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Investigation of the pyrene/*N*,*N*′-diethylaniline exciplex by photoacoustic calorimetry and fluorescence spectroscopy

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Abstract

The formation and deactivation of the pyrene/*N*,*N*′-diethylaniline exciplex has been studied in *n*-alkanes by stationary and time resolved experiments with photoacoustic calorimetry (PAC) and fluorescence spectroscopy. At 0.1 M concentration of *N*,*N*′-diethylaniline a biexponential kinetics approximately applies. The formation of the exciplex occurs with rise times ranging from 0.50 ns in *n*-pentane to 2.9 ns in *n*-hexadecane. Its decay has an average lifetime of 89 ns. Hereby, fluorescence, intersystem crossing and internal conversion participate with quantum yields $\Phi_{FC}=0.39$, $\Phi_{TC}=0.27$, and $\Phi_{IC}=0.34$, respectively. The reaction volume of exciplex formation bare of electrostriction contributions has been determined by PAC to $\Delta V_C-\Delta V_{el}=-22\ \mathrm{cm^3\,mol^{-1}}$. The two principal contributions to the overall reaction volume ΔV_C are solvent effects: (1) the volume of contact complex formation ΔV_{cc} and (2) the volume contraction of the solvent around the created dipole ΔV_{el}. The contribution of bond formation to ΔV_C is negligibly small. A direct proportionality between ΔV_{el} and the thermoelastic parameter X of the solvent has been found for *n*-alkanes at 25°C. This is the reason why reaction volumes and enthalpies determined by PAC in the series of *n*-alkanes are generally free of electrostriction contributions: structural volume changes are directly obtained, overall reaction enthalpies are only obtained after an appropriate correction. This surprising result demonstrates that the electrostriction corrections of PAC results in *n*-alkanes performed in the past are wrong.

Keywords: Exciplex; Photoacoustic calorimetry; Fluorescence; Lifetimes; Quantum yields; Reaction enthalpies; Reaction volumes; Contact complex formation

1. Introduction

Only a few years after the discovery of the pyrene excimer by Förster and Kasper [1], reaction volumes ΔV_C of excimer and exciplex formation have been determined in stationary and time-resolved high pressure fluorescence studies. Large negative but in part distinctly scattering ΔV_C data have been published for several aromatic molecules [2–5]. The forward reaction is diffusion-controlled. The scatter of the ΔV_C data resulting from stationary emission experiments could be a consequence of the influence of the solvent viscosity, if the excited states equilibrium would not have been fully established. Furthermore, in time-resolved emission experiments the accurate separation of the rate constants of forward and backward reaction, required for the calculation of the equilibrium constant, is sometimes problematic [5]. Therefore, it seemed interesting to try as alternative method photoacoustic calorimetry (PAC), which allows the determination of reaction volumes and enthalpies of photoinduced processes. Measurements have to be performed under controlled variation of the thermoelastic parameter X of the solvent, either by varying the temperature of aqueous systems or by changing the solvent in the series of *n*-alkanes at constant temperature [6–10]. Using these techniques a variety of reactions such as fragmentation, proton release and uptake, hydrogen bridge formation, electron transfer, and conformational change have been studied [6–19]. Just recently, intramolecular exciplex formation of donor–acceptor compounds was investigated by Braslavsky and coworkers using PAC [20,21], and by Morais and Zimmt using the closely related method of picosecond optical calorimetry [22]. *Intramolecular* exciplex formation requires only low concentrations, since the ground state reactant is covalently bound to the excited reactant. In contrast, *intermolecular* excimer and exciplex formation demands very high concentrations of the ground state reactant in order to shift the excited states equilibrium completely to the excited complex. In the present work we extend the PAC method for the first time to this type of reaction.

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2. Experimental

Pyrene (Aldrich 99%) was crystallized twice from methanol. *N*,*N*′-diethylaniline (DEA, Aldrich >99%) was purified by column chromatography with Al_2O_3 The reference compound 2-aminobenzophenone (ABP, 99.8% Fluka) was used as received. *n*-Pentane, *n*-heptane, *n*-nonane, *n*-dodecane and *n*-hexadecane (all from Aldrich) and *n*-hexane (Riedel-de-Häen) were of the highest purity available. Stationary emission spectra were recorded with deoxygenated solutions on a 650-40 fluorescence spectrometer (Perkin–Elmer) and were corrected for the wavelength-dependent spectral sensitivity of the instrument. The front-face PAC set-up was already described [23–25]. As excitation source we used a MSC 1600 N_2 laser from LTB (pulse width 0.5 ns, pulse energy 0.7 mJ). The acoustic signals were detected by a Panametrics A103S (1 MHz) ceramic transducer, amplified by an Ortec 9306 1 GHz preamplifier and fed to a Tektronix TDS 620A storage oscilloscope. The PAC apparatus was thermostated to 25±0.3°C. To detect a possible contamination of the deoxygenated solutions by residual O_2, which could lead to a reduction of the exciplex lifetime and to corresponding changes in the heat evolution in the PAC experiments, we measured the actual exciplex lifetime before and after each PAC experiment by a AD 110 silicon avalanche diode from opto-electronics with a rise time of 0.6 ns. The fluorescence cell was directly connected by tubes with the PAC cell. The signals were stored with the TDS 620A. The apparatus function was obtained by irradiating a layer of MgO with N_2 laser pulses and recording the reflected light by the set-up. Acoustic signals were averaged typically over 100 laser shots. For each measurement, the laser pulse energy dependence was examined. Only linearly energy-dependent results were employed. Signal analysis was performed by using the program Sound Analysis 3000 version 1.13 (Quantum Northwest). In the series of PAC experiments the concentrations of pyrene and DEA were 2×10^{-4} and 0.1 M, respectively. The absorption of DEA was negligible at the excitation wavelength of 337.1 nm. Reference solutions contained also DEA in 0.1 M concentration and were optically matched to within ±0.5%. The addition of 0.1 M DEA had no influence on the velocity of sound and consequently on the adiabatic compressibility of the *n*-alkanes. Since the adiabatic compressibility is only by about 30% smaller than the isothermal compressibility κ [11], one can assume that κ remains unchanged upon the addition of 0.1 M DEA. The amplitudes ϕ of energy normalized PAC waves of reference solutions with and without 0.1 M DEA were in the limits of uncertainty the same for each solvent. Due to the proportionality $X \sim \kappa\phi$ [11], we assume that the addition of 0.1 M DEA does not change the value of X. Two independent series of PAC experiments were performed in six *n*-alkane solvents.

3. Results

3.1. Fluorescence spectroscopy

The quantitative evaluation of time-resolved PAC data by means of the commercial software requires decay kinetics, which can be described by a sum of exponentials. Since the pyrene/DEA exciplex is formed in an equilibrium reaction from the excited monomer, the kinetics of both transients is, however, more complicated [26]. The kinetics become simplified, if the excited state equilibrium is completely shifted to the exciplex side. Then, a consecutive exponential decay model can approximately be applied. Fig. 1 compares the fluorescence spectrum of pyrene (1) in 10^{-6} M concentra-

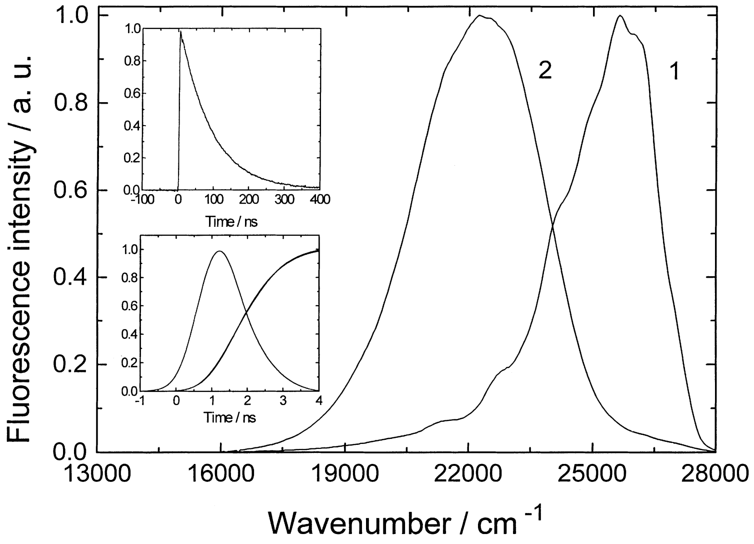

Fig. 1. Fluorescence spectra of solutions of 10^{-6} M pyrene (1), and of 2×10^{-4} M pyrene and 0.1 M DEA (2) in *n*-pentane. Upper inset: exciplex decay in *n*-pentane, τ_C=80.3 ns. Lower inset: apparatus function, rise of the exciplex and fit in *n*-pentane. Rise time 0.50 ns.

