

SOLUTE-SOLVENT EXCIPLEXES IN THE PHOTOINDUCED FORMATION OF RADICAL IONS OF 4-*N,N*-DIMETHYLAMINO-BENZONITRILE AND RELATED COMPOUNDS

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Summary

Measurements of laser-pulse-induced transient optical absorptions and transient electrical conductance reveal that excitation of 4-*N,N*-dimethylaminobenzonitrile and related compounds in acetonitrile or water at 308 nm leads to formation of radical cations of the solutes. In acetonitrile the cations are formed in a single-photon process via a singlet state solute-solvent exciplex, whereas in water they are formed mainly by a biphotonic process. It follows from the transient absorptions of the compounds in cyclohexane, 1,4-dioxane and acetonitrile that the solutes in their lowest electronic triplet state do not form exciplexes with these solvents.

1. Introduction

The photoinduced formation of radical ions of aromatic compounds in polar solvents is a topic of wide interest. Our aim is to gain insight into the catalytic role of the solvent in the monophotonic formation of the ions, when the excitation energy is much less than the first ionization energy of the solute in vacuum. In previous publications on the role of solute-solvent interactions in the anomalous fluorescence of 4-*N,N*-dimethylaminobenzonitrile (DMABN; I, Fig. 1) we suggested that solute-solvent exciplexes are precursors of the radical cation of DMABN [1] and we provided some evidence in support of this suggestion [2]. The present paper focuses attention on the formation of radical ions via solute-solvent exciplexes in the case of the compounds DMABN, 3,5-*N,N*-tetramethyl-4-aminobenzonitrile (3,5-TMABN; II, Fig. 1) and 1-methyl-6-cyano-1,2,3,4-tetrahydroquinoline (1M6CTHQ; IV, Fig. 1). The orientation of the $N-(CH_3)_2$ group relative to the phenyl ring is different in the solute-solvent complexes of these compounds [1-4]. If the solute in the singlet state solute-solvent exciplex has a conformation with the $N-(CH_3)_2$ group

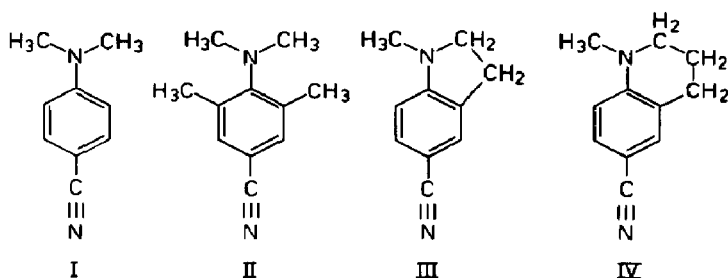


Fig. 1. Structural formulae relevant to the paper.

coplanar to or at right angles to the phenyl ring, they are denoted by 1E_1 and 1E_2 respectively. The compound DMABN may yield exciplexes of both type 1E_1 and 1E_2 , whereas 3,5-TMABN only yields type 1E_2 . In the case of compounds III and IV no anomalous fluorescence has been observed, although there is some evidence that IV is able to form solute-solvent exciplexes of type 1E_1 [2 - 4].

As in our previous papers we shall refer to emitting states and quantities associated with the normal and anomalous fluorescence by labelling them with N and A respectively.

The intermolecular interaction which leads to the binding of the constituents in the solute-solvent exciplexes of these compounds gains much of its strength from the overlap of lone pair orbitals on the N-(CH₃)₂ group and on the solvent. For a discussion of this matter we refer to our previous work [2]. In a study of the anomalous fluorescence from 9,9'-bianthryl we discovered that this compound also may form solute-solvent exciplexes with a variety of solvents which act as precursors of the radical cation of the compound [5]. The case of 9,9'-bianthryl illustrates that the formation of solute-solvent exciplexes is not restricted to solutes and solvents with lone pair electrons.

