

Application of high-accuracy time-resolved laser spectroscopy to the study of diffusion-controlled triplet-triplet annihilation

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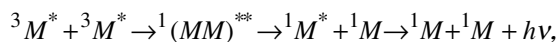
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The kinetics of the diffusion-controlled triplet-triplet annihilation of anthracene was investigated with the time-resolved laser spectroscopy. The analysis of the decays of delayed fluorescence with the standard Smoluchowski model leads to an artificial dependence of the annihilation radius from the delay (starting point of evaluation). The intuitive-empirical modification of the so-called short-time term in Smoluchowski equation (based on the treatment of the triplet-triplet annihilation as a non-Fickian diffusion) is proposed. A brief comparison is presented between standard Smoluchowski and modified models for anthracene. The limits of the approximation used are discussed and the way of further progress is suggested.

Keywords: laser spectroscopy, signal processing and mathematical modelling, non-Fickian diffusion, triplet-triplet annihilation (TTA).

1. Introduction

The triplet-triplet annihilation (TTA) [1] is observed as a p-type delayed fluorescence caused by the process



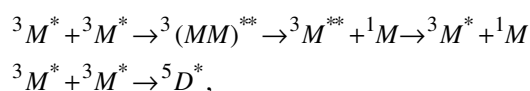
where ${}^3M^*$ indicates the molecule in the T_1 state, ${}^1M^*$ is the molecule in the S_1 state and 1M in the ground state, $h\nu$ indicates the energy of the emitted photon. The kinetics is described with a simple approximation (valid if the first order decay of molecules in the triplet state is dominant) for the decay of p-type delayed fluorescence

$$I_{DF}(t) = (C_0)^2 k_{2A}(t) e^{-2k_T t}, \quad (1)$$

where k_T is the first order decay constant of molecules in the T_1 state ($k_T = 1/\tau_T$), C_0 is the initial concentration of molecules in the T_1 state and $k_{2A}(t)$ is the rate parameter of the diffusion-controlled second order reaction. In a previous paper [2], the $k_{2A}(t)$ expression taken directly from the Smoluchowski model [3] was used. This kind of treatment makes the description of TTA relatively simple, but does not provide any deep insight into the process. It requires also the extremely unfavourable and difficult experimental

conditions for obtaining acceptable agreement between theory and experiment.

Let us first compare the most important simplifications of this description with other models. The first assumption concerns the probability of the contact reaction, in the Smoluchowski model it is 100% which means that molecules in contact react immediately. The Collins-Kimball (CK) model [4] allows the molecules which are in so-called contact pair to diffuse away before the reaction occurs, so the probability of the contact reaction in the CK model is below 100%. This type of behaviour has a minor influence on the description of a decay discussed in this work, because it should result in a constant factor multiplying the right side of Eq. (1). So, in the fitting procedure it is automatically included in the amplitude. A similar situation occurs also for other channels of TTA



where ${}^3M^{**}$ and ${}^5D^*$ denote the molecule in its higher triplet state and in the quintet state, respectively. The first channel should reduce the intensity of the delayed fluorescence without any influence on its time dependence [5] because it leads to homogeneous decrease in the molecules in the T_1 state. The lifetimes of the molecules ${}^3M^{**}$ which is converted to ${}^3M^*$ via internal conversion is negligible on the time scale of the diffusion controlled TTA. The encounter

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pairs $^1(MM)^{**}$ and $^3(MM)^{**}$ have too short lifetime to allow interconversion between spin states of different multiplicity [6]. The second one is generally not occurring in aromatic molecules, because the sum of the energies of two T_1 states is usually lower than the energy of a $^5D^*$ state [7].

The next simplification in the description of TTA is the use of a single parameter, the annihilation radius which describes the spatial feature of the reaction. The simplification results in the reduction of the rate equation for the local density $\rho(r,t)$ to the Fick's equation. The TTA process occurs via the exchange (Dexter) mechanism [8], so the reaction depends on the overlap of orbitals. More realistic models of TTA should take into account distance-dependent interactions (DDI). The basic idea of a model including DDI was introduced by Wilemski and Fixman [9]. The TTA can be regarded as a kind of energy transfer process. Butler and Piling discussed this type of reaction in terms of long- and short-range interactions [10]. They applied the original Fick's equation in the following way:

- the diffusion term in the Fick's equation was used to describe short-range interaction,
- the additional term was introduced to describe the long-range interaction. This term in Butler and Piling's treatment describes the distance-dependent features of the process.

