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The unusual temperature dependence of the fluorescence intensity and lifetime of anthracene in ethanol

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Abstract

Anthracene in ethanol shows an unusual temperature dependence of the fluorescence quantum yield and lifetime: both fluorescence parameters pass through a maximum at approx. 180 K but they follow the usual Arrhenius kinetic when anthracene is dissolved in 2-methylpentane or other hydrocarbons. In literature, several models of explanation have been presented but no decision has been made which may be the right one. We present new data about the temperature-dependent fluorescence properties and T_1 population of anthracene in ethanol. On the basis of these data, we conclude that a modified kinetic scheme with a deactivating channel via an exciplex between excited anthracene and ethanol rationalizes the findings best.

Keywords: Anthracene; Fluorescence; Fluorescence quantum yield; Lifetime; Solvent effects; Temperature dependence; Triplet population

1. Introduction

The normal temperature dependence of fluorescence of anthracene derivatives in ethanol shows an increasing fluorescence intensity and lifetime when the temperature is lowered. For example, for meso-anthracenes the fluorescence quantum yields and fluorescence lifetimes vs. temperature follow an s-shaped dependence and reach a constant value at low temperatures. This constitutes Arrhenius behavior. Arrhenius parameters have often been used in locating the position of excited energy levels [1–11]. Surprisingly, the parent substance anthracene shows an unusual temperature dependence of the fluorescence intensity in various solvents.

Bowen [1] who was the first to investigate the temperature dependence of the fluorescence intensity of anthracene and derivatives found negative and positive temperature coefficients in different solvents between +70 and −70°C. He proposed a kinetic scheme (see Scheme 1) in which a complex (A*...S) between excited anthracene (A*) and a solvent molecule (S) is formed which requires an activation energy on dissociation (E_2). This type of excited complex was later termed "exciplex". In a purely formal manner (no values for the activation energies, no spectral evidence for the existence of excited anthracene–solvent complexes), Bowen showed that with the assumption of two further processes which need an activation energy, namely the intersystem crossings of excited anthracene (E_d) and excited anthracene–solvent complex (E_3), the overall temperature dependence of the fluorescence intensity could lead to maxima or minima depending on the values of E_2 and E_3 (maximum if $E_2 > E_3$, minimum if $E_2 < E_3$). The parent anthracene in ethanol as a solvent is a special case. Bowen found a normal temperature dependence of the fluorescence intensity Φ_F in this solvent between +30 and −50°C which he could describe by $(1/\Phi_F - 1) = 11 \exp(-890\,\text{cal mol}^{-1}/RT)$.

But when Pantke and Labhart [12] and at the same time Bräuchle [13] extended their measurements of the fluorescence quantum yield of anthracene in ethanol to lower temperatures they found that the fluorescence quantum yield increases in this solvent from 0.28 at room temperature to a maximum value of 0.37 at −93°C (180 K) and decreases to 0.33 at −153°C (120 K). This is in sharp contrast to the fluorescence quantum yield of anthracene in 2-methylpentane and in other alkanes where the yield increases in an s-shaped dependence from 0.30 at room temperature to a constant value (0.53 at 130 K in 2-methylpentane), thus showing Arrhenius type behavior.

Pantke and Labhart explained this strange behavior of anthracene in ethanol with a constant activation energy E_0 but with energy-dependent S_1–T_n transition probabilities, $w(E)$. Whereas they take in the systems exhibiting Arrhenius behavior the transition probability as $w(E) = 0$ below the E_0 threshold and $w(E) = A$ for $E > E_0$ they introduce an additional transition probability at low energies for anthracene in ethanol. With $w(E) = \frac{1}{2}A$ for $E < 0.85E_0$, $w(E) = 0$ for $0.85E_0 < E < E_0$ and $w(E) = A$ for $E > E_0$, and

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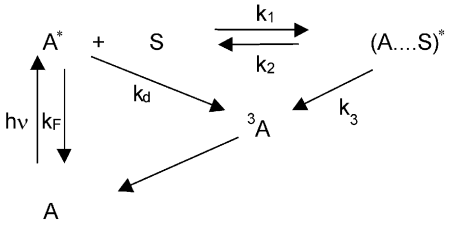

Scheme 1.

with $A = 2.14 \times 10^8\,s^{-1}$ and $E_0 = 27\,kcal\,mol^{-1}$, Pantke and Labhart can simulate a maximum curve. No physical evidence or concept for this low energy ISC probability is given.