The experimental results which will be discussed in this paper have been obtained from measurements of fluorescence lifetimes, pulse-laser-induced transient optical absorptions and transient electrical conductance.

2. Experimental details

The synthesis and the purification of the compounds have been described previously [1]. Spectrograde solvents were used to make solutions for spectroscopic investigations. Fluorescence spectra were recorded using a spectrofluorometer (Hitachi-Perkin-Elmer MPF2A) and were corrected for instrumental distortions. Quinine sulphate in 1 N sulphuric acid ($\Phi_F = 0.55$) was used as a standard in the determination of fluorescence quantum yields. Fluorescence decay was studied by exciting the solution with a laser pulse at 265 nm (30 ps full width at half-maximum (FWHM)) and by following the temporal profile of the emission in real time by means of a detection system consisting of a photodiode and a 500 MHz transient digitizer (Tektronix

model R 7912) which provides a rise time of the whole instrument of 800 ps. The solutions used in the fluorescence decay studies were deoxygenated by purging with argon gas. The measurement of photoinduced transient electrical conduction has been described previously [5]. The solution in the conduction cell is excited between the electrodes with a pulse from an excimer laser (Lambda Physik EMG500) at 308 nm and a pulse width of 10 ns FWHM. The solutions used in the studies of transient photoconduction had an optical density of 0.30 at 308 nm.

To prevent even small changes in the solutions after laser excitation, the samples in the conduction cell were renewed after each laser pulse. The laser energy entering the conduction cell was monitored by deflecting a small fraction of it via a beam splitter onto a photodiode. The total laser energy entering the conductance cell was determined with a solution of a photochemical actinometer (Aberchrome 540 in toluene) [6] in the cell.

The intensity of the fluorescence emitted by the solution in the conduction cell was observed, in the direction perpendicular to the laser beam and the electric field, by means of a photodiode connected to the transient digitizer. Care was taken by appropriate masking to prevent stray light from the laser from entering the photodiode. The fluorescence was attenuated and filtered with an interference filter to assure a linear response of the photodiode and to restrict the observation to the fluorescence band of the solute.

Transient optical absorptions induced by laser excitation were studied by means of an excite-and-probe technique described previously [7]. The sample is excited with a pulse from the excimer laser and the transient absorption of monochromatic light emerging from a pulsed xenon lamp is followed in real time.

When required, the solutions used in the studies of transient absorptions were deoxygenated by repeated freeze-pump-thaw cycles. All the solutions used in the transient absorption studies had an equal optical density at 308 nm.

3. Results and discussion

Excitation of DMABN (I, Fig. 1) in acetonitrile with a 308 nm (FWHM, 10 ns) laser pulse induces a transient component in the electrical conduction of the solution. The leading edge of the transient conduction signal is completely determined by the time integral of the laser pulse which means that the lowest triplet state may be excluded as a doorway to the charged species because the lifetime of T_0 is 35 ns in the air-saturated solution. The induced conduction decays according to second-order kinetics over a period of several microseconds.

Two different kinds of experiments were performed to establish whether the mobile charges are produced monophotonically or multiphotonically. The two types of experiments were performed with solutions of equal absorbance at 308 nm in the photoconduction cell. In one experiment the

variation of the peak height $j(0)$ of the transient photoconduction, *i.e.* the signal height immediately after termination of the laser pulse, with the time integral I_L of the laser pulse is determined.

The result shown in Fig. 2 indicates that the initial concentration of mobile charged species is proportional to the first power of the total number N_p of photons entering the cell. In the other experiment the variation in the intensity of the anomalous fluorescence at 460 nm with I_L was determined over the same range of I_L covered in the first experiment. The result is a proportionality between the fluorescence intensity and the first power of I_L , as shown in Fig. 3. Since the anomalous fluorescence can be excited monophotonically, Fig. 3 provides evidence for the absence of non-linear effects in the absorption which could arise from depletion of the ground state population. Therefore, we may conclude from Fig. 2 that mobile