In the case of Dexter mechanism the additional term, describing the overlap of molecular orbitals as a function of the distance r , has the form $A\exp(-Br)$, where A and B are the constant factors. Piling and Rice [11] examined the energy transfer for different values of diffusion coefficient. They showed that the Smoluchowski type of the formula for $k_{2A}(t \rightarrow \infty)$ is a good approximation only in a limited range of viscosity but, even in this case, the "real" radius of interaction must be replaced by an "effective" one. For the very high viscosities, long-range mechanism of the energy transfer can effectively compete with the diffusional energy transfer (short-range mechanism). So, the conditions for stationary diffusion cannot be established and the Smoluchowski type of expression for $k_{2A}(t)$ breaks down. The review of the models describing the kinetics of diffusion-controlled reactions was published by Noyes [12].

In this paper, the description of TTA process is limited to the simplest possible formalism, namely the complex spatial feature of interaction is reduced to an average distance representing the whole spectrum of distances with different overlaps of orbitals. We start from the Smoluchowski formula for the rate parameter for diffusion-controlled reactions. The modification takes into account the coexistence of the first order decay of T_1 and diffusion controlled TTA, namely the influence of the first order decay on the, so-called, short-time effect. In the text, the phrase "redistribution effect" will be used interchangeably with "short-time effect".

In order to make the discussion of the introduced change as simple as possible we do not discuss in details the, so-called, anti-Smoluchowski behaviour. This type of the kinetics results from the modified initial conditions

(taking into account the role of Förster type of energy transfer during the population of the molecules in the T_1 state) which were introduced in one of the previous papers [2]. The differences in the kinetics of TTA, caused by both types of initial conditions are important in the initial part of the decay only. One can avoid the detailed description of the, so-called, anti-Smoluchowski behaviour (the initial rise of the delayed fluorescence observed instead of a fast decay predicted for standard Smoluchowski model) [2], because it should not affect the introduced modification. In this work, the following terms will be used:

- Smoluchowski time range – for the time interval of a decay where the rate parameter $k_{2A}(t)$ has practically the same time dependence for both types of initial conditions,
- anti-Smoluchowski time range – for the part of a decay where the time dependence of $k_{2A}(t)$ resulting from the modified initial conditions is significantly different than that obtained for standard Smoluchowski initial conditions.

2. Description of the model

Although Smoluchowski's original work [3] was applied to the coagulation of colloids, it is widely used to describe the kinetics of diffusion-controlled reactions, e.g., fluorescence quenching [13]. In this treatment, the diffusion-controlled reaction, $A + A \rightarrow C$, is not associated with other channels of the decay of the reacting species. Smoluchowski analyzed evolution of the local density $\rho(r,t)$, (r is the distance from the selected particle and t is the time) from the initial state, $\rho(r,t=0)$, to the steady (stationary) state, $\rho(r,t \rightarrow \infty)$. Using the initial conditions describing the statistical distribution of the reacting particles at the initial time ($t=0$)

$$\begin{aligned} \rho(r,t=0) &= 0 & \text{for } r \leq R_A \\ \rho(r,t=0) &= \rho_0 & \text{for } r > R_A \end{aligned}$$

and the boundary condition describing the contact reaction (100% efficient trapping) occurring when the distance between reacting species equals R_A

$$\rho(R_A,t) = 0 \quad \text{for } t > 0.$$

Smoluchowski obtained his famous formula which can be expressed in terms of the rate parameter $k_{2A}(t)$

$$k_{2A}(t) = 4\pi R_A D_T \left(1 + \frac{R_A}{\sqrt{\pi D_T t}} \right), \quad (2)$$

where D_T is the relative diffusion coefficient of the species A. This rate parameter consists of two parts:

- the stationary part describing the diffusion in the steady state distribution of the particles represented by "1" in brackets,

- the non-stationary part describing a so-called short-time (redistribution) effect – represented by $R_A/(\pi D_T t)^{1/2}$ in parenthesis.

The assumptions made by Smoluchowski result in the asymptotic behaviour of the local density of the particles A

$$\rho(r, t \rightarrow \infty) = \rho_0 \left(1 - \frac{R_A}{r} \right) \xrightarrow{r \rightarrow \infty} \rho_0,$$

which means that the local concentration of the substrates remains practically unchanged for large distances from the selected particle.