Table 1
Results of the time-resolved and stationary emission experiments

Solvent	τ_M[a] (ns)	Φ_{FC}[b]	τ_C[c] (ns)	k_{FC}[d] (10^6 s$^{-1)}$	E_{FC}[e] (cm^{-1})	ΔG_C[f] (cm^{-1})	λ[g] (cm^{-1})
Pentane	0.50	0.361	80.3	4.50	22070	25900	4223
Hexane	0.61	0.374	85.4	4.38	21960	25670	4064
Heptane	0.88	0.368	87.9	4.19	21860	25640	4065
Nonane	1.20	0.404	90.8	4.45	21830	25650	4124
Dodecane	1.86	0.403	93.9	4.29	21860	25650	4110
Hexadecane	2.86	0.417	95.1	4.38	21750	25540	4065

[a] Uncertainty: ±0.15 ns.
[b] Uncertainty: ±5%.
[c] Uncertainty: ±3%.
[d] Uncertainty: ±5%.
[e] Uncertainty: ±160 cm^{-1}.
[f] Uncertainty: ±140 cm^{-1}.
[g] Uncertainty: ±140 cm^{-1}.

tion in *n*-pentane with the fluorescence spectrum of a sample of 2×10^{-4} M pyrene and 0.1 M DEA in *n*-pentane (2). Spectrum 2 consists almost exclusively of exciplex fluorescence at this DEA concentration.

The upper inset in Fig. 1 shows the corresponding time-resolved exciplex fluorescence in a longer time scale. Since the equilibrium is almost completely shifted to the exciplex, its decay time is the excited complex lifetime of τ_C=80.3 ns in *n*-pentane[1]. The lower inset in Fig. 1 presents the apparatus function, the rise of the exciplex and the corresponding fit in a fast time scale. Using convolution techniques with a biexponential rise and decay kinetics and a fixed value τ_C=80.3 ns for the decay time constant, we determined the rise time of the exciplex emission in *n*-pentane to 0.50±0.15 ns. The risetime of the exciplex corresponds to the singlet state lifetime τ_M of the pyrene monomer in the presence of 0.1 M DEA. The formation of the pyrene/DEA exciplex is a diffusion-controlled reaction. Using Smoluchowski's equation and assuming the encounter distance as 5 Å, Knibbe et al. calculated the corresponding rate constant as 1.65×10^{10} M^{-1} s^{-1} in hexane [27]. From τ_M=0.61 ns at 0.1 M DEA in *n*-hexane, see Table 1, we obtain 1.64×10^{10} M^{-1} s^{-1}, in agreement with their result. The lifetime of the lowest excited pyrene singlet state S_1 in the absence of quenchers is τ_M^0=450 ns in alkanes [28]. By using time-resolved measurements an estimate of the quantum yield of exciplex formation affords $\Phi_{CM} \approx 1 - \tau_M/\tau_M^0$ [26,28]. With the rise times listed in Table 1 we obtain $\Phi_{CM} \approx 1.00$ for the *n*-alkanes, indicating the almost complete shift of the equilibrium to the exciplex (see Footnote 1). Therefore, it seems that the simple double exponential kinetic model can be used for the evaluation of the PAC experiments at 0.1 M DEA.

Table 1 summarizes the principal results of the emission measurements. The exciplex rise time τ_M increases from 0.50 ns in *n*-pentane to 2.86 ns in *n*-hexadecane. The fluorescence and the triplet quantum yields Φ_{FM} and Φ_{TM} of the pyrene monomer are very low in the presence 0.1 M DEA. They can be estimated from $\Phi^0_{FM} = 0.65$ and $\Phi^0_{TM} = 0.35$ by $\Phi_{TM} \approx \Phi^0_{TM}\left(\tau_M/\tau^0_M\right)$ and $\Phi_{FM} \approx \Phi^0_{FM}\left(\tau_M/\tau^0_M\right)$ [28]. The exciplex fluorescence quantum yields Φ_{FC} as well as the lifetimes τ_C increase slightly and similarly from *n*-pentane to *n*-hexadecane. Thus, the rate constant of exciplex fluorescence has a constant value of k_{FC}=4.4×10^6 s^{-1} in the *n*-alkanes used. The pure exciplex spectrum is obtained by subtracting from spectrum 2 the properly scaled monomer fluorescence spectrum 1. From the spectra we calculate the average energy of the fluorescence photons in the *n*-alkanes for the pyrene monomer as E_{FM}=299±2 kJ mol^{-1} and for the excited complex as E_{FC}=262±2 kJ mol^{-1}. The energy of the S_1 state of pyrene is obtained from the 0–0 transition of high resolution fluorescence spectra as E_S=322±1 kJ mol^{-1}.

The free energy of exciplex formation ΔG_C and the overall reorganization energy λ, which is the sum of the reorganization energies associated with the solvent (λ_s) and with a single averaged high frequency skeletal mode of frequency ν_ν (λ_ν) can be obtained from an analysis of the shape and position of the exciplex emission spectrum [29–31]. Fitting the experimental exciplex spectrum by the analytical expression given by Gould et al. [30,31], we obtain the fit parameters ΔG_C and λ, as described earlier [32,33]. Table 1 lists the values of ΔG_C and λ, which both vary only slightly in the series of *n*-alkanes. Thus, we calculate the average values ΔG_C=25 670±140 cm^{-1} (307±2 kJ mol^{-1}) and λ=4110±140 cm^{-1} (49±2 kJ mol^{-1}). According to the model of Gould et al., the sum of E_{FC} and λ should be equal to ΔG_C [31]. In the limits of mutual experimental uncertainty, this is actually the case.

3.2. Photoacoustic calorimetry

PAC measures the pressure waves following laser pulse excitation of a sample relative to a reference, which completely and very quickly converts the absorbed photon

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[1] Symbols describing the exciplex kinetics are designated in analogy to Birks. For e.g. τ_C is the excited complex lifetime, Φ_{CM} is the quantum yields of complex formation.

Table 2
Parameters of evaluation of the time-resolved photoacoustic experiments

Solvent	ϕ_1[a]	ϕ_2[a]	X[b] ($cm^3\,kJ^{-1}$)	$f_1(X)$ ($kJ\,mol^{-1}$)	$f_2(X)$ ($kJ\,mol^{-1}$)	ΔV_{el} ($cm^3\,mol^{-1}$)
Pentane	0.161	0.415	1.117	297.7	241.7	−16.7
Hexane	0.144	0.434	0.935	303.7	251.9	−15.2
Heptane	0.119	0.450	0.831	312.6	256.0	−13.3
Nonane	0.106	0.442	0.696	317.5	262.9	−11.1
Dodecane	0.100	0.445	0.592	319.7	263.9	−9.6
Hexadecane	0.093	0.441	0.524	322.3	266.2	−8.5

[a] Uncertainties resulting from the biexponential fit: ±0.01.
[b] [10].

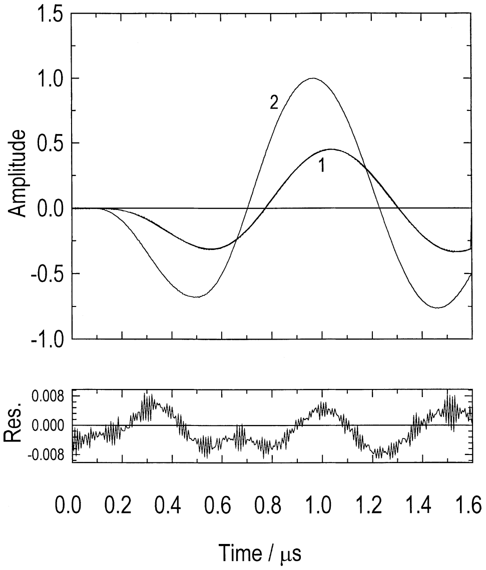

Fig. 2. Normalized PAC waves of sample solution 2×10^{-4} M pyrene and 0.1 M DEA (1) and reference solution ABP and 0.1 M DEA (2) in *n*-pentane. Fit covers the sample wave. Fixed parameters: τ_1=0.5 ns, τ_2=80.3 ns, fit parameters ϕ_1=0.152, ϕ_2=0.418.

energy into heat [34]. Fig. 2 shows the acoustic waves of (1) sample solution 2×10^{-4} M pyrene with 0.1 M DEA and (2) reference solution ABP with 0.1 M DEA obtained in *n*-pentane.