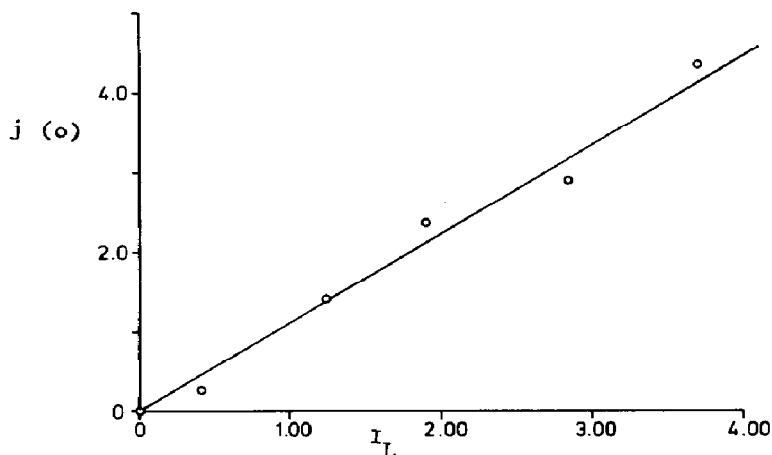


Fig. 2. Laser-pulse-induced transient conduction $j(0)$ at $t = 0$ of a solution of DMABN in acetonitrile as a function of the intensity I_L of the laser.

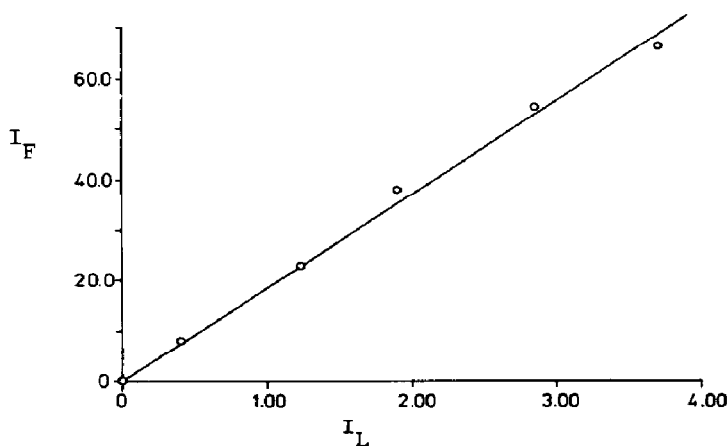


Fig. 3. Intensity I_F of the fluorescence of a solution of DMABN in acetonitrile in the electrical conductivity cell as a function of the intensity I_L of the laser used to induce transient electrical conduction.

acetonitrile. Since the potential energy of the reference calomel electrode is 4.5 eV [8], the ionization energy E_I^+ of 3,5-TMABN in acetonitrile may be calculated as $E_I^+ = eE_{1/2}^{\text{ox}} + 4.5$ eV, i.e. $E_I^+ = 6.4$ eV. The energy E_S^- of solvation of the ion $(\text{CH}_3\text{CN})_2^-$ is 2.4 eV [8]. The excitation energy $\Delta E_{0,0}$ of the 0-0 transition of 3,5-TMABN in acetonitrile is 4.0 eV. ΔG may be estimated as $\Delta G = E_I^+ - E_S^- - \Delta E_{0,0}$ which yields $\Delta G \approx 0$. The rate constants k_i for electron transfer reactions in which $\Delta G \approx 0$ are in the range $5 \times 10^5 \text{ s}^{-1} \leq k_i \leq 10^9 \text{ s}^{-1}$ [9]. According to mechanism (I) the quantum yield Φ_{ion} of photoionization is given by

$$\Phi_{\text{ion}} = \frac{k_i}{k_0(\text{N}) + k_i + k_e} \quad (3)$$

Taking the relations $k_E + k_i \geq 4 \times 10^{11} \text{ s}^{-1}$ and $k_0(\text{N}) = 10^9 \text{ s}^{-1}$ into account we obtain $\Phi_{\text{ion}} \leq 2.5 \times 10^{-3}$. Note that Φ_{ion} in eqn. (3) represents the quantum yield of geminate ion pairs. The yield $\Phi_{\text{ion}}^{\text{m}}$ of mobile ions at the end of the laser pulse is generally smaller than Φ_{ion} , owing to charge recombination within geminate pairs.