In the experimental determination of the decay of a delayed fluorescence the time window t_w necessary to obtain a good fit should be at least equal to about $5(\tau_T/2)$. In this case the decrease in the concentration of molecules, due to the first order decay, is equal to $1/\exp(-2.5) \sim 10$ times. This results in different evolution of the local concentration of reacting molecules in comparison with a standard Smoluchowski behaviour (cf. Fig. 1), namely the evolution of local density is caused by two associated phenomena: first order decay and TTA. This kind of behaviour is known as a non-Fickian diffusion [14] and is investigated in polymer membranes [15,16], where two reactions: sorption and diffusion through the membrane are associated. If rate parameters of both processes are comparable, the coexistence of sorption and diffusion must be introduced into the description of the behaviour of the whole system. Although the non-Fickian diffusion plays an important role, e.g., in biology [17] or in medicine [18] no suitable model of this phenomenon was developed up to now [19]. The ki-

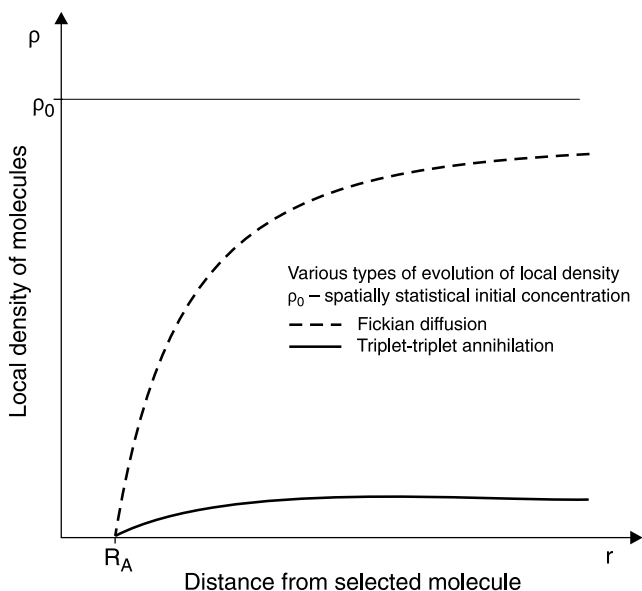


Fig. 1. Comparison of the local density as a function of distance: dashed line – Smoluchowski type distribution after $t = 2.5\tau_T$, solid line – TTA after $t = 2.5\tau_T$. The initial concentration of the particles $\rho(r, t = 0)$ equals 0 for $r \leq R_A$ and ρ_0 for $r \geq R_A$. The initial conditions: spatially random distribution of the particles are the same for both processes.

netics is described with the standard Fick's treatment supplemented with expressions describing the cooperative working of associated relaxation phenomena. For example: in the case of polymer membranes the diffusion coefficient is a function of concentration of penetrants, interaction among penetrants and and interaction between penetrants and membrane [15].

The TTA can be interpreted in terms of non-Fickian diffusion, because the delayed fluorescence results from two coexisting processes: first order decay of molecules in the triplet state and their diffusion-controlled annihilation. However, in this particular case the effects of coexistence of both processes are observed even if the first order decay is strongly dominant, because the p-type delayed fluorescence originates only from those molecules, which take part in the second order reaction. Thus, the phosphorescence containing the “direct information” about first order reaction is cut off.

The system in which TTA takes place, should be characterized by two types of concentrations: average $\rho(t)$, and local $\rho(r;t)$. A simplifying assumption, that the first order decay of molecules in the T_1 state is dominant, means that the description of the coexistence of the first and second order processes is reduced to “local effects”, namely, the first order process influences both types of concentrations $\rho(t)$ and $\rho(r;t)$, whereas TTA is introduced in the description of $\rho(r;t)$ only and has no influence on $\rho(t)$. This simplification results in the approximation of the evolution of the average concentration as described by a monoexponential function: $\rho(t) = \rho_0 \exp(-k_T t)$. The kinetics of TTA should be determined by diffusion of two molecules in the T_1 state which, in turn, is influenced by the evolution of the average concentration discussed above. The stationary part of the rate parameter (Eq. 2) will not be changed. The situation is different for the redistribution part of $k_{2A}(t)$. The term $(\pi D_T t)^{1/2}$ is proportional to the total amount of molecules which diffuse during the period from the initial instant ($t = 0$) to the actual instant ($t > 0$) due to the redistribution effect [3]. It means that the redistribution part of $k_{2A}(t)$ is inversely proportional to the total amount of molecules which diffuse from the beginning of the process to the actual moment t . This is consistent with an intuitive approach which suggests that the contribution of the non-stationary part to the total rate parameter $k_{2A}(t)$ should decrease in time in the same way as the amount of the molecules which can contribute to that (redistribution) effect. In the case of TTA the non-stationary part of the rate parameter must describe the coexistence of two processes:

- the spatial redistribution, as in Smoluchowski original model;
- the first order decay of the molecules in the T_1 state.