Signal 2 serves as the apparatus function. Signal 1 is shifted as compared to signal 2, indicating the presence of a transient species, i.e. the pyrene/DEA exciplex, with a lifetime fitting into the time window of the PAC set-up. In such a case, signals have to be analyzed by convolution of the apparatus function with a suited pressure evolution function *P*(*t*) [20,24,25,35,36]. Since Φ_{CM} is almost unity, the decay kinetics is simplified. A fast and quantitative relaxation to the exciplex occurs which is followed by its slow decay. The pressure evolution function is approximated by the sum of two exponentials in Eq. (1).

$$P(t) = \left(\frac{\phi_1}{\tau_1}\right)\exp\left(-\frac{t}{\tau_1}\right) + \left(\frac{\phi_2}{\tau_2}\right)\exp\left(-\frac{t}{\tau_2}\right) \qquad (1)$$

The first exponential describes the pressure evolution during the fast relaxation to the exciplex. Since the lower limit of time resolution of our PAC set-up amounts to about 25 ns with the 1 MHz transducer, the relaxation to the exciplex is detected integrally as fast pressure wave. The second exponential corresponds to the decay of the exciplex. Thus, $\tau_1=\tau_M$ and $\tau_2=\tau_C$ have been used as fixed parameters in the convolution procedures. The quality of such fits is demonstrated by the fit curve of Fig. 2, which practically covers the wave 1, and by the corresponding plot of residuals. The values of ϕ_1 and ϕ_2 are collected in Table 2.

Since the amplitude ϕ_1 of the fast pressure wave is not only caused by thermal relaxation but also by chemically induced volume changes occurring on the way to the exciplex, Eq. (2) holds true [8,10,11,20].

$$\phi_1 = \frac{E_L - \Phi_{CM}\Delta H_C - \Phi_{FM}E_{FM} - \Phi_{TM}E_T}{E_L} + \frac{\Phi_{CM}\Delta V_C}{E_L X} \qquad (2)$$

E_L=354.8 kJ mol^{-1} denotes the molar energy of the laser photons, E_T=203 kJ mol^{-1} is the triplet state energy of pyrene [26], and ΔH_C and ΔV_C are the reaction enthalpy and the reaction volume of the exciplex formation from the ground states of pyrene and DEA, respectively. $X=\alpha/(\rho c_P)=dV/dH$ is determined by the thermal expansion coefficient α, the density ρ, and the specific heat c_P of the solution. Eq. (2) is rearranged to get Eq. (3), where the experimentally accessible quantities are put together in the function $f_1(X)$.

$$f_1(X) = \frac{\{(1-\phi_1)E_L - \Phi_{FM}E_{FM} - \Phi_{TM}E_T\}}{\Phi_{CM}} = \Delta H_C - \frac{\Delta V_C}{X} \qquad (3)$$

The S_1 state of pyrene has similar to the ground state negligible dipole or quadrupole moments. This conclusion is drawn from the fact that E_S decreases only by 1 kJ mol^{-1} in going from nonpolar to polar solvents [37]. In the reaction of the nonpolar pyrene with the weakly polar DEA a highly polar exciplex is formed, which leads to a strong rearrangement of solvent molecules caused by electrostatic interactions. Around the newly created dipole a reorientation of the solvent molecules and a solvent contraction takes place, which becomes particularly important in nonpolar solvents.

Table 3
Values of solvent dielectric functions and isothermal compressibility

Solvent	ϵ	q	$10^5\kappa$[a] (bar^{-1})	$10^5 q_P$ (bar^{-1})	$10^4 q_T$[b] (K^{-1})	Tq_T-q
Pentane	1.841	0.1796		2.78[c]	−2.37	−0.250
Hexane	1.886	0.1857	16.72	2.53	−2.10	−0.248
Heptane	1.925	0.1907	14.40	2.22	−1.90	−0.247
Nonane	1.970	0.1964	11.77	1.85	−1.71	−0.247
Dodecane	2.021	0.2025	9.87	1.59	−1.57	−0.249
Hexadecane	2.058	0.2068	8.67	1.42	−1.46	−0.250

[a] [43].

[b] Derived from the values of α given in [10].

[c] Value extrapolated using the linear correlation of q_P with q, including the data for n-octane and n-decane.

Therefore, the electrostriction effects have to be considered in the evaluation of the PAC measurements. Kirkwood's theory yields Eq. (4) as relation for the free energy ΔG_{el} of electrostatic interaction of a point dipole in the center of a spherical cavity of radius r in a solvent of dielectric constant ϵ [38,39].

$$\Delta G_{\mathrm{el}} = -N_{\mathrm{A}}\left(\frac{\mu^2}{r^3}\right) q \tag{4}$$

Here, N_{A} is Avogadro's number, μ and r are the dipole moment and the radius of the spherically assumed solute molecule, and $q=(\epsilon+1)/(2\epsilon+1)$. The pressure and temperature derivatives of ΔG_{el} yield the corresponding volume and entropy effects ΔV_{el} and ΔS_{el} in Eqs. (5) and (6) [39,40].

$$\Delta V_{\mathrm{el}} = -N_{\mathrm{A}}\left(\frac{\mu^2}{r^3}\right) q_P \tag{5}$$

$$\Delta S_{\mathrm{el}} = N_{\mathrm{A}}\left(\frac{\mu^2}{r^3}\right) q_T \tag{6}$$

The parameters q_P and q_T are related to the pressure and temperature derivatives of ϵ: $q_P=3(2\epsilon+1)^{-2}(\mathrm{d}\epsilon/\mathrm{d}P)_T$, $q_T=3(2\epsilon+1)^{-2}(\mathrm{d}\epsilon/\mathrm{d}T)_P$. Finally, the enthalpy of solvation of the dipole is calculated via $\Delta H_{\mathrm{el}}=\Delta G_{\mathrm{el}}+T\Delta S_{\mathrm{el}}$ by Eq. (7).

$$\Delta H_{\mathrm{el}} = N\left(\frac{\mu^2}{r^3}\right)(Tq_T - q) \tag{7}$$

The parameters q_P and q_T are accurately known only for a small number of liquids. However, they can be calculated for nonpolar solvents like alkanes on the basis of the Clausius–Mosotti equation from the isothermal compressibility κ and from α by $q_P=(\epsilon-1)(\epsilon+2)\kappa/(2\epsilon+1)^2$ and $q_T=-(\epsilon-1)(\epsilon+2)\alpha/(2\epsilon+1)^2$ [20,41]. The change of the polarity parameter $N_{\mathrm{A}}(\mu^2/r^3)$ upon formation of the pyrene/DEA exciplex was determined in a study of the solvatochromic shift of the fluorescence as 60 kJ mol^{-1} [42]. The values of the of ϵ, q, q_P, and q_T are listed in Table 3.

It has recently been shown for the first time by Wegewijs et al. that the calculation of the electrostriction volume ΔV_{el} by Eq. (5) leads to realistic values for nonspherical dipole molecules in n-alkanes [21]. $\Delta V_{\mathrm{el}}=-160\pm30\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ was determined for the highly polar charge-transfer (CT) state of a rigid donor-bridge-acceptor compound in n-heptane by PAC measurements. With the change of $N_{\mathrm{A}}(\mu^2/r^3)$ of 760 kJ mol^{-1} the calculation resulted in $\Delta V_{\mathrm{el}}=-167\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ for n-heptane. Thus, it seems reasonable to use the above given Eqs. (4)–(7) to estimate the pure electrostriction effects ΔG_{el}, ΔS_{el}, ΔH_{el}, and ΔV_{el} in n-alkanes.