Bräuchle assumed that the triplet terms shift against the singlet terms when the temperature is lowered which should result in temperature-dependent activation energies. He proposed two models: (1) a lowering of the activation energy for the $S_1 \rightarrow T_1$ process and an increasing activation energy for the $S_1 \rightarrow T_2$ process with decreasing temperature and (2) a constant activation energy for the ISC process between room temperature and 200 K, and between 200 and 100 K a lowering of the activation energy to half of its value at 200 K.

Tanaka and Osugi [14] explained the strange solvent and temperature dependence of the fluorescence of anthracene by the fact that the energy gap between S_1 and T_2 is in the order of vibrational quanta. In systems with small energy gaps the density of states in the final state is small and thus the vibrational overlap (Franck-Condon factors) is sensitive to the energy difference of initial and final states. Thus, depending on the value of the gap between S_1 and T_2 at room temperature the lowering of the temperature and S_1 energy could result first in decreasing then increasing (maximum in Φ_F) or always decreasing FC factors (Φ_F increases steadily).

We recognize that four models have been proposed: (i) the exciplex model by Bowen, (ii) a model assuming constant activation energies but additional transition probability at low energy (Pantke/Labhart), (iii) a model assuming an energy gap variation leading to temperature-dependent activation energies (Bräuchle) and (iv) a model assuming an energy gap variation leading to changes in the FC factors (Tanaka/Osugi). We may add a fifth explanation: at room temperature the weakly absorbing ^1L_b-state lies approx. $1100\,cm^{-1}$ above the strongly absorbing ^1L_a-state [15]. Newer vibrational resolved two-photon spectroscopy places the ^1L_b-state of the free anthracene molecule only $350\,cm^{-1}$ above the ^1L_a-state [16,17]. A maximum in the fluorescence quantum efficiency vs. temperature could thus be explained if the ^1L_b-state shifts at low temperatures below the ^1L_a-state. This term inversion should result in different natural fluorescence lifetimes at high and low temperatures.

It is obvious that the attempts of Pantke/Labhart, Bräuchle and Tanaka/Osugi to explain the unusual temperature dependence of the fluorescence intensity of anthracene in ethanol are based on pure simulation parameters and, if right, should be supported by the specific molecular properties of anthracene and ethanol: The transition probabilities $w(E)$ and the threshold energy value E_0 (Pantke/Labhart model) should be a characteristic feature of the vibrational levels of the S_1 term of anthracene in ethanol and the shift of S_1 with temperature (Bräuchle model) should be visible in the UV spectra.

As Pantke/Labhart, Bräuchle and Tanaka/Osugi assume that only fluorescence and intersystem crossing are active as deactivation channels, whereas Bowen suggests an additional radiationless deactivation channel via the excited anthracene/solvent complex, one should be able to discriminate between the models by measuring the triplet population vs. temperature. A maximum value of the fluorescence quantum yield should be accompanied by a minimum of the triplet population at the same temperature if the Pantke/Labhart, Bräuchle and Tanaka/Osugi models are right, but not, if Bowen's model is right.

In order to clarify this situation we decided to measure (i) the shift of absorbance and fluorescence bands (test of term shifts), (ii) the fluorescence lifetimes (test of term inversion) and (iii) the population of the T_1-state of anthracene in ethanol down to very low temperatures.

2. Materials and methods

2.1. Materials

Anthracene (99.9%) from Aldrich and anthracene-d_{10} from Merck were used as received. Zone-melted anthracene gave identical results. Spectroscopic grade solvents (Aldrich, Fluka or Merck Uvasol) were used as received. Triacetin (glyceroltriacetate) from Aldrich was refluxed in acetanhydrid before use in order to esterificate the remaining free OH groups and subsequently distilled at low pressure.