To sum up: the first order decay of molecules in the T_1 state should be represented in Eq. (1) not only as the term $\exp(-2k_T t)$, but also should include a correction of the redistribution part of $k_{2A}(t)$. The first order decay can be treated as independent from the redistribution process (dif-

fusion). In this case the total amount of molecules which can take part in non-stationary diffusion will decrease as described by the function $\exp(-k_T t)$, so the term $(\pi D_T t)^{1/2}$ in $k_{2A}(t)$ should be replaced by the product of $(\pi D_T t)^{1/2}$ and $\exp(-k_T t)$. Finally, the modified rate parameter should have the form

$$k_{2A}(t) = 4\pi R_A D_T \left(1 + \frac{R_A}{e^{-k_T t} \sqrt{\pi D_T t}} \right). \quad (3)$$

3. Experimental technique and data evaluation

3.1. Substances

Anthracene was purified by vacuum sublimation and subsequent zone-refining. Solvent mixture: *cis/trans*-dimethylcyclohexane (*c/t*-DMCH) was prepared as described earlier [20]. The solution was degassed by 15 freeze-pump-thaw cycles. The concentration of anthracene, about 2×10^{-5} M, was calculated from the absorption spectrum measured at room temperature.

3.2. Apparatus

The scheme of experimental the setup is presented in Fig. 2. An Ar⁺ laser (Spectraphysics, Model 2045) was used as an excitation source. The laser beam passed the chopper Ch1 (homemade, 50 Hz), and then the set of prisms BP, where $\lambda = 363.3$ nm (TEM 00) was selected. After leaving BP the laser pulses were reflected from mirrors M1 and M2 and passed through the chopper Ch2 (home-made, 5 Hz) which was synchronized in phase with Ch1. The second chopper reduced the number of pulses by a factor of 10, then the beam passed the blends B1 and B2, was reflected from mirror M3, passed two blends (B3 and B4), was reflected from mirrors M4 and M5 and was focused by the lens L1 onto the first disc of the fast chopper Ch3 (home-made, 1000 Hz). At the other side of the disc the beam was again collimated by the lens L2. The L1 to L2 ratio of focal lengths was 1:2 (100:200 mm). After passing the first disc of the fast chopper, the excitation pulse was prepared, its half width being 31 μ s. The excitation pulse was further reflected from the mirrors M6, M7 and M8 in order to reach a proper position to excite the solution in the cell from the side. The exciting beam was reflected from mirrors M12 and M13 back into the cell in order to increase the intensity of delayed fluorescence. The pathway (about 1.5 m) was much longer than the coherence length of the laser (about 50 mm). The light from the excited area of the cell was focused onto the second disc of the fast chopper by achromatic lenses L3 and L4. The image of the excited area was converted from horizontal to vertical direction by mirrors M10 and M11. Both discs of the fast chopper were adjusted to generate a break (dead time) between the end of the excitation pulse and the beginning of

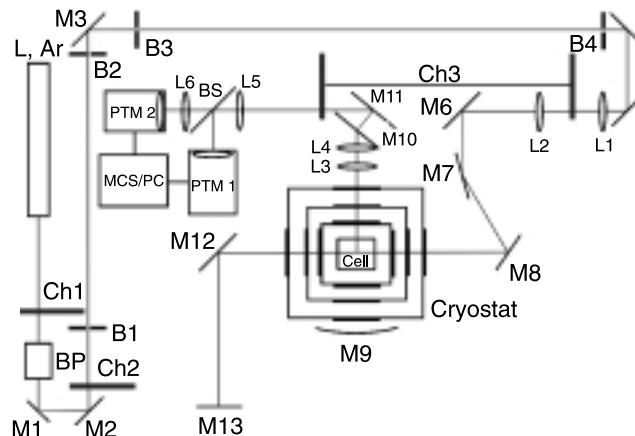


Fig. 2. Experimental set-up: L, Ar – laser Ar⁺, BP – Brewster prisms, B1÷B4 – blends, L1÷L6 – lenses, M1÷M13 – mirrors, Ch1, Ch2, Ch3 – choppers, BS – beam splitter, PTM1 and PTM2 – photomultipliers, and MCS/PC- multichannel scaler/computer.