We can estimate the value of $\Phi_{\text{ion}}^{\text{m}}$ from the peak height $j(0)$ of the transient conduction signal of the solutions of the compounds I, II and IV in acetonitrile. The current density is given by

$$j(t) = \mathcal{F}(C_+(t)\mu_+ + C_-(t)\mu_-)E \quad (4)$$

where \mathcal{F} is Faraday's constant, $C_+(t)\mu_+$ and $C_-(t)\mu_-$ are the products of concentration C and mobility μ of the positive and negative charge carriers respectively and E is the externally applied electric field.

The concentration of ions may be obtained if μ_+ and μ_- are known. The positive charge carrier is undoubtedly the cation of the solute. We assume that the radical cations of DMABN, 3,5-TMABN and 1M6CTHQ have equal mobilities and for these ions we estimate $\mu_+ = 5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is a value found for cations in liquids with a viscosity comparable with that of acetonitrile [10]. In the solutions saturated with air the negative charge carrier O_2^- was formed by electron transfer from $(\text{CH}_3\text{CN})_2^-$ to oxygen. The value of μ_- in the case of O_2^- is estimated as $9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Using the quoted values of μ_+ and μ_- and the number of photons N_a absorbed in the solution we obtain from eqn. (4) the values of $\Phi_{\text{ion}}^{\text{m}}$ given in Table 1. The

TABLE 1

Fluorescence lifetime τ_F , maximum quantum yield $\Phi_{\text{ion}}^{\text{m}}$ of mobile ions, rate constant k_1^{m} for formation of mobile ions and maximum optical density OD_{max} of the radical cations between 17 000 and 22 000 cm^{-1} in the case of solutions of compounds I, II and IV in acetonitrile

Solute	τ_F ($\times 10^{-9}$ s)	$\Phi_{\text{ion}}^{\text{m}}$	k_1^{m} (s^{-1})	OD_{max}
DMABN (I)	4.0	1.3×10^{-2}	3.3×10^6	0.013
3,5-TMABN (II)	3.3	1.1×10^{-2}	3.3×10^6	0.013
1M6CTHQ (IV)	2.8	0.9×10^{-2}	3.2×10^6	0.019

values $k_i^m = \Phi_{\text{ion}}^m / \tau_F$ are also presented in this table. The quantum yields are larger than the estimated maximum of Φ_{ion} which could be achieved by direct formation of ions from $S_1(N)$. We conclude that the ions are formed from the exciplexes 1E_1 and 1E_2 .

3.1. Transient optical absorptions of the compounds DMABN, 3,5-TMABN and 1M6CTHQ

In Fig. 4 the transient absorption spectra immediately after the laser pulse are shown for deoxygenated solutions of compounds I, II and IV in acetonitrile. In the oxygenated solutions in acetonitrile, part of the transient spectrum has disappeared at about 150 ns after termination of the laser pulse. The remaining components of the spectra are shown in Fig. 5. The remaining part of the spectrum of DMABN is nearly identical with the spectrum of the radical cation of DMABN in a glassy ethanol matrix [11]. Therefore, the spectra in Fig. 5 have to be attributed to the radical cations of the compounds I, II and IV. This is in accordance with the observed second-order decay of these spectra, *i.e.* the inverse of the optical density OD is a linear function of time, which is expected for a decay due to a homogeneous charge-recombination reaction. The second-order decay indicates that the radical cations do not react with oxygen.