Anthracene solutions ranged from 2×10^{-6} to $4 \times 10^{-6}\,mol\,l^{-1}$ and were degassed by at least five freeze–pump–thaw cycles. A cryocooler (Cryophysics Model 21) or a CryoVac liquid nitrogen cryostat allowed to adjust constant temperatures (±1 K) which were determined by a gold–iron thermocouple which was placed in a thin glass tube in the solutions or by a Pt-100 resistance.

2.2. Spectroscopic measurements

Absorption spectra at room temperature were recorded with a Zeiss (DMR 10) spectrophotometer. Absorption spectra at low temperatures were registered with a Beckman (M VI) spectrophotometer with an attached low temperature unit (CTC 250).

For the determination of fluorescence spectra a fluorimeter of Farrand (type MK1) was used which was modified to accept for low temperature fluorescence spectra the head of the Cryophysics cryocooler. The fluorescence was detected at right angles at 420 nm.

The fluorescence lifetimes were determined with the time correlated single photon counting (SPC) technique. A

N_2-filled thyratron gated flashlamp (Edinburgh instruments model 199F, half-width ca. 3 ns) in combination with the optical unit of the model 5000U of IBH was used to excite the solutions at 337 nm. The lamp profile was sampled by scattering the lamp with an aqueous solution of LUDOX at room temperature and taken to be the same for all temperatures. Analysis of the data was performed with the reconvolution software of IBH and the quality of fit for a monoexponential decay was checked by the reduced χ^2-values which were below 1.2 in the temperature range between room temperature and 130 K but increased steadily at lower temperatures (e.g. 1.8 at 110 K) and fits for biexponential decays became possible with slightly smaller χ^2-values. A biexponential decay can be caused by exciplex kinetics (see Section 5). However, the increased density of the frozen medium causes scattering of the exciting light pulse. This also may lead to a biexponential decay with a τ_1 value comparable to the τ of the flashlamp.

For excitation of anthracene in triplet–triplet transient absorption measurements we used the radiation at 337 nm (half-width: ca. 7 ns; pulse energy: approx. 9 mJ) of an excimer laser (Lambda-Physics EMG 500) filled with a He/N_2-mixture. The light source for the detection of the T_1–T_n absorption of anthracene (detection light) was a pulsed (discharge of capacitors of an Applied Photophysics module model 411) Xe lamp (Hanovia 250 W). Unfortunately, the anthracene fluorescence and the T_1–T_n absorption occur in the same wavelength range. Although great care was applied in order to separate the radiation of the two sources it was not possible to measure the transient absorption within the first microsecond after the laser flash. An estimation of the possible loss of triplet concentration during the first microsecond can be made by analyzing the following processes:

1. Deactivation of T_1 molecules by ground-state anthracene via a triplet-excimer $^3(AA)^*$.
2. Deactivation of T_1 molecules by triplet–triplet annihilation.
3. O_2 is a very effective quencher of triplet molecules.

A detailed analysis of these processes shows that they can decrease the initial triplet concentration by not more than 1%. Thus, T_1 concentrations were determined from the transient absorbance ca. 1 μs after the laser flash. Due to the constancy of the absorbance at the exciting wavelength of 337 nm (see Fig. 1), it is not necessary to apply a temperature-dependent density correction to the triplet–triplet absorbancies.

3. Results

3.1. Temperature dependence of absorption and fluorescence spectra

Fig. 1 shows the absorption spectra of anthracene in ethanol at different temperatures. The vibrational maxima shift to longer wavelengths at lower temperature. At 337 nm the absorbance is nearly constant, a consequence of the compensating effects of the increase of the density of ethanol and the shift of the absorption when the temperature is lowered. The fluorescence maxima also shift to longer wavelengths at lower temperature but to a lesser degree than the absorption maxima (Fig. 2).