The data of Table 3 show that the differences $Tq_T-q\approx-0.25$ and thus ΔH_{el} (Eq. (7)) remain constant in the series of n-alkanes. Therefore, we conclude that the enthalpy of exciplex formation ΔH_{C}, which is the intercept (INT) of the plot of $f_1(X)$ versus $1/X$ (Eq. (3)), is actually constant in the series of n-alkanes. However, the corresponding slope (SL) ΔV_{C} cannot be constant, because of the distinct variation of the electrostriction volume ΔV_{el} (Eq. (5)), which ranges from −16.7 (n-pentane) to $-8.5\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ (n-hexadecane), see Table 2, and which additively contributes to ΔV_{C}, vide infra. The variation of ΔV_{C} can be taken into account by Eq. (8), or by Eq. (9), derived by simple addition of the same term $\Delta V_{\mathrm{el}}/X$ to both sides of Eq. (3).

$$f_1(X) + \frac{\Delta V_{\mathrm{el}}}{X} = \Delta H_{\mathrm{C}} - \left(\frac{\Delta V_{\mathrm{C}} - \Delta V_{\mathrm{el}}}{X}\right) \tag{8}$$

$$f_1(X)X + \Delta V_{\mathrm{el}} = \Delta H_{\mathrm{C}}X - (\Delta V_{\mathrm{C}} - \Delta V_{\mathrm{el}}) \tag{9}$$

If ΔH_{C} and $\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}}$ remain constant in the series of n-alkanes, linear correlations of $f_1(X)+\Delta V_{\mathrm{el}}/X$ versus $1/X$ (Eq. (8), SL$=-(\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}})$, INT$=\Delta H_{\mathrm{C}}$) and $f_1(X)X+\Delta V_{\mathrm{el}}$ versus X (Eq. (9), SL$=\Delta H_{\mathrm{C}}$, INT$=-(\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}})$) are expected.

The amplitude ϕ_2 of the time-resolved recorded slow pressure wave corresponds to the decay of the exciplex, which occurs only by fluorescence, by internal conversion (IC), and by intersystem crossing (ISC) to the pyrene triplet state with quantum yield Φ_{TC}. These three processes lead to dissociation of the exciplex. Since the dissociation products of the exciplex are identical with its educts, with the only exception that pyrene is S$_1$-excited as educt but T$_1$-excited or nonexcited as product, the corresponding reaction volume should be $-\Delta V_{\mathrm{C}}$. ϕ_2 is given by Eq. (10), which rearranges to Eq. (11).

$$\phi_2 = \Phi_{\mathrm{CM}}\frac{\Delta H_{\mathrm{C}} - \Phi_{\mathrm{FC}}E_{\mathrm{FC}} - \Phi_{\mathrm{C}}E_{\mathrm{T}}}{E_{\mathrm{L}}} - \frac{\Phi_{\mathrm{CM}}\Delta V_{\mathrm{C}}}{E_{\mathrm{L}}X} \tag{10}$$

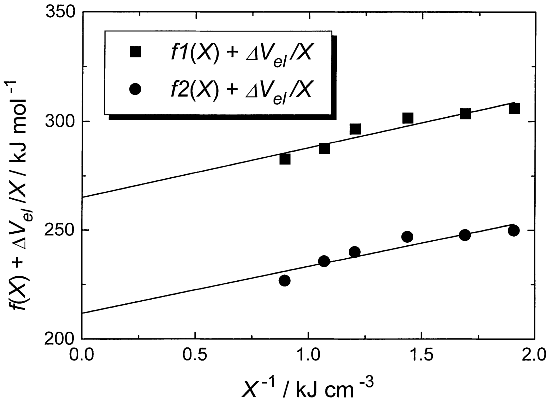

Fig. 3. Correlations of $f_1(X)+\Delta V_{\mathrm{el}}/X$ (upper) and $f_2(X)+\Delta V_{\mathrm{el}}/X$ (lower) vs. $1/X$. $f_1(X)=\{(1-\phi_1)E_{\mathrm{L}}-\Phi_{\mathrm{FM}}E_{\mathrm{FM}}-\Phi_{\mathrm{TM}}E_{\mathrm{T}}\}/\Phi_{\mathrm{CM}}$, $f_2(X)=\phi_2 E_{\mathrm{L}}/\Phi_{\mathrm{CM}}+\Phi_{\mathrm{FC}}E_{\mathrm{FC}}$. Straight lines result from linear least squares fits.

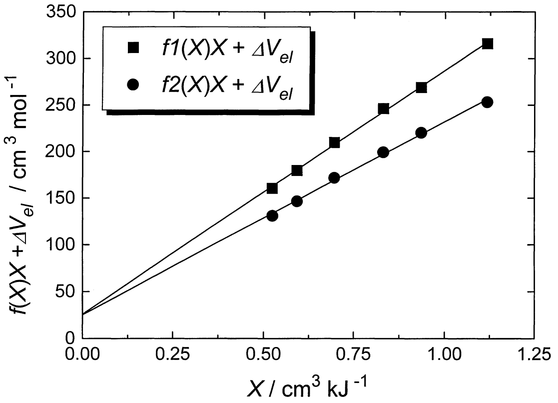

Fig. 4. Correlations of $f_1(X)X+\Delta V_{\mathrm{el}}$ (upper) and $f_2(X)X+\Delta V_{\mathrm{el}}$ (lower) vs. X. $f_1(X)=\{(1-\phi_1)E_{\mathrm{L}}-\Phi_{\mathrm{FM}}E_{\mathrm{FM}}-\Phi_{\mathrm{TM}}E_{\mathrm{T}}\}/\Phi_{\mathrm{CM}}$, $f_2(X)=\phi_2 E_{\mathrm{L}}/\Phi_{\mathrm{CM}}+\Phi_{\mathrm{FC}}E_{\mathrm{FC}}$. Straight lines result from linear least squares fits.

$$\begin{aligned} f_2(X) &= \frac{\phi_2 E_{\mathrm{L}}}{\Phi_{\mathrm{CM}}} + \Phi_{\mathrm{FC}} E_{\mathrm{FC}} \\ &= \Delta H_{\mathrm{C}} - \Phi_{\mathrm{TC}} E_{\mathrm{T}} - \frac{\Delta V_{\mathrm{C}}}{X} \end{aligned} \tag{11}$$

Again it has to be considered that ΔV_{C} varies in the series of *n*-alkanes because of the variation of ΔV_{el}, whereas ΔH_{C} remains constant. Therefore, we derive Eqs. (12) and (13), which can be used to separate the enthalpic and volumetric contributions.

$$f_2(X) + \frac{\Delta V_{\mathrm{el}}}{X} = \Delta H_{\mathrm{C}} - \Phi_{\mathrm{TC}} E_{\mathrm{T}} - \frac{\Delta V_{\mathrm{C}} - \Delta V_{\mathrm{el}}}{X} \tag{12}$$

$$\begin{aligned} f_2(X)X + \Delta V_{\mathrm{el}} &= (\Delta H_{\mathrm{C}} - \Phi_{\mathrm{TC}} E_{\mathrm{T}})X \\ &\quad -(\Delta V_{\mathrm{C}} - \Delta V_{\mathrm{el}}) \end{aligned} \tag{13}$$

Data of X, $f_1(X)$, $f_2(X)$, as well as ΔV_{el} are given in Table 2. Fig. 3 shows the correlations according to Eqs. (8) and (12). Roughly linear correlations are obtained. Linear least squares fits result in very similar slopes of $-(\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}})=22.9\pm4.0\,\mathrm{cm^3\,mol^{-1}}$ (Eq. (8)) and $21.5\pm4.1\,\mathrm{cm^3\,mol^{-1}}$ (Eq. (12)). The enthalpic contributions are obtained as intercepts $\Delta H_{\mathrm{C}}=265\pm3\,\mathrm{kJ\,mol^{-1}}$ (Eq. (8)) and $\Delta H_{\mathrm{C}}-\Phi_{\mathrm{TC}}E_{\mathrm{T}}=212\pm4\,\mathrm{kJ\,mol^{-1}}$ (Eq. (12)).

