ^{3}phenanthrene* under the same experimental conditions and with about the same experimental expenditure as the rate constants γ_{TTA} and γ_{TET}. The interpretation of the viscosity-dependence of γ_{TTA} and γ_{TET} would be independent of the Stokes-Einstein equation (39), in contrast to previous investigations [49 − 52]. Such an investigation could

bring to light to what extent the notion of a constant encouter distance R_0 is meaningful in TTA and TET [53]. $\gamma_{TTA} \cong \frac{4}{9} \gamma_{TET}$ at low viscosity and $\gamma_{TTA} \cong \gamma_{TET}$ at high viscosity would indicate the presence of a rate-limiting spin-statistical factor at low viscosity, when the triplet pair correlation time is short compared to the spin-lattice relaxation time.

(III) With solutions of aromatic hydrocarbons in *n*-alkanes of about the same molecular length some anomaly in the temperature-dependence of the DC is expected. Solid solutions of aromatic hydrocarbons in *n*-alkanes exhibit a peculiarity which is known as the Shpol'skii effect [54]: The spectrum of the fluorescence $S_1 \rightarrow S_0$ or phosphorescence $T_1 \rightarrow S_0$ of such solutions consists at low temperature (4 K) of sharp lines or multiplets of sharp lines because only a few spectroscopically distinct molecular environments of solute molecules occur. One may expect that already in the liquid solution, at temperatures just above the melting point, some short-range orientational order is present [55], and this should be reflected also in an anomalous temperature-dependence of the DC (as compared to the temperature-dependence of the DC, predicted by the Stokes-Einstein equation (39)).

5.4. On the existence of triplet excimers

The existence of triplet excimers of aromatic hydrocarbons in liquid solutions was the subject of theoretical [56] and experimental [57 − 61] investigations. Three kinds of experimental results were regarded as evidence for the existence of triplet excimers: Concentration quenching of the triplet state [57], the appearance of new bands in the phosphorescence spectrum [58 − 60], and the appearance of new bands in the $T_n \leftarrow T_1$ absorption spectrum [61]. We do not believe that these experimental results really prove the existence of triplet excimers. In all cases the observed effects can easily be explained by the presence of an impurity. With respect to the explanation of concentration quenching by triplet excimer formation, a detailed criticism can be found in [62]. With respect to new bands in the phosphorescence spectrum we simply mention that the distinction between triplet excimer phosphorescence and the sensitized phosphorescence of an impurity is difficult; in one case [60], even the nature of the impurity is obvious (biacetyl or some similar compound). Finally, in the transient

absorption spectrum in [61] strong negative absorption is found in a spectral range, in which ground-state molecules do not yet absorb.

It should be possible to solve the problem of the existence or non-existence of triplet excimers of aromatic hydrocarbons in liquid solutions in the following way:

(a) The concentration quenching of the triplet state should be studied very carefully. A sample preparation technique similar to that of Tsai and Robinson [42] should be used.

(b) In the investigation of the concentration-dependence of the phosphorescence spectrum one should look in the first place for small spectral changes and not for new bands because it is not at all obvious why the triplet excimer phosphorescence spectrum should be very different from the triplet monomer phosphorescence spectrum.

(c) If experimental conditions can be found under which triplet excimers are the dominating triplet species then the DC of the triplet energy should decrease with increasing concentration of molecules in the ground state, as indicated in Section 5.2. The practical application of the method probably would be restricted to systems with very rapid equilibration of excited monomers and excimers (compared to the diffusion-relaxation time $1/\delta$ in (29)).