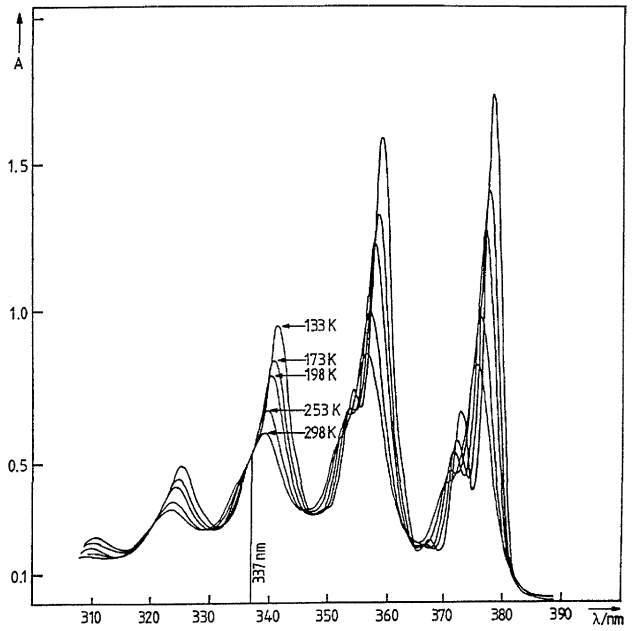

Fig. 1. Absorption spectra of anthracene in ethanol (10^{-5} mol l^{-1}) at different temperatures.

3.2. Fluorescence lifetimes of anthracene in hydrocarbons and alcohols

Fig. 3 shows the experimental fluorescence lifetimes τ_F of anthracene in 2-methylpentane which we determined by SPC as monoexponential decays, and the fluorescence quan-

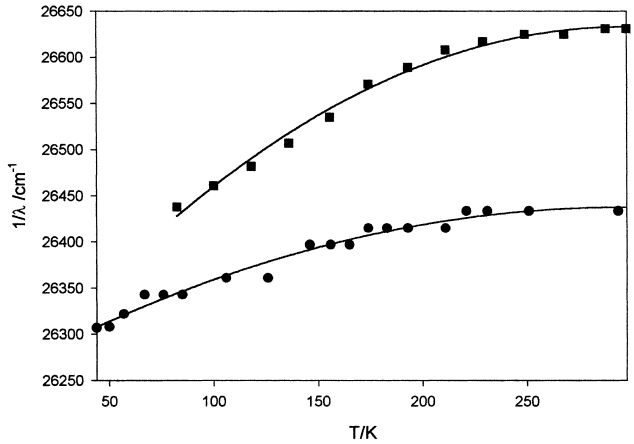

Fig. 2. Wavelength shift of the absorption bands (■) and fluorescence bands (●) of anthracene in ethanol vs. temperature.

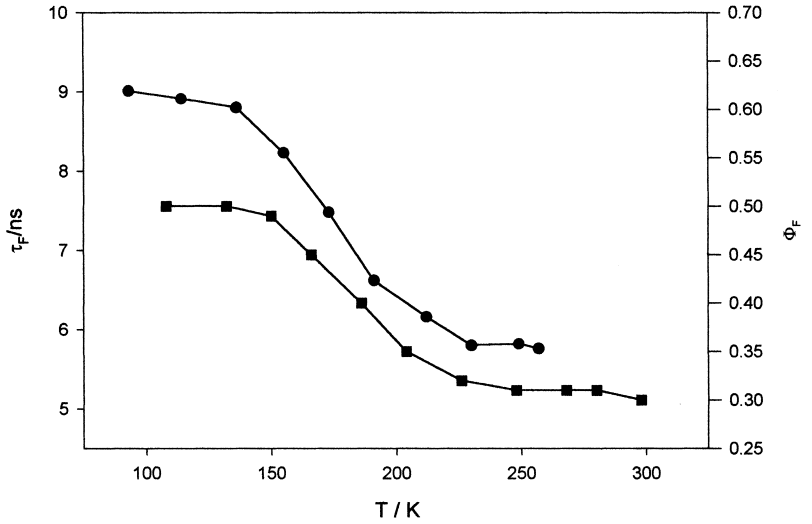

Fig. 3. Fluorescence quantum yields Φ_F (■) [12] and fluorescence lifetimes τ_F (●) of anthracene in 2-methylpentane vs. temperature.

tum efficiencies Φ_F measured by Pantke and Labhart [12] in 2-methylpentane at different temperatures. The s-shaped graphs are parallel and we call this the normal behavior which is also observed in methylcyclohexane/isopentane (1:3 (v/v)).