the measurement of the emission. The aim was to remove the prompt fluorescence of the compound under study. The dead time was about 2 μ s, two orders of magnitude larger than the lifetime of the prompt fluorescence. After passing the second disc of Ch3 the emission was divided into two beams by a beam splitter BS. In order to obtain optimal conditions for the splitting of the emission, BS was placed inside of the set of achromatic lenses L5 and L6. The decay time of phosphorescence was measured on a PTM1 photomultiplier (Hamamatsu, R1464); the decay of the delayed fluorescence was measured on a PTM2 photomultiplier (Hamamatsu, 9125 A). The spectral ranges were selected by filters. In the case of phosphorescence, the cut-off filter F1 (RG655, 2 mm) was used. The delayed fluorescence was selected by an interference filter F2 with the maximum of the transmission at 317 nm and a halfwidth of 17 nm (AHF analysentechnik, D 377/17). The signals from both photomultipliers were registered on a multichannel analyzer (7882, Dual Input Multiscaler/TOF/Photon Counter, FAST ComTech GmbH) controlled by a PC computer. The mirror M9 was used to increase the measured signal.

Delayed fluorescence and phosphorescence decays were measured in parallel in order to get the kinetic parameters from both emissions under the same experimental conditions.

3.3. Evaluation procedure

There are two important moments in each decay:

- The first one is the “end” of the anti-Smoluchowski time range (see Fig. 3).
- A final instant of the so-called short-time effect. It means that for longer times the decay of the delayed fluorescence goes mainly via the stationary part, and can be satisfactorily approximated by the monoexponential function only (see Fig. 3).

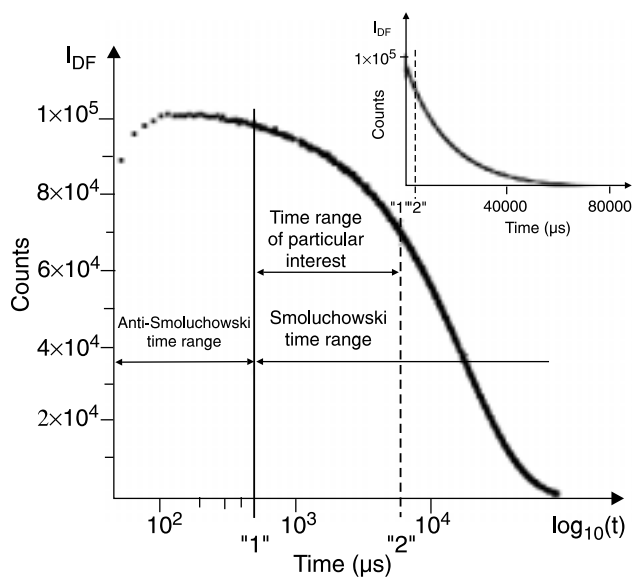


Fig. 3. Schematic representation of the important instants of a decay: “1” – the “end” of the anti-Smoluchowski time range, “2” – the final instant of the short-time effect. The time is represented in logarithmic scale in order to expand the initial part of the decay, illustrating important time ranges. In the insert, time is plotted in linear scale.

The main attention of this work is focused on the part of a decay between the “end” of the anti-Smoluchowski time range and the final instant of, so-called, short-time effect (see Fig. 3).

Three types of curves were fitted to the measured decays of the delayed fluorescence:

monoexponential

$$I_{DF}(t) = P_1 e^{-t/P_3}, \quad (4)$$

standard-Smoluchowski

$$I_{DF}^S(t) = P_1 \left(1 + \frac{P_2}{\sqrt{t}} \right) e^{-t/P_3}, \quad (5)$$

and the modified model

$$I_{DF}^M(t) = P_1 \left(1 + \frac{P_2}{e^{-k_T t} \sqrt{t}} \right) e^{-t/P_3}. \quad (6)$$

P_1 , P_2 and P_3 are the fitting parameters.

The phosphorescence decays were analyzed assuming a monoexponential function in order to obtain the first order decay rate constant k_T . This value was used in $I_{DF}^M(t)$ [k_T in the denominator of the second component in brackets Eq. (6)].

The points from the beginning of the measured curve of delayed fluorescence were systematically cut off with the step of 10 points. This procedure was applied to the function described in Eq. (4) in order to find the final instant of the short-time effect. Generally, after 5–8 ms, the monoexponential fit describes the decay satisfactorily. For Eqs. (5) and (6), the same procedure as for Eq. (4) was applied in order to find the final instant of the anti-Smoluchowski time range.