Acknowledgement

Appendix

It has to be shown that with the boundary condition (22) and with (15) a function $f(x, t)$ of the form

$$f(x, t) = f_0(t) + f_1(t) \cos(2 \pi x/d) \qquad (44)$$

is a sufficient approximation for $c(x, t)$ (for the present purpose). The solution $c(x, t)$ of the partial differential equation (9) with the boundary condition (22) can be expanded into a Fourier series

with time-dependent coefficients,

$$c(x, t) = f_0(t) + f_1(t) \cos(1\,\xi) + f_2(t) \cos(2\,\xi) + \cdots$$
$$+ f_k(t) \cos(k\,\xi) + \cdots, \qquad (45)$$

where $\xi = 2\,\pi\,x/d$. From (22) follows

$$f_0(0) = f_1(0) = c_0, \qquad (46)$$

$$f_2(0) = \cdots = f_k(0) = \cdots = 0. \qquad (47)$$

The intensity of the DF is proportional to $\langle c^2(x, t) \rangle_x$,

$$\langle c^2(x, t) \rangle_x = f_0^2(t) + \frac{1}{2} f_1^2(t) + \frac{1}{2} f_2^2(t) + \cdots$$
$$+ \frac{1}{2} f_k^2(t) + \cdots. \qquad (48)$$

Now it is to show that the functions $f_j(t)$ $(j = 1, 2, \ldots)$ contain the factor p^{j-1}, and that for this reason only the first two terms in the series expansion (45) have to be taken into account. The argument is given for the term $f_2(t) \cos(2\,\xi)$ in (45). Because of (47) this term can only arise from the x-dependence of TTA. In order to get an upper bound for the relative magnitude of $f_2(t)$ with respect to $f_1(t)$, it is assumed that $f_0(t) = f_1(t)$ = constant and that the increase of $|f_2(t)|$ is limited only by equilibration of concentration due to diffusion. Then the rate of change of $c(x, t)$ due to TTA is

$$v_{\text{TTA}}(x, t) = -\gamma\, c_0^2 \,(1 + \cos(1\,\xi))^2 \qquad (49)$$
$$= -\gamma\, c_0^2 \,(1 + 2 \cos(1\,\xi) + \cos^2(1\,\xi))$$
$$= -\gamma\, c_0^2 \left(\frac{3}{2} + 2 \cos(1\,\xi) + \frac{1}{2} \cos(2\,\xi) \right).$$

Fick's second law requires

$$\cos(2\,\xi)\, \mathrm{d}f_2(t)/\mathrm{d}t = -\frac{1}{2}\,\gamma\, c_0^2 \cos(2\,\xi) \qquad (50)$$
$$+ D\, f_2(t)\, d^2 \cos(2\,\xi)/\mathrm{d}x^2$$

or, with (24),

$$\mathrm{d}f_2(t)/\mathrm{d}t = -\frac{1}{2}\,\gamma\, c_0^2 - 4\,\delta f_2(t). \qquad (51)$$

Finally, with (47) the solution of (51) is

$$f_2(t) = -(\gamma\, c_0^2/8)(1 - e^{-4\delta t})$$
$$= -p\, c_0\, \frac{\beta}{8\,\delta}\,(1 - e^{-4\delta t}), \qquad (52)$$

and in the steady state

$$f_2 = -p\, c_0\,(\beta/8\,\delta). \qquad (53)$$

Moreover, since in the determination of diffusion coefficients usually the condition $\delta \geq 3\,\beta$ is fulfilled,

$$|f_2| = p\,c_0(\beta/8\,\delta) \leq p\,c_0(1/24) = p(1/24)f_1 . \quad (54)$$

(54) means that for practical purposes even $|f_2| \ll f_1$ holds if (15) is valid.

The systematic derivation of the correct approximate expressions for $f_0(t)$ and $f_1(t)$ in (44),

and thus of (26), is somewhat lengthy. However, the correctness of the approximation (26) is easily checked by insertion of (26) into (9): all terms $p^\mu \cos(\nu\,\xi)$ with $\mu + \nu \leq 2$ cancel; the only remaining term is

$$\frac{1}{2}\,\beta\,p\,c_0\,e^{-(2\beta+2\delta)t}\cos(2\,\xi) .$$

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