Note that the spectra of the radical cations of compounds I and IV have their peaks at about the same wavelength, but the peak in the case of the radical cation of compound II is shifted to the red. From this we conclude that the dimethylamino group in DMABN^+ is coplanar with the phenyl ring. In Table 1 the heights OD_{max} of the maxima in the absorptions in Fig. 5 are listed. Neither Φ_{ion}^m nor OD_{max} vary much from one compound to the other. The part of the transient spectrum in Fig. 4 which has disappeared in the

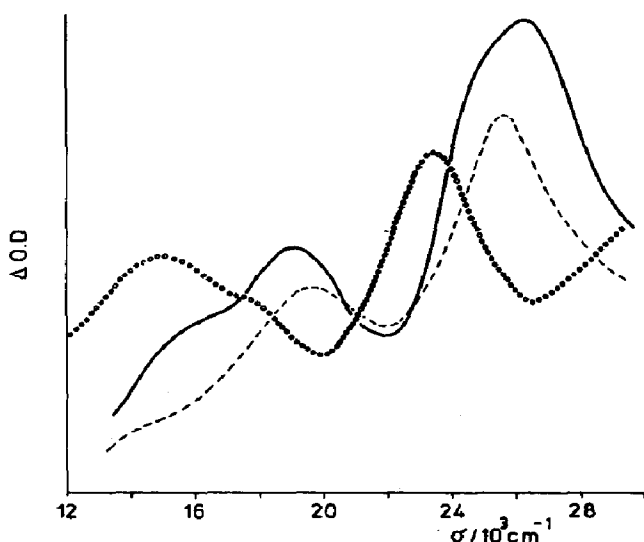


Fig. 4. Transient absorption spectra in acetonitrile immediately after the laser pulse: —, DMABN; ○○○, 3,5-TMABN; ---, 1M6CTHQ.

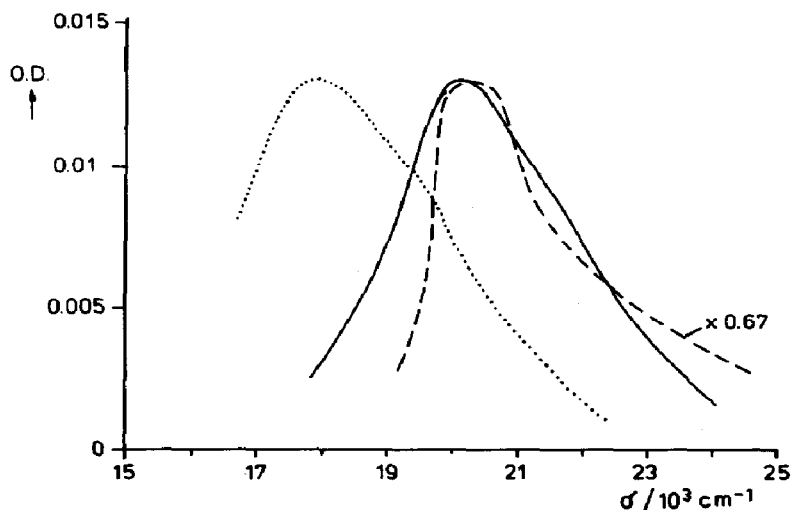


Fig. 5. Spectra of the radical cations in acetonitrile: —, DMABN; ·····, 3,5-TMABN; ---, 1M6CTHQ.