The annihilation radius R_A was calculated from the P_2 parameter [$R_A = P_2(\pi D_T)^{1/2}$]. The diffusion coefficients of anthracene in hexane and methylcyclohexane were taken from literature [21] and extrapolated to our experimental conditions, using Stokes-Einstein-type equation and the measured viscosities of the cis/trans-DMCH solvent mixture. The viscosities of cis/trans-DMCH were measured with a home-built viscosimeter described previously [22] (in the temperature range 132–150 K the viscosity changes over three orders of magnitude, from 1068 mPas to 105639 mPas). The values of the first order rate constant calculated from the delayed fluorescence, k_T^{df} , [$k_T^{df} = 2/P_3$, cf. Eqs. (5) and (6)] were compared with those obtained from phosphorescence decay, k_T .

4. Results and discussion

Figure 4 presents the annihilation radius R_A and first order rate constants k_T^{df} and k_T obtained for the decay at 146 K as a function of the starting point of evaluation, t_0 . For both models (standard Smoluchowski and the modified one) the symptoms of anti-Smoluchowski behaviour in the region up to about 500 μ s after excitation are observed. The annihilation radius R_A [Fig. 4(a)] increases from the value of about 0.6 nm to about 0.88 nm.

For larger t_0 , the differences in both models become significant. In the standard Smoluchowski model the annihilation radius further grows up with the time of starting point (t_0) and reaches the value of about 1.2 nm. In the case of modified model the R_A values are placed around 0.9 nm and, for t_0 between 1 ms and 8 ms, R_A can be treated as nearly constant or even has a weak tendency to decrease with the increase in t_0 . One should notice the increase in the experimental error (ΔR_A) with the increase in the time of starting point. This behaviour is a result of the decrease in the contribution of the redistribution effect to the total decay.

The differences between the values of the first order rate constant calculated from different models of TTA and from phosphorescence decay are very small in comparison with absolute values (not larger than 0.4%). The ordinate in Fig. 4(b) is expanded in the range between 29.33 s^{-1} and 29.51 s^{-1} in order to distinctly show the differences. The behaviour of k_T^{df} in the anti-Smoluchowski time range corresponds to that of R_A . It means: the fast decrease in k_T^{df} with increasing delay of the starting point of evaluation is observed for both models in the time range up to 500 μ s. In the Smoluchowski time range the values of the rate constant k_T^{df} calculated from Eq. (5) slowly decrease with the increase of t_0 and for starting point greater than 5 ms tend to values smaller than k_T . The values of k_T^{df} obtained from standard Smoluchowski model are almost equal to that of k_T . In the modified model k_T^{df} reaches, for the Smoluchowski time range, a plateau which is placed slightly above the k_T (about 0.4%). This plateau can be treated as exactly constant within an experimental error which is very small $\sim 0.02\%$. The difference between val-