In Fig. 4, the same fluorescence parameters of anthracene (Φ_F from Pantke and Labhart or Bräuchle) are shown for anthracene in ethanol (max. 5 vol.% water). Also in this solvent the variation in τ_F with temperature parallels the temperature dependence of Φ_F and both parameters pass through a maximum at approx. 180 K. Addition of water (10 vol.%) to ethanol yielded a maximum of τ of 6.5 ns at 190 K.

To study the intensively discussed influence of the refractive index on the fluorescence lifetimes [18–24] we multiplied the τ-values by (n_T^2/n_{298}^2), where n_T is the refractive index at temperature T and n_{298} at 298 K. This correction leads to higher τ_F-values but the maximum in τ_F still exists.

A strong increase of the viscosity of ethanol begins at the temperature of the maximum of the fluorescence lifetime and one may suspect an interdependence. Therefore, we investigated this possible influence by measuring τ_F in triacetin (glyceroltriacetate) which has a strong increase of the viscosity at ca. -20°C (Fig. 5) and forms a glass. But Fig. 5 reveals no maximum at the glass point of triacetin. So the fluorescence feature is no viscosity effect.

This strange behavior seems to appear only in alcohols. As we need solvents which transform to glasses at low temperatures (rigid solvents) we could not use methanol. However, propanol-1 is a suitable solvent. In Fig. 5, the fluorescence lifetimes vs. temperature of anthracene in propanol-1 are included and they also pass through a maximum (6.3 ns at 190 K). τ_F of anthracene-d_{10} in ethanol passes through a very flat maximum of $\tau = 5.8$ ns at ca. 220 K.

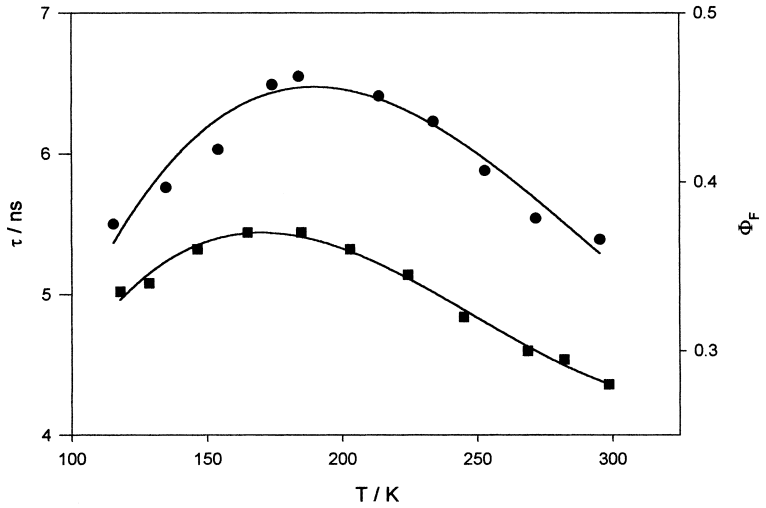

Fig. 4. Fluorescence quantum yields Φ_F (■) [12,13] and fluorescence lifetimes τ (●) of anthracene in ethanol vs. temperature.

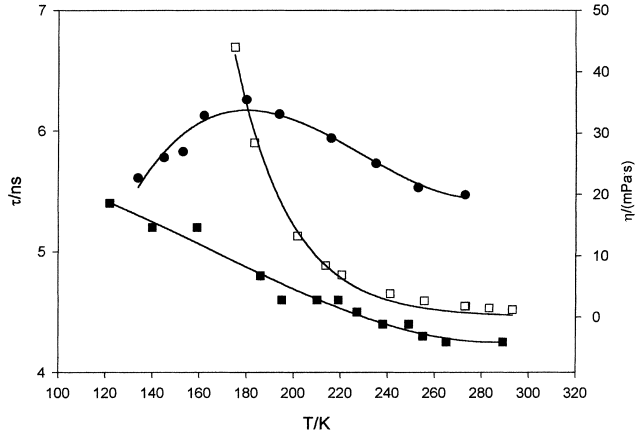

Fig. 5. Fluorescence lifetimes τ of anthracene in triacetin (■) and in propanol-1 (●) vs. temperature; (□) viscosity of triacetin vs. temperature.