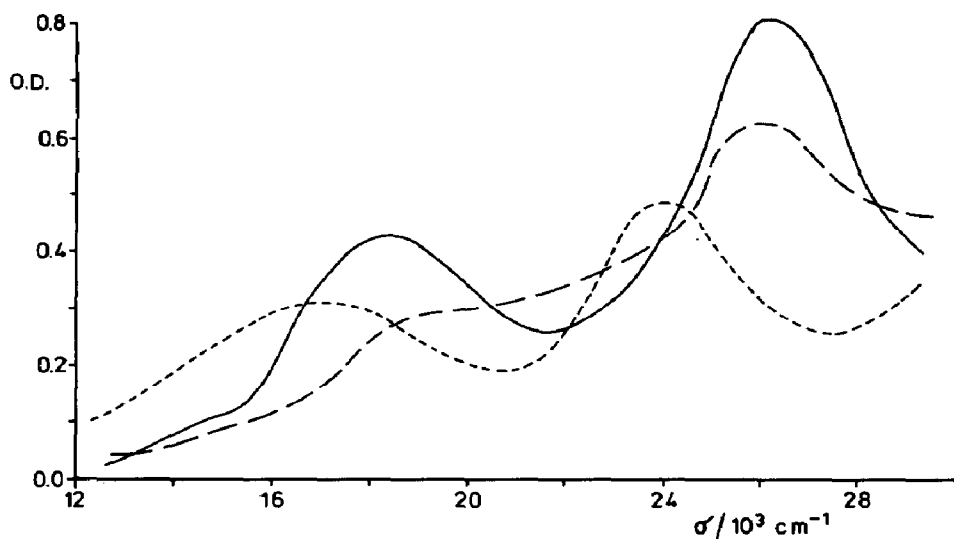


Fig. 6. Triplet-triplet absorption spectra of the solutions in cyclohexane: —, DMABN; ---, 3,5-TMABN; - · - ·, 1M6CTHQ.

oxygenated solution is nearly the same as the transient spectrum of the compound in cyclohexane shown in Fig. 6. Since ions are not formed in the solution in cyclohexane and the spectra in Fig. 6 persist for more than $50 \mu\text{s}$ when the solution is deoxygenated, the spectra have to be attributed to the solutes in the lowest triplet state T_0 . This conclusion is supported by the fact that the lifetime of the spectra in Fig. 6 may be reduced with the addition of triplet state quenchers such as 1,3-cyclohexadiene and 1,1,2,2-tetramethyldiazetidene dioxide.

By comparing Figs. 4 and 5 we conclude that the radical cation contributes less than 5% of the absorbance in Fig. 4, which may therefore be regarded as the absorption spectrum of the solute in its T_0 state in acetonitrile. Comparison of Figs. 4, 6 and 7 leads to the conclusion that the triplet state spectrum of compounds I and IV is almost unaffected on changing the solvent from cyclohexane to either acetonitrile or 1,4-dioxane, whereas the change in solvent is accompanied by a red shift of the long wavelength band in the triplet state spectrum of compound II. This red shift probably arises from the formation of exciplexes of compound II in its lowest triplet state with 1,4-dioxane and acetonitrile. In their lowest triplet state the compounds I and IV evidently do not form thermally stable exciplexes with the solvent.

In a previous paper [1] we reported quenching of the normal and the anomalous fluorescence of DMABN by electron acceptors such as SF_6 and CCl_4 , which is accompanied by formation of the radical cation of DMABN. Here we shall consider the reaction of DMABN in its triplet state T_0 and in its exciplex state 1E_2 in acetonitrile with CCl_4 in order to obtain another estimate of the quantum yield Φ_{ion}^m .

Figure 8 shows that the reduction of the lifetime of the triplet state absorption by CCl_4 at 500 nm is accompanied by an enhancement of the long-lived absorption at the same wavelength originating from the radical cation $DMABN^+$. Figure 9 displays the absorbance of the radical cation at 150 ns after termination of the laser excitation when the solution contains no CCl_4 and also when it contains 7×10^{-3} M CCl_4 and the remaining conditions are the same in the two cases. This proves that there are two pathways to the radical cation, one independent of the presence of CCl_4 and the other involving an interaction with CCl_4 . The radical anion CCl_4^- formed in the electron transfer reaction with the exciplex disproportionates into a CCl_3 radical and the ion Cl^- [12]. Since in the presence of CCl_4 no decay of the