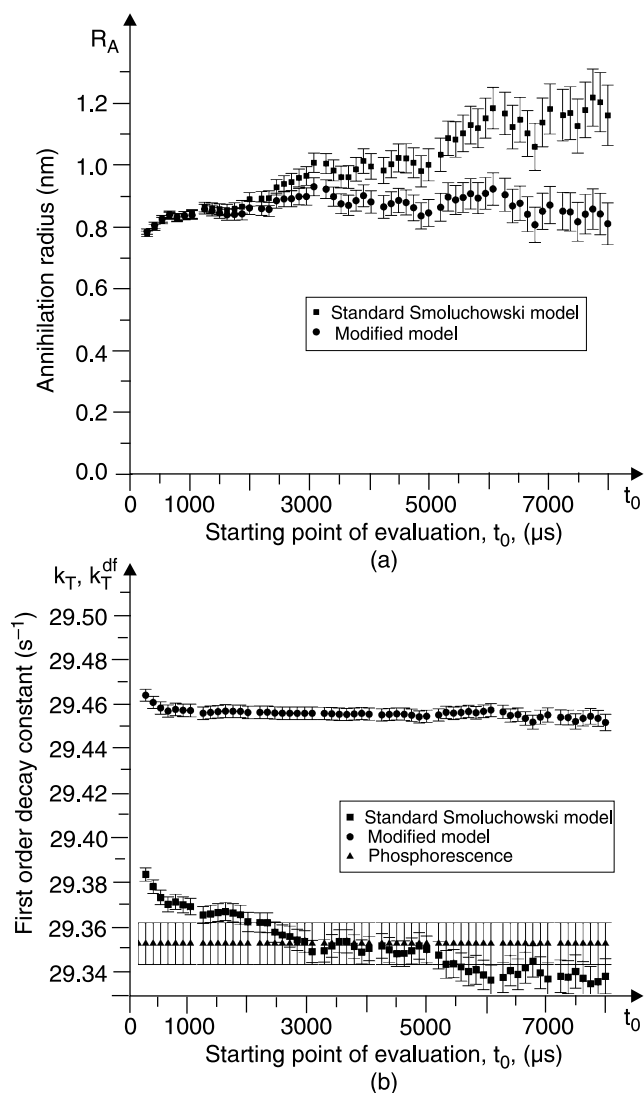


Fig. 4. Results of fits obtained for different starting points of the evaluation with the standard Smoluchowski model and the modified model. Upper part (a) presents the changes of the annihilation radius R_A , the lower one (b) the first order rate constant k_T^{df} . The first order rate constant obtained from a monoexponential fit of phosphorescence decay (k_T) is also shown in part (b).

ues of the first order rate constant obtained from the modified model of TTA and the phosphorescence decay is caused by the simplified description of TTA and will be discussed below.

In Fig. 5, there is presented the annihilation radius R_A , calculated from the modified model, as a function of the temperature. In the temperature range 132–136 K a slight increase in the annihilation radius with increase in temperature can be observed. Above 136 K R_A can be treated as nearly constant, its value varies from 0.8 nm to 0.9 nm. The dimensions of an ellipsoidal Onsager cavity estimated from crystallographic data [23], contact radii of hydrogen and carbon atoms [24] with an empirical addition of 0.04 nm [25] are $a_x = 0.60$ nm, $a_y = 0.39$ nm, and $a_z = 0.22$ nm. The average value $r_0 = (a_x a_y a_z)^{1/3}$

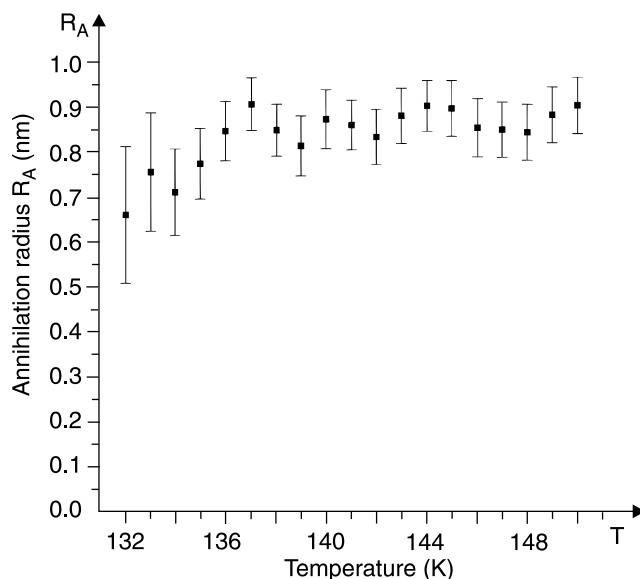


Fig. 5. The temperature dependence of the annihilation radius obtained from the modified model with application of the extrapolated diffusion coefficients.

equals 0.37 nm. The values of the average radius calculated from semi-axes of the Onsager cavity used in solvatochromic study of aminoanthracenes [26] vary from 0.34 nm to 0.37 nm. The contact radius of anthracene was estimated to be placed between 0.34 nm and 0.39 nm [27]. The annihilation radius R_A should be compared with the double radius of Onsager spherical cavity. The values of R_A obtained from the function described in Eq. (6) are slightly larger than the corresponding value calculated from the parameters reported in literature, 0.8–0.9 nm vs. 0.68–0.78 nm.

The comparison of temperature dependence of the first order rate constants, k_T^{df} (calculated from the modified model) and k_T is presented in Fig. 6. Similar to Fig. 4(b), the ordinate is expanded (the range between 28.7 s^{-1} and 29.7 s^{-1} is presented) in order to show the small differences between k_T^{df} and k_T . The first order rate constant obtained from phosphorescence decay decreases with temperature in the whole investigated range. In contrast, the temperature dependence of the first order decay calculated from delayed fluorescence, k_T^{df} is more complicated. It decreases with the decrease in temperature in the range 150–141 K, then it is almost constant down to 138 K and slightly increases with further decrease in temperature down to 132 K. The values of k_T^{df} are slightly larger in comparison with those of k_T in the whole investigated temperature range (see Fig. 6).