3.3. Fluorescence lifetimes of anthracene in mixtures of 2-methylpentane and ethanol

So far τ_F of anthracene vs. temperature shows a maximum in ethanol but not in 2-methylpentane. What is the effect of mixing these solvents? We determined τ_F of anthracene in three different mixtures of 2-methylpentane and ethanol with mole fractions $x_{ethanol}$ (see Fig. 6) of 0.57, 0.63 and 0.70. It is obvious that the maximum of τ_F shifts to higher temperatures and becomes flatter when the amount of ethanol is increased.

3.4. Triplet–triplet absorption of anthracene in ethanol vs. temperature

When, on cooling, we measured the T_1–T_n absorbance of anthracene in ethanol at single wavelengths (6.4 nm bandwidth) we found either a constant increase of absorbance

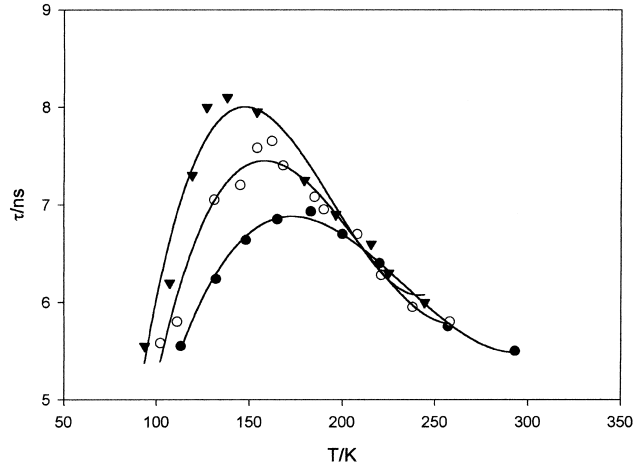

Fig. 6. Fluorescence lifetimes τ_F of anthracene in mixtures of ethanol and 2-methylpentane vs. temperature at different mole fractions x of ethanol: (▼) $x_{ethanol} = 0.57$; (○) $x_{ethanol} = 0.63$; (●) $x_{ethanol} = 0.70$.

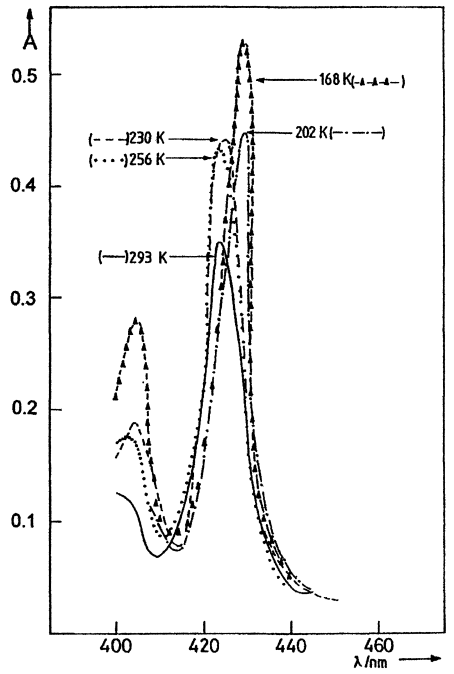

Fig. 7. Triplet–triplet absorption spectra of anthracene in ethanol vs. temperature.

(at 428 nm) or first an increase and then a decrease with a maximum at 260 K (at 420 nm) or with a maximum at 200 K (at 432 nm). The reason for this strange temperature dependence became clear when we measured the T_1–T_n spectrum between 400 and 450 nm at several temperatures (Fig. 7).