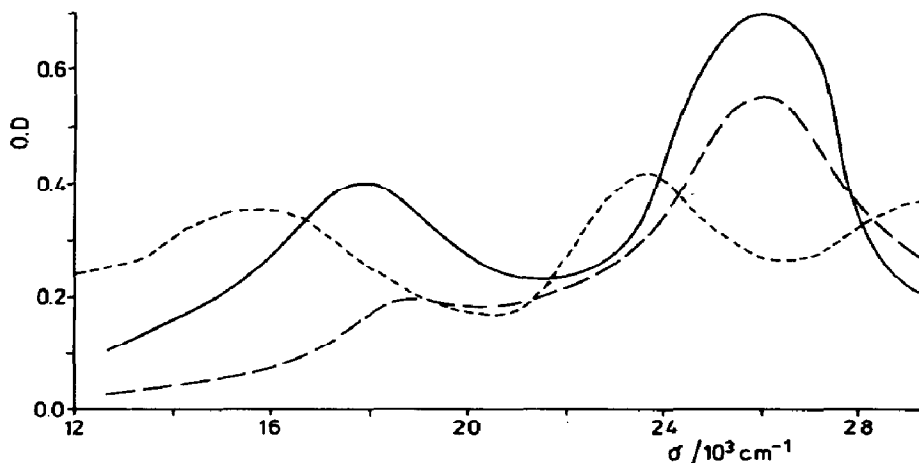


Fig. 7. Triplet-triplet absorption spectra of the solutions in 1,4-dioxane: —, DMABN; ---, 3,5-TMABN; - · - ·, 1M6CTHQ.

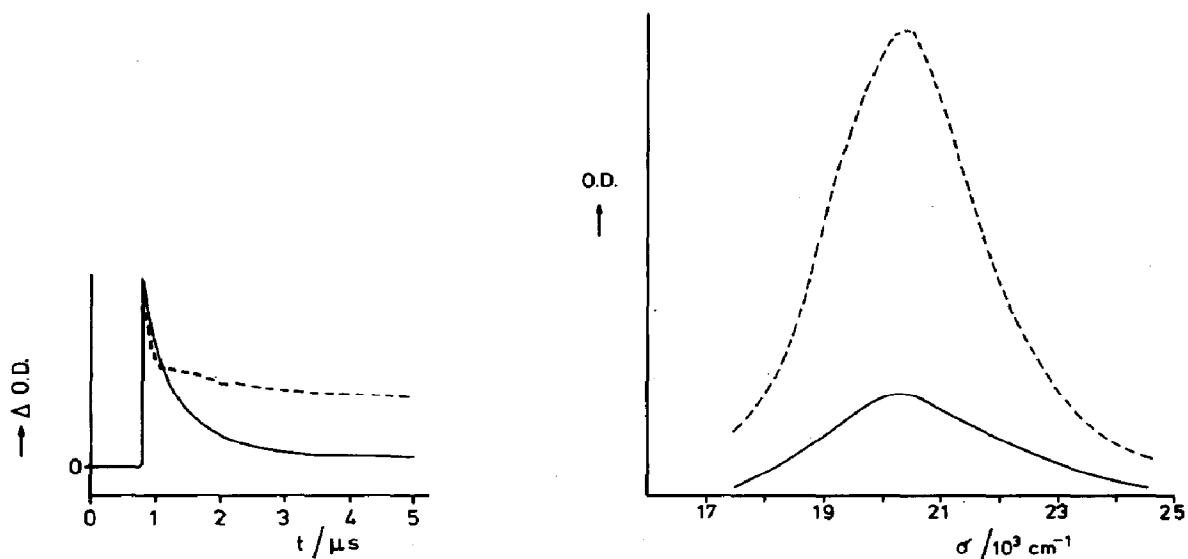
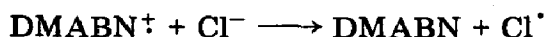


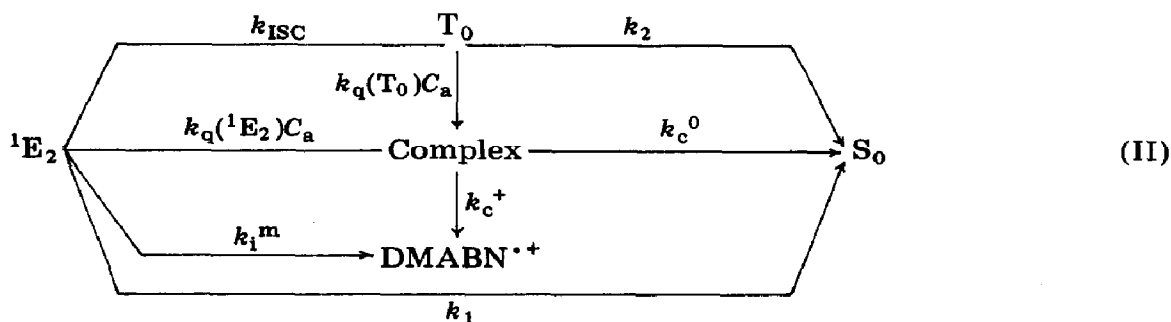
Fig. 8. Transient absorption signal of a solution of DMABN in acetonitrile at 500 nm. The fast decaying component is due to the triplet state and the slowly decaying component is due to the radical cation: —, without CCl_4 ; ---, with a concentration of $5 \times 10^{-4} \text{ M CCl}_4$.

Fig. 9. Spectrum of the radical cation of DMABN in acetonitrile: —, without CCl_4 ; ---, with a concentration of $7 \times 10^{-3} \text{ M CCl}_4$.

absorption due to the cations is observed for at least $100 \mu\text{s}$ we conclude that the anions $(\text{CH}_3\text{CN})_2^-$ or O_2^- which are formed via direct ionic dissociation of the exciplex transfer their charge to CCl_4 , resulting in the single neutralization reaction



which is expected to be much slower than the neutralization of the cation by $(\text{CH}_3\text{CN})_2^-$ or O_2^- . The enhancement of the radical ion yield by CCl_4 could also be detected as an enhancement of the transient electrical conductance of the solution. Mechanism (II) describes how the radical cation is formed and may be used to express the quantum yield of ions in terms of rate constants and the concentration C_a of the electron acceptor EA.



The enhancement in the quantum yield of the radical cation owing to the presence of EAs will be denoted $\Delta\Phi_{\text{ion}}^m$. According to mechanism (II) it is given by

$$\Delta\Phi_{\text{ion}}^m = \frac{\beta k_q(^1E_2)C_a}{k_q(^1E_2)C_a + K} + \Phi(T_0) \frac{\beta k_q(T_0)C_a}{k_q(T_0)C_a + k_2} \quad (5)$$

where

$$\Phi(T_0) = \frac{k_{\text{ISC}}}{k_q(^1E_2)C_a + K} \quad (6)$$

$$K \equiv k_i^m + k_1 + k_{\text{ISC}} \quad (7)$$

and

$$\beta \equiv \frac{k_c^+}{k_c^+ + k_c^0} \quad (8)$$

From the quenching of the anomalous fluorescence we obtain the rate constant $k_q(^1E_2)$ for the reaction of CCl_4 with the exciplex 1E_2 and from the reduction of the lifetime of T_0 we obtain the rate $k_q(T_0)$ for reaction of CCl_4 with the triplet state molecule. The values obtained are $k_q(^1E_2) = 1.7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_q(T_0) = 1.0 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The values $k_1 + k_i^m = 1.5 \times 10^8 \text{ s}^{-1}$ and $k_{\text{ISC}} = 1 \times 10^8 \text{ s}^{-1}$ have been determined previously [3] and our present work yields $k_2 = 2.9 \times 10^7 \text{ s}^{-1}$. If the values of the rate constants just quoted are entered into eqns. (4) - (6), it may be shown that $1/\Delta\Phi_{\text{ion}}^m$ varies almost linearly with $1/C_a$ at least in the range $0 \leq C_a \leq 10^{-1} \text{ M}$. This is illustrated in