The comparison of the first order rate constants k_T and k_T^{df} shows that two problems must be discussed: very small but systematic difference between the values obtained from delayed fluorescence and phosphorescence in the temperature range 141–150 K and the strange behaviour of k_T^{df} in the temperature range 132–138 K, where k_T^{df} increases with cooling.

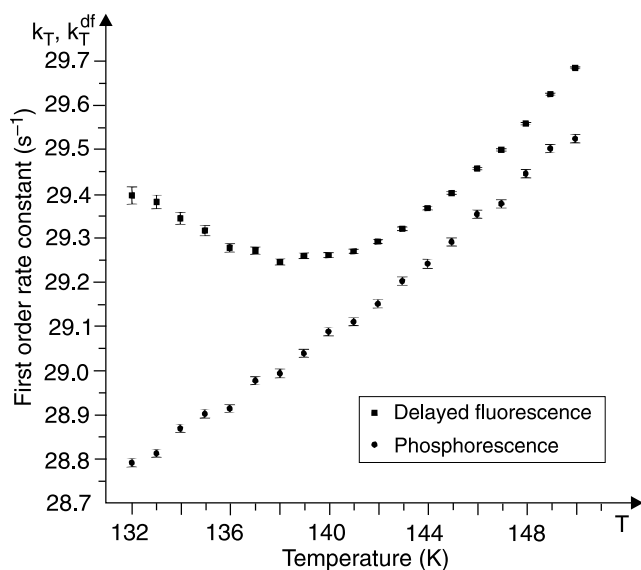


Fig. 6. The temperature dependence of the first order decay constant measured directly from phosphorescence (monoexponential function), and from delayed fluorescence (modified model).

The possible explanation of the temperature dependence of k_T^{df} in the temperature range 132–138 K can be the breaking down of Smoluchowski type of description at high viscosities. Butler and Pilling compared the numerical solution of the equation for diffusion accompanied by Dexter [28] or Förster [29] type of energy transfer with analytical approximate solutions like Smoluchowski expression (Eq. 2). The conclusion can be summarized as follows: if the diffusion coefficient is large enough, the Smoluchowski type formula provides a good approximation of the rate parameter $k_{2A}(t)$. However, for diffusion coefficient below a so-called critical value (at high viscosities) the reasonable description of the kinetics of such systems in the intermediate time range must be done by numerical solution of the rate equation including both: short- and long-range interaction (cf. comparison of DDI and the Smoluchowski treatment in the introduction) although for long times the conditions for stationary diffusion could be established. Since the Dexter type of interaction is effective at shorter distances than the Förster type energy transfer, the critical diffusion coefficient in processes like TTA should be smaller. This nonapplicability of the Smoluchowski treatment can result in small deviations of the behaviour of kinetic parameters (obtained from the Smoluchowski type of treatment) from the expected temperature dependencies, as observed for R_A or k_T^{df} in the temperature range 132–138 K, due to high accuracy of the measurements. Since no evidence for microcrystals formation was observed even under extreme experimental conditions: the solution was cooled down for time longer than 20 hours, the abnormal temperature dependence of R_A and k_T^{df} cannot be associated with simple experimental artifacts.

In the intermediate temperature range, namely 138–141 K, the tendency to the abnormal temperature dependence of R_A and k_T^{df} can be treated as ambiguous.

The comparison of k_i and k_T^{df} in the temperature range between 141–150 K shows that the evaluation procedure introduces a very small but systematic difference between them. The weak point of the model seems to be the assumption that the first order decay is dominant. This approximation results in the description of both, the phosphorescence and delayed fluorescence with monoexponential functions. If the precision of the measurement is high enough, the contribution of the second order decay of triplet states to the total decay can be no longer treated as negligible in the rate equation for the average density. In such a case both processes (first and second order reactions) must contribute to the model describing the decay of average density of molecules in the triplet state [30]. In turn, the intensity of the delayed fluorescence in diffusion controlled TTA should be no longer proportional to $\exp(-2kt)$.

The discussion of the model extended to non-monoexponential decay of molecules in the T_1 state will be the subject of a separate paper.

5. Conclusions

Finally, let us state that, the proposed correction of the short time effect removes the artificial growing up of the annihilation radius with the starting point of evaluation obtained with the use of the standard Smoluchowski model. The values of k_T^{df} calculated from the modified model are slightly larger than those of k_T in the whole temperature range where Smoluchowski-type of treatment is applicable. This small but systematic shift can reflect the fact that the influence of both processes on the system under study cannot be precisely described by monoexponential decay.

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