Both linear fits of the correlations according to Eqs. (9) and (13) meet almost the same intercept with $-(\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}})=25.9\pm2.7\,\mathrm{cm^3\,mol^{-1}}$ (Eq. (9)) and $25.2\pm2.8\,\mathrm{cm^3\,mol^{-1}}$ (Eq. (13)), see Fig. 4. The slopes amount to $\Delta H_{\mathrm{C}}=261\pm5\,\mathrm{kJ\,mol^{-1}}$ (Eq. (9)) and $\Delta H_{\mathrm{C}}-\Phi_{\mathrm{TC}}E_{\mathrm{T}}=207\pm6\,\mathrm{kJ\,mol^{-1}}$ (Eq. (13)). The apparently better quality of these correlations is the consequence of a forced linearization. To answer the question which of these correlations lead to the more realistic results, we performed experiments with a synthetic set of data calculated by $f_1=260+20/X$. Linear fits according to Eqs. (8) and (9) reproduce, of course, the values 260 and 20. If we add to the data a similar scatter as found experimentally, i.e. positive deviations in the center and negative deviations at both ends, compare Fig. 3, then the fits according to Eqs. (8) and (9) lead to different results: INT=260 and SL 19.0 (Eq. (8)) and INT=22.6 and SL 255 (Eq. (9)). Therefore, we conclude that the fit parameters of the correlations of Fig. 3, i.e., $\Delta H_{\mathrm{C}}=265\pm3\,\mathrm{kJ\,mol^{-1}}$ and $-(\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}})=22.9\pm4.0\,\mathrm{cm^3\,mol^{-1}}$ (Eq. (8)) and $\Delta H_{\mathrm{C}}-\Phi_{\mathrm{TC}}E_{\mathrm{T}}=212\pm4\,\mathrm{kJ\,mol^{-1}}$ and $-(\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}})=21.5\pm4.1\,\mathrm{cm^3\,mol^{-1}}$ (Eq. (12)) are more realistic. In the limits of uncertainty both slopes of Fig. 3 are equal, confirming the consistency of the evaluation of the PAC measurements with respect to the reaction volume. We obtain the mean value of the reaction volume of the pyrene/DEA exciplex formation bare of electrostriction contributions $\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}}=-22\,\mathrm{cm^3\,mol^{-1}}$. The difference of both intercepts of Fig. 3 yields $\Phi_{\mathrm{TC}}E_{\mathrm{T}}=53\pm5\,\mathrm{kJ\,mol^{-1}}$. According to Eqs. (8) and (12) $f_1(X)-f_2(X)=\Phi_{\mathrm{TC}}E_{\mathrm{T}}$ holds true for each solvent. Actually, the differences scatter only slightly around the average value $\Phi_{\mathrm{TC}}E_{\mathrm{T}}=55\pm2\,\mathrm{kJ\,mol^{-1}}$. With $E_{\mathrm{T}}=203\,\mathrm{kJ\,mol^{-1}}$ $\Phi_{\mathrm{TC}}=0.27\pm0.03$ results as average value of the quantum yield of exciplex ISC in *n*-alkanes. Taking the mean value of $\Phi_{\mathrm{FC}}=0.39\pm0.02$ the quantum yield of IC of the exciplex is $\Phi_{\mathrm{IC}}=0.34\pm0.04$. Finally, we calculate with the average excited complex lifetime $\tau_{\mathrm{C}}=89\pm5$ ns the following rate constants for the three deactivation channels of the exciplex in *n*-alkanes: $k_{\mathrm{FC}}=(4.4\pm0.3)\times10^6\,\mathrm{s^{-1}}$, $k_{\mathrm{TC}}=(3.0\pm0.3)\times10^6\,\mathrm{s^{-1}}$, and $k_{\mathrm{IC}}=(3.8\pm0.5)\times10^6\,\mathrm{s^{-1}}$.

4. Discussion

4.1. Correction for electrostriction of PAC results obtained in n-alkanes

During analysis we discovered that photoacoustic measurements in the series of *n*-alkanes generally yield reaction volumes bare of electrostriction contributions $\Delta V_{\mathrm{C}}-\Delta V_{\mathrm{el}}$. This surprising result is caused by the almost perfect direct proportionality of q_P with X for *n*-alkanes at 25°C. The data of Tables 2 and 3 already demonstrate a strong linear correlation of q_P with X. Inclusion of the data for n-octane and n-decane yields $q_P=(1.9\pm0.6)\times10^{-6}+(2.4\pm0.1)\times10^{-5}X$. Thus, the relation $\Delta V_{\text{el}}=-10^{-1}N_{\text{A}}(\mu^2/r^3)(0.2+2.4X)$ $\text{cm}^3\,\text{mol}^{-1}$ results, if $N_{\text{A}}(\mu^2/r^3)$ is given in $\text{kJ}\,\text{mol}^{-1}$ and X in $\text{cm}^3\,\text{kJ}^{-1}$. Since the intercept of that relation is only small and since X is not smaller than $0.524\,\text{cm}^3\,\text{kJ}^{-1}$ (n-hexadecane), the approximately constant ratio $\Delta V_{\text{el}}/X\approx-0.24N_{\text{A}}(\mu^2/r^3)$ $\text{kJ}\,\text{mol}^{-1}$ holds true. Since $X=\text{d}V/\text{d}H$, we derive $\Delta H_{\text{el}}=\Delta V_{\text{el}}/X$. As a matter of fact, the values of $\Delta H_{\text{el}}\approx-0.25N_{\text{A}}(\mu^2/r^3)\,\text{kJ}\,\text{mol}^{-1}$ are also approximately constant in the series of n-alkanes, vide infra. Consequently, we obtain Eq. (14) from Eq. (8).

$$f_1(X) = \Delta H_{\text{C}} - \Delta H_{\text{el}} - \frac{\Delta V_{\text{C}} - \Delta V_{\text{el}}}{X} \tag{14}$$

Since $\Delta V_{\text{C}}-\Delta V_{\text{el}}$ as well as $\Delta H_{\text{C}}-\Delta H_{\text{el}}$ can be assumed to be constant in the series of n-alkanes, Eq. (14) tells us that linear correlations of $f_1(X)$ with $1/X$ can generally be expected in the series of n-alkanes even in the case of strong electrostriction effects. Thus, in contrast to the current interpretation, slope and intercept of linear correlations of $f_1(X)$ or $f_2(X)$ with $1/X$ are volumetric and enthalpic quantities free of electrostriction contributions. This is a very surprising but important conclusion.

Correction for electrostriction by ΔV_{el} is only necessary, if overall reaction volumes ΔV_{C} are of interest. Overall reaction enthalpies ΔH_{C} are only obtained after addition of $\Delta H_{\text{el}}\approx-0.25N_{\text{A}}(\mu^2/r^3)$. Therefore, the knowledge of the change of the polarity parameter $N_{\text{A}}(\mu^2/r^3)$ during reaction is necessary for the determination of overall reaction volumes and enthalpies but not for structural volume changes. For example, we obtain from our data of $f_1(X)$ the slope $-(\Delta V_{\text{C}}-\Delta V_{\text{el}})=23.7\pm4.2$ which is only $0.8\,\text{cm}^3\,\text{mol}^{-1}$ larger than the result obtained with Eq. (8). We calculate the reaction enthalpy of exciplex formation $\Delta H_{\text{C}}=265\,\text{kJ}\,\text{mol}^{-1}$ by adding $\Delta H_{\text{el}}\approx-0.25N_{\text{A}}(\mu^2/r^3)=-15\,\text{kJ}\,\text{mol}^{-1}$ to the intercept value $280\pm4\,\text{kJ}\,\text{mol}^{-1}$. These conclusions are also valid for the results of correlations of $f_1(X)X$ or $f_2(X)X$ with X. This finding demonstrates that the electrostriction corrections of PAC results in n-alkanes performed in the past are wrong, e.g., [10,11,20]. The corrections of the reaction volumes are superfluous, if only structural volume effects are of interest, whereas corrections of the reaction enthalpies are necessary.

The magnitude of the electrostriction correction depends on the change of $N_{\text{A}}(\mu^2/r^3)$. Therefore, the results of a PAC study on the photoinduced formation of a ‘giant dipole’ charge-transfer (CT) state with a change of $N_{\text{A}}(\mu^2/r^3)$ by $760\,\text{kJ}\,\text{mol}^{-1}$ by Wegewijs et al. will be used for an illustration of our conclusions [21]. Taking their amplitudes ϕ_1 of the pressure waves evolving in the fast and complete formation of the CT state in n-alkanes we calculate values of $f_1(X)=(1-\phi_1)E_{\text{L}}$. The correlation of $f_1(X)$ with $1/X$ is actually linear and yields as intercept $506\pm5\,\text{kJ}\,\text{mol}^{-1}$. Normally, this energy would be attributed to the reaction enthalpy of the formation of the CT state. However, it is obvious that this interpretation makes no sense, since this energy is much larger than the molar energy of the exciting laser photons $E_{\text{L}}=388\,\text{kJ}\,\text{mol}^{-1}$. However, Eq. (14) tells us that ΔH_{C} is obtained from the intercept after addition of $\Delta H_{\text{el}}\approx-0.25N_{\text{A}}(\mu^2/r^3)=-190\,\text{kJ}\,\text{mol}^{-1}$. We calculate $\Delta H_{\text{C}}\approx316\,\text{kJ}\,\text{mol}^{-1}$ which agrees rather well with the estimate of $\Delta H_{\text{C}}=286\pm35\,\text{kJ}\,\text{mol}^{-1}$ of Wegeweijs et al. [21]. The slope of the plot of $f_1(X)$ with $1/X$ amounts to $-23\pm10\,\text{cm}^3\,\text{mol}^{-1}$. This small volume effect is the reaction volume of CT state formation bare of electrostriction contributions according to Eq. (14). Actually, a pure structural contribution of the reaction volume near by zero is expected for the formation of the CT state of the rigid donor-bridge-acceptor compound investigated. Considering the uncertainty of the ϕ_1 data we state fair agreement. Thus, the results of this PAC study convincingly confirm our conclusions.