It is obvious that at lowering the temperature the bands shift to longer wavelengths and the width decreases which leads to a strong increase of ε_{max} and dependent on wavelength, an increase or decrease of ε_λ. Therefore, single wavelength measurements are deceptive and we determined the areas under the spectra representing as relative-state population or Φ_{ISC}. These areas relative to room temperature are depicted in Fig. 8 together with the calculated temperature

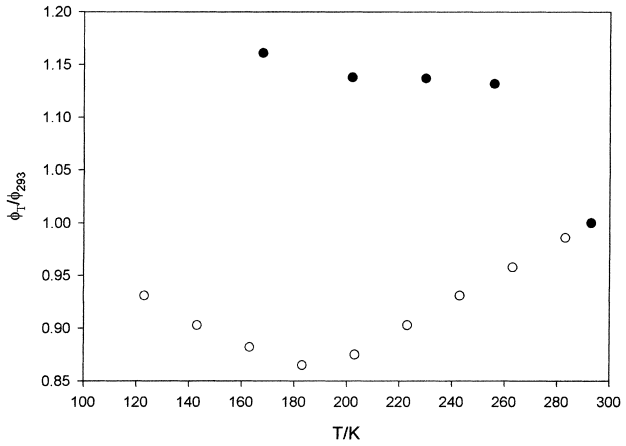

Fig. 8. Triplet–triplet absorption of anthracene in ethanol vs. temperature: (●) experimental values relative to room temperature; (○) $(1 - \Phi_F(T))/\Phi_{293}$) vs. temperature ($\Phi_F$-values from Pantke/Labhart).

dependence of the triplet population assuming $\Phi_F + \Phi_{ISC} = 1$ and using the Φ_F-values of Pantke and Labhart. The discrepancy is evident.

4. Discussion

4.1. Temperature-dependent term positions

The energy gap between S_1 and T_2 of anthracene lies between 650 and 800 cm^{-1} [25–27] at room temperature. The temperature-dependent shifts of the absorbance and fluorescence maxima are much smaller (at most 150 cm^{-1} between 298 and 80 K, Fig. 2). Thus, it is very unlikely that in the relevant temperature region the S_1-state falls below the T_2-state.

4.2. Fluorescence lifetimes

4.2.1. Radiative lifetimes of anthracene in ethanol

The radiative lifetimes calculated by $\tau_r = \tau_F/\Phi_F$ of anthracene in ethanol using our experimental τ_F-values and the Φ_F-values determined by Pantke and Labhart (see Fig. 3) lie between 18.9 and 20.7 ns, after correction with the square of the refractive index between 20.5 and 22.2 ns. The variation is within the error of ±2 ns, the sum of the individual errors of the quantum efficiencies and lifetime measurements. This means that a term inversion between ^1L_b and ^1L_a does not take place. A term inversion should result in a great change of the τ_r-values because the two states have very different transition moments. There is another argument against a term inversion: no new band is visible at the long wavelength side of the low temperature absorption spectra (see Fig. 1).

4.2.2. Fluorescence lifetimes of anthracene-d_{10} in ethanol

In general, the fluorescence lifetimes become longer on deuteration of a fluorescing molecule as the FC factors of the radiationless internal conversion (IC) become less favorable. The smaller lifetimes of anthracene-d_{10} in solutions in ethanol and the maximum at higher temperature compared to anthracene-h_{10} demonstrates an inverse deuterium effect [27]. The rate of intersystem crossing is greater in anthracene-d_{10} than in anthracene-h_{10} because the Franck-Condon vibrational overlap between states in S_1 and T_2 is larger for the per-deuterated compound. This finding is in favor of the Tanaka/Osugi [14] model.

4.2.3. Fluorescence lifetimes of anthracene in ethanol/2-methylpentane mixtures

The observation of the variation of the temperature of the τ_F-maximum with the EtOH-fraction of the mixtures is taken as a hint to the existence of an equilibrium between excited anthracene–ethanol complexes and ethanol molecules, and is thus in favor of the exciplex model.