4.2. Energetics

The electrostriction effect on the free energy of exciplex formation ΔG_{C} varies only slightly in the series of n-alkanes. The values of ΔG_{el} calculated according to Eq. (4) range from -10.8 (n-pentane) to $-12.4\,\text{kJ}\,\text{mol}^{-1}$ (n-hexadecane). This result is in line with the almost constant data of ΔG_{C} obtained in the analysis of the exciplex spectra which vary in the same series from 309.7 to $305.4\,\text{kJ}\,\text{mol}^{-1}$. The S_1 state of pyrene has no or only a negligible dipole moment [37]. Thus, electrostatic interactions with the solvent are very small. Therefore, neither significant reorientation of the surrounding solvent molecules nor volume contraction occurs after excitation on the way to the relaxed S_1 state. Hence, the S_1 state energy should be equal to the enthalpy ΔH_{S} and the free energy ΔG_{S} of the formation of the equilibrated S_1 state from ground state pyrene: $\Delta G_{\text{S}}=\Delta H_{\text{S}}=E_{\text{S}}=322\,\text{kJ}\,\text{mol}^{-1}$ and thus, $\Delta S_{\text{S}}=0$. With the value $\Delta G_{\text{C}}=307\,\text{kJ}\,\text{mol}^{-1}$, obtained in the analysis of the exciplex spectrum we calculate $\Delta G^*=\Delta G_{\text{C}}-\Delta G_{\text{S}}=-15\,\text{kJ}\,\text{mol}^{-1}$ for the formation of the pyrene/DEA exciplex from S_1 state pyrene and DEA. This value is in good agreement with the free reaction energy $\Delta G^*=-13\,\text{kJ}\,\text{mol}^{-1}$ resulting from the corresponding equilibrium constant $K=177\,\text{M}^{-1}$ determined by Knibbe et al. in hexane [27]. Thus, it is demonstrated that equilibrium constants of excimer or exciplex formation are accessible from the analysis of the fluorescence spectra of the excited monomer and complex.

Temperature dependent stationary emission experiments in paraffin resulted in $\Delta H^*=-35\,\text{kJ}\,\text{mol}^{-1}$ [27]. With our value of ΔG^* we calculate $\Delta S^*=-76\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$. $\Delta H_{\text{S}}+\Delta H^*$ yields $\Delta H_{\text{C}}=287\,\text{kJ}\,\text{mol}^{-1}$, which is much larger than $\Delta H_{\text{C}}=265\,\text{kJ}\,\text{mol}^{-1}$ found in the present PAC study. It seems that the value of ΔH_{C} resulting from the PAC study is significantly too small. The average energy of the fluorescence photons of the exciplex amounts to E_{FC}=262±2 kJ mol^{-1}. Since fluorescence leads without solvent reorientation from the relaxed exciplex state to a nonrelaxed Franck–Condon position in the repulsive ground state, solvent reorganization with a corresponding negative enthalpy change $\Delta H_{\mathrm{R}}=-\Delta H_{\mathrm{C}}+E_{\mathrm{FC}}$ has to occur upon returning to the thermally equilibrated pyrene and DEA molecules. Therefore, ΔH_{C} must be distinctly larger than E_{FC}. We recently determined a value of $\Delta H_{\mathrm{R}}=-21$ kJ mol^{-1} for the deactivation of the CT state of 9,9′-bianthryl (BA) ($N_{\mathrm{A}}(\mu^2/r^3)$=92 kJ mol^{-1}) in *n*-hexane [32]. Taking into account the smaller value of $N_{\mathrm{A}}(\mu^2/r^3)$=60 kJ mol^{-1} of the pyrene/DEA exciplex, $\Delta H_{\mathrm{R}}\approx-14$ kJ mol^{-1} could be realistic for the exciplex but not $H_{\mathrm{R}}=-3$ kJ mol^{-1}. Thus, we conclude that the value of ΔH_{C} obtained in this PAC study is at least by 10 kJ mol^{-1} too small.

We have once more analyzed our PAC experiments in detail looking for possible artifacts. However, we found no experimental errors perhaps with exception of the evaluation of the PAC signals. Normally, the separation of the fast and slow contributions to the acoustic wave is no big problem in time-resolved PAC, if the time window of the PAC set-up is properly chosen and the suited kinetic model is used. We have previously demonstrated that it is possible to obtain an accurate separation of the amplitudes ϕ_1 and ϕ_2 of the fast and slow contributions in biexponential decays and even to correctly separate the fast, intermediate, and slow contributions to the PAC signal in a triexponential decay by use of the available programs [36]. However, as mentioned above, the kinetics of the formation and decay of an exciplex significantly differs from a sequential biexponential kinetics. Unfortunately, only the latter kinetics can be handled by the commercial evaluation software. Perhaps it is the use of the only approximately correct kinetic model, which results in a systematically too large value of ϕ_1 and consequently too small value of ΔH_{C}. However, a decrease of ϕ_1 would require a corresponding increase of ϕ_2 to reproduce the overall PAC signal, i.e. $\phi_1+\phi_2$=constant. Then, the values of $f_1(X)$ and $f_2(X)$ would change, however, the difference $f_1(X)-f_2(X)=\Phi_{\mathrm{TC}}E_{\mathrm{T}}$ would still remain constant. Thus, the values of $\Phi_{\mathrm{TC}}E_{\mathrm{T}}$ should be free from the above suspected systematical errors.

The data allow the calculation of the complete thermodynamic cycle of formation and decay of the pyrene/DEA exciplex. Fig. 5 illustrates the thermodynamic aspects of the pyrene/DEA photophysics in *n*-alkanes by means of a free energy diagram. The free energy of the radiative fragmentation of the exciplex into ground state molecules consists of contributions due to exciplex fluorescence and ground state reorganization: $-\Delta G_{\mathrm{C}}=\Delta G_{\mathrm{FC}}+\Delta G_{\mathrm{R}}$. Fluorescence leads from the relaxed exciplex to a nonrelaxed Frank–Condon position on the S_0 potential curve without solvent reorientation. Therefore, $\Delta G_{\mathrm{FC}}=\Delta H_{\mathrm{FC}}=-E_{\mathrm{FC}}=-262\pm2$ kJ mol^{-1} holds true. Reorganization subsequently occurs on the ground state surface with $\Delta G_{\mathrm{R}}=-\Delta G_{\mathrm{C}}-\Delta G_{\mathrm{FC}}=-45\pm3$ kJ mol^{-1}, which agrees in the mutual limits of uncertainty with the negative value of the overall reorganization energy of 49±2 kJ mol^{-1}. The T_1 state of pyrene has most probably the same zero dipole moment as S_1 and S_0 [37]. Therefore, its energy E_{T}=203 kJ mol^{-1} is equal to ΔH_{T} and ΔG_{T}.

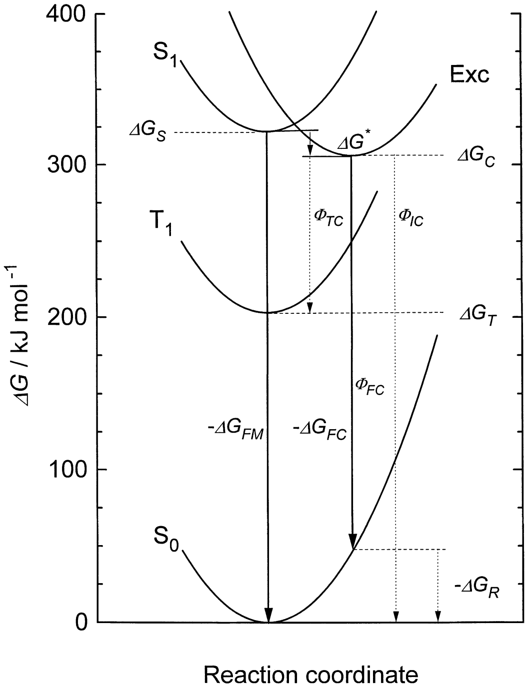

Fig. 5. Free energy diagram of the photophysics of the formation and deactivation of the pyrene/DEA exciplex in *n*-alkanes.

4.3. Exciplex decay kinetics

Fluorescence, ISC to the T_1 state of pyrene, and IC contribute with similar probability to the overall deactivation of the exciplex as can be seen from the corresponding rate constants $k_{\mathrm{FC}}=4.4\times10^6$ s^{-1}, $k_{\mathrm{TC}}=3.0\times10^6$ s^{-1}, and $k_{\mathrm{IC}}=3.8\times10^6$ s^{-1}. The rather large rate constant of ISC of the exciplex in *n*-alkanes looks at first glance surprising. There are only few data which can be used for a meaningful comparison. The pyrene excimer has almost the same energy gap between the excimer state and the pyrene triplet, for which 81 kJ mol^{-1} results from ΔH_{S}=322 kJ mol^{-1}, $\Delta H^*=-38$ kJ mol^{-1} [28], and the known value of ΔH_{T}. The corresponding energy gap amounts to 84 kJ mol^{-1} for the pyrene/DEA exciplex. All rate constants have separately been determined as $k_{\mathrm{FC}}=10.5\times10^6$ s^{-1}, $k_{\mathrm{TC}}=1.8\times10^6$ s^{-1}, and $k_{\mathrm{IC}}=6.8\times10^6$ s^{-1} for the excimer in ethanol, whereas in cyclohexane besides $k_{\mathrm{FC}}=11.6\times10^6$ s^{-1} only the sum $k_{\mathrm{TC}}+k_{\mathrm{IC}}=3.9\times10^6$ s^{-1} is known [28]. The rate constants for radiationless decay of the pyrene excimer decrease with decreasing solvent polarity. If ISC as well as IC decrease by the same factor, then ISC of the excimer occurs with $k_{\mathrm{TC}}\leq1\times10^6$ s^{-1} in nonpolar solvents. Thus, it seems that in nonpolar solvents ISC is faster for the polar pyrene/DEA exciplex (μ=12 D [42]) than for the nonpolar excimer.

Actually, CT interactions are known to promote ISC in exciplexes as for example in the quenching of the triplet states of electron donors by O_2 [44], as well as the quenching of singlet oxygen by ground state electron donors [45,46].

4.4. Reaction volume

The findings that the correlations of Fig. 3 have the same slope and the correlations of Fig. 4 meet the same intercept strongly support the validity of the reaction volumes determined in the present PAC study. The average value is obtained as $\Delta V_C - \Delta V_{el} = -22\,cm^3\,mol^{-1}$. With $\Delta V_{el} = -15\,cm^3\,mol^{-1}$, see Table 2, we obtain $\Delta V_C = -37\,cm^3\,mol^{-1}$ for the pyrene/DEA exciplex in *n*-hexane. Stationary fluorescence measurements in *n*-hexane as a function of hydrostatic pressure resulted in $\Delta V^* = -32\,cm^3\,mol^{-1}$ for the formation of exciplex from S_1 excited pyrene and DEA [47]. Since the S_1 state of pyrene has the same dipole moment and van der Waals volume like the ground state $\Delta V^* = \Delta V_C$ should hold true. Thus, in the mutual limits of uncertainty the results of both methods agree and a common average of $\Delta V_C - \Delta V_{el} = -20\,cm^3\,mol^{-1}$ is obtained.

Until now a rather simple hypothesis is mostly used for the interpretation of reaction volumes. In a rough approximation ΔV is considered as a sum of an intrinsic component, which is assumed to be equivalent to the change ΔV_{vdW} of the pure van der Waals volumes, and a solvation component, which is believed to represent all volume changes associated with changes in polarity, electrostriction, and dipole interactions during the reaction, i.e. ΔV_{el} [48]. However, there exists a significant third contribution, which mostly is overlooked. According to Yoshimura and Nakahara, the formation of a contact complex is accompanied by a volume contraction already in the complete absence of any attractive interaction [49]. The addition of a solute to a solvent leads to a perturbation of the packing of the solvent molecules in the liquid, causing a reduced packing fraction in the direct solvent shell of the solute molecules in the absence of electrostatic interactions. Hereby, the overall volume increase is proportional to the surface of the solute. If two separate solute molecules form a contact complex, the overall surface, which is exposed to the solvent is smaller for the contact complex than for the separate molecules. Consequently, the overall volume of the solvent shells of lower packing fraction decreases, which leads to a negative volume of contact complex formation ΔV_{cc}. Firestone and Smith arrived at very similar conclusions in the analysis of Diels–Alder reaction volumes [50]. They found that about 85% of the loss of volume that occurs during the reaction results from the loss of empty space surrounding the molecules and not from the reaction itself. The quantitative treatment of the problem by Yoshimura and Nakahara leads to Eq. (15) [49,51–53].

$$\Delta V_{cc} = \left(\frac{d\gamma}{dP}\right)\Delta S_{vdW} + \Delta\nu\kappa RT \tag{15}$$

Here, $(d\gamma/dP)$ is the pressure derivative of the interfacial tension between the solvent and the hard walls of the solute molecules, ΔS_{vdW} is the overall change of the molar surface of the hard core (van der Waals) molecules participating in the reaction, $\Delta\nu$ is the sum of the stoichiometric numbers, and κRT is the translational contribution to the partial molar volume. Eq. (15) reveals that the volume of contact complex formation ΔV_{cc} contains a solvent structure perturbation term and a translational contribution. ΔV_{cc} can be of considerable magnitude. Therefore, it is absolutely necessary for a meaningful interpretation of reaction volumes, although the effect of ΔV_{cc} still presently is ignored [48,54], to consider the value of ΔV_{cc} as third contribution of ΔV.

$$\Delta V = \Delta V_{vdW} + \Delta V_{cc} + \Delta V_{el} \tag{16}$$

Very different mechanistic conclusions can be obtained [11,55–58]. For example, it has been shown by us in an analysis of reaction volumes of excimer formation that no or only a negligible negative contribution ΔV_{vdW} to ΔV results, if the values of ΔV_{cc} are taken into account [56]. These results contradict early interpretations of these reaction volumes, which assumed $\Delta V = \Delta V_{vdW}$ [2,3,59]. It was argued that a reduction of the distance between both parallel planar aromatic molecules in the contact complex by about 0.5 Å would occur upon excimer bond formation, which would be sufficient to explain quantitatively the magnitude of ΔV. However, this vivid mechanistic interpretation neglects the weakness of the excimer bond and the strong increase of the repulsive potential below the collision distance preventing a significant further decrease of the intermolecular distance.

The interpretation of the reaction volume of the formation of the pyrene/DEA exciplex follows the lines given for the excimers [56]. We obtained $\Delta V_C - \Delta V_{el} = \Delta V_{vdW} + \Delta V_{cc} = -20\,cm^3\,mol^{-1}$. Eq. (15) is used for the estimation of ΔV_{cc}. It is assumed that only those contact complexes can react, in which both planar molecules form a sandwich conformation. Then, the reduction ΔS_{vdW} of the solute surface exposed to the solvent is calculated as the area of the flat surface of the aromatic molecule per mole. Yoshimura and Nakahara derived for alkanes dissolved in carbon tetrachloride at 25°C the value $(d\gamma/dP) = 3.6\times10^{-11}$ m [52]. In default of other data we take this as a general value for nonpolar organic solvents. The diameter of the disk-shaped benzene molecule amounts to about 6 Å. Thus, we calculate for the formation of a benzene sandwich contact complex with complete coverage of the planar surfaces at room temperature $\Delta S_{vdW} = -3.4\times10^5\,m^2\,mol^{-1}$, $\Delta\nu\kappa RT = -2.6\,cm^3\,mol^{-1}$ and $\Delta V_{cc} = -15\,cm^3\,mol^{-1}$. The planar surface of naphthalene is about 1.5-fold, and that of pyrene about two-fold larger than the planar surface of benzene leading to estimates of $\Delta V_{cc} = -21$ (naphthalene) and $\Delta V_{cc} = -27\,cm^3\,mol^{-1}$ (pyrene). The maximum coverage of about 75% of the planar pyrene surface is obtained in the pyrene/DEA exciplex, when the DEA molecule lies in the long axis sandwich-like on the pyrene moiety. Therefore, $\Delta V_{cc} \approx -21\,cm^3\,mol^{-1}$ is estimated for such a configuration. This value is almost equal to $\Delta V_{\mathrm{vdW}}+\Delta V_{\mathrm{cc}}=-20\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$, indicating no contribution of ΔV_{vdW} to the reaction volume. For an exciplex configuration with a smaller coverage a small negative value of ΔV_{vdW} would result. Thus, we arrive at similar conclusions as in the case of excimers: there exists no or only a negligibly small negative contribution of bond formation to ΔV in the formation of exciplexes. Therefore, a significant further reduction of the distance of the planar aromatic molecules in the sandwich configuration does not take place upon formation of the weak excimer and exciplex bonds.