4.3. Temperature-dependent triplet population of anthracene in ethanol

Instead of decreasing with lower temperatures and running through a minimum as requested by the demand that the sum of fluorescence quantum yield and triplet quantum yield be 1 [28], the triplet population increases from room temperature to 180 K by ca. 14%. This increase of triplet yield which is accompanied by an increase of the fluorescence quantum yield when the solution is cooled can only be rationalized if the sum of triplet yield and fluorescence quantum yield at room temperature is smaller than 1. This is confirmed by the measurements of Compton et al. [29] who determined the triplet quantum yield for anthracene in ethanol as 0.58 at room temperature which adds up to 0.86 together with the fluorescence quantum yield of 0.28 measured by Pantke/Labhart. Thus, a further temperature-dependent process is operating. We, therefore, have to add a radiationless deactivation process from S_1 with an activation energy E_4 in the kinetic scheme of Bowen. This direct IC process is already frozen at 260 K.

The further increase of triplet yield which we observe when the temperature is lowered below 180 K can only occur at the expense of the fluorescence yield. Therefore, the fluorescence yield and the fluorescence lifetime must run through a maximum at 180 K!

The kinetic analysis of the scheme on the assumption of steady-state conditions for the concentration of anthracene–ethanol–exciplexes leads to the following expression for the temperature dependence of the fluorescence lifetime:

$$\tau_F = \frac{1}{k_F + k_{ISC}\, e^{-E_{ISC}/RT} + k_4\, e^{-E_4/RT} + k_1 k_3/(k_2\, e^{(E_3-E_2)/RT} + k_3)} \quad (1)$$

This is Bowen's [2] expression for $\Phi_F = \tau_F k_F$ with $k_{ISC} = k_d$, but with the additional term $k_4 \exp(-E_4/RT)$. Provided that $E_2 > E_3$, i.e. exciplex formation is exothermic, Eq. (1) describes a maximum in τ_F vs. temperature.

5. Conclusions

In Section 1, we have listed five attempts to give a rationale for the unusual temperature dependence of the fluorescence of anthracene. On the grounds of the small shifts of the $S_0 \rightarrow S_1$ and T_1–T_n absorption as well as the $S_1 \rightarrow S_0$ fluorescence bands we can exclude the propositions based on an energy shift of the S_1 and T_2 states, i.e. the term inversion model and Bräuchle's suggestion. The Tanaka/Osugi model cannot be ruled out as there even small shifts of state energies may cause considerable changes in the ISC rate and the deuterium effect is primarily on the FC factors. The Pantke/Labhart approach is totally inaccessible to experimental testing, it is a pure construct for fitting the data.

The fact that the unusual temperature dependence of the anthracene fluorescence occurs only in alcohols and in mixtures with alcohol and not in other polar solvents is the significant piece of evidence. Note also that the alcohol concentration is important: the temperature of the maximum of the fluorescence lifetime is the higher, the higher the alcohol content. This observation suggests that an exciplex between excited anthracene and alcohol opens a new deactivating channel. Compared to the well-known exciplexes between excited anthracene and amines (ionization energy for ethylamine: 8.9 eV) this exciplex is less stable (ionization energy of ethanol: 10.5 eV). This is in agreement with the observation of the exciplex only at high concentrations of alcohol and at low temperatures.

The excited complex between anthracene and ethanol which we postulate with Bowen in this work as a deactivating species does not emit and therefore its existence cannot be proven by a direct observation. However, it should cause a biexponential fluorescence decay. Indeed, a biexponential fit of the fluorescence decay curves according to $I = A + B_1 \exp(-\tau_1/t) + B_2 \exp(-\tau_2/t)$ is possible with $\tau_1 = 1 \pm 0.3$ ns and τ_2 mimicking the familiar maximum curve (5.4 ns at 296 K, 6.7 ns at 210 K and 5.8 ns at 134 K). The B_1-values are negative as required by exciplex kinetics [30]. However, the χ^2-values are essentially equal to those of a monoexponential fit of the decay curves which has been favored in the course of this work. This does not mean exclusion of the existence of an exciplex, as Birks [31] has shown that exciplex kinetics at high temperature can often be described by a single exponential and as in our SPC measurements at low temperatures the χ^2-values are higher and less discriminative. Thus, the first suggestion published by Bowen, with a slight modification according to our work is the most probable one.

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