5. Conclusions

Time-resolved PAC investigations in the series of *n*-alkanes can be used for a reliable determination of reaction volumes of exciplex formation, if the excited states equilibrium is shifted far to the exciplex side. The two principal contributions to the overall reaction volume are solvent effects: the volume of contact complex formation and the contraction of the solvent around the created dipole, whereas the contribution of bond formation is negligibly small. Direct proportionality between ΔV_{el} and the thermoelastic parameter X has been found for *n*-alkanes at 25°C. This relation effects that the reaction volumes and enthalpies determined by PAC in the series of *n*-alkanes are free of electrostriction contributions. Structural volume changes are directly obtained. Overall reaction enthalpies require an appropriate correction. This surprising result demonstrates that the electrostriction corrections of PAC results in *n*-alkanes performed in the past are wrong.

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References

[1] T. Förster, K. Kasper, Z. Phys. Chem. N. F. 1 (1959) 275.
[2] H. Braun, T. Förster, Ber. Bunsenges. Phys. Chem. 70 (1966) 1091.
[3] H. Braun, T. Förster, Z. Phys. Chem. N. F. 78 (1972) 40.
[4] P.C. Johnson, H.W. Offen, J. Chem. Phys. 56 (1972) 1638.
[5] M. Okamoto, M. Sasaki, J. Phys. Chem. 95 (1991) 6548.
[6] J. Westrick, J.L. Goodman, K.S. Peters, Biochemistry 26 (1987) 8313.
[7] W.P. Leung, K.C. Cho, S.K. Chau, C.L. Choy, Chem. Phys. Lett. 141 (1987) 20.
[8] M.S. Herman, J.L. Goodman, J. Am. Chem. Soc. 111 (1989) 1849.
[9] J. Morais, J. Ma, M.B. Zimmt, J. Phys. Chem. 95 (1991) 3885.
[10] R.R. Hung, J.J. Grabowski, J. Am. Chem. Soc. 114 (1992) 351.
[11] R. Schmidt, M. Schütz, Chem. Phys. Lett. 263 (1996) 795.
[12] A. Losi, C. Viappiani, Chem. Phys. Lett. 289 (1998) 506.
[13] G. Bonetti, A. Vecli, C. Viappiani, Chem. Phys. Lett. 269 (1997) 268.
[14] C.D. Borsarelli, S.E. Braslavsky, J. Phys. Chem. B 101 (1997) 6036.
[15] C.D. Borsarelli, S.E. Braslavsky, J. Phys. Chem. B 102 (1998) 6231.
[16] T. Gensch, S.E. Braslavsky, J. Phys. Chem. B 101 (1997) 101.
[17] C.D. Borsarelli, H. Corti, D. Goldfarb, S.E. Braslavsky, J. Phys. Chem. A 101 (1997) 7718.
[18] C.D. Borsarelli, S.E. Braslavsky, J. Phys. Chem. A 103 (1999) 1719.
[19] T. Gensch, M.S. Churio, S.E. Braslavsky, K. Schaffner, Photochem. Photobiol. 63 (1996) 719.
[20] B. Wegewijs, J.W. Verhoeven, S.E. Braslavsky, J. Phys. Chem. 100 (1996) 8890.
[21] B. Wegewijs, M.N. Paddon-Row, S.E. Braslavsky, J. Phys. Chem. A 102 (1998) 8812.
[22] J. Morais, M.B. Zimmt, J. Phys. Chem. 99 (1995) 8863.
[23] R. Dunsbach, R. Schmidt, J. Photochem. Photobiol. A: Chem. 85 (1995) 275.
[24] L.A. Melton, T. Ni, Q. Lu, Rev. Sci. Instrum. 60 (1989) 3217.
[25] L.G. Arnault, R.A. Caldwell, J.E. Elbert, L.A. Melton, Rev. Sci. Instrum. 63 (1992) 5381.
[26] J.B. Birks, D.J. Dyson, I.H. Munro, Proc. R. Soc. London, Ser. A 275 (1963) 575.
[27] H. Knibbe, D. Rehm, A. Weller, Ber. Bunsenges. Phys. Chem. 73 (1969) 839.
[28] J.B. Birks, Acta Phys. Polon. 34 (1968) 603.
[29] R.A. Marcus, J. Phys. Chem. 93 (1989) 3078.
[30] I.R. Gould, R.H. Young, R.E. Moody, S.J. Farid, J. Phys. Chem. 95 (1991) 2068.
[31] I.R. Gould, D. Noukakis, L. Gomez-Jahn, R.H. Young, J.L. Goodman, S.J. Farid, Chem. Phys. 176 (1993) 439.
[32] M. Schütz, R. Schmidt, J. Phys. Chem. 100 (1996) 2012.
[33] D.W. Marquardt, J. Soc. Ind. Appl. Math. 11 (1963) 431.
[34] S.E. Braslavsky, G.E. Heibel, Chem. Rev. 92 (1992) 1381.
[35] J. Rudzki-Small, L.J. Libertini, E.W. Small, Biophys. Chem. 42 (1992) 29.
[36] R. Schmidt, M. Schütz, J. Photochem. Photobiol. A: Chem. 103 (1997) 39.
[37] S.L. Murov, I. Carmichael, L.H. Gordon, Handbook of Photochemistry, Dekker, New York, 1993, p. 44.
[38] J.G. Kirkwood, J. Chem. Phys. 2 (1934) 351.
[39] E.J. Whalley, Chem. Phys. 38 (1963) 1400.
[40] H. Hartmann, H.-D. Brauer, H. Kelm, G. Rinck, Z. Phys. Chem. N. F. 61 (1968) 53.
[41] H.A. Schwarz, J. Phys. Chem. 97 (1993) 12954.
[42] H. Beens, H. Knibbe, A. Weller, J. Chem. Phys. 47 (1967) 1183.
[43] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 74th Edition, CRC Press, Boca Raton, 1993.
[44] F. Wilkinson, A.A. Abdel-Shafii, J. Phys. Chem. A. 101 (1997) 5509.
[45] B.M. Monroe, J. Phys. Chem. 81 (1977) 1861.
[46] F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 24 (1995) 663.
[47] P. Pollmann, D. Rehm, A. Weller, Ber. Bunsenges. Phys. Chem. 79 (1975) 692.
[48] R. van Eldik, T. Asano, J.W. le Noble, Chem. Rev. 89 (1989) 549.
[49] Y. Yoshimura, M. Nakahara, J. Chem. Phys. 81 (1984) 4080.
[50] R.A. Firestone, G.M. Smith, Chem. Ber. 122 (1989) 1089.
[51] Y. Yoshimura, J. Osugi, M. Nakahara, Ber. Bunsenges. Phys. Chem. 89 (1985) 25.
[52] Y. Yoshimura, M. Nakahara, Ber. Bunsenges. Phys. Chem. 89 (1985) 426.
[53] Y. Yoshimura, M. Nakahara, Ber. Bunsenges. Phys. Chem. 89 (1985) 1004.
[54] A. Drljaca, C.D. Hubbard, R. van Eldik, T. Asano, M.V. Basilevsky, W.J. le Noble, Chem. Rev. 98 (1998) 2167.
[55] Y. Yoshimura, Y. Kimura, M. Nakahara, Ber. Bunsenges. Phys. Chem. 92 (1988) 1095.
[56] R. Schmidt, J. Phys. Chem. A 102 (1998) 9082.
[57] R. Schmidt, K. Seickel, H.-D. Brauer, Ber. Bunsenges. Phys. Chem. 94 (1990) 1100.
[58] M. Hild, H.-D. Brauer, Ber. Bunsenges. Phys. Chem. 100 (1996) 1210.
[59] P. Pollmann, A. Weller, Ber. Bunsenges. Phys. Chem. 77 (1973) 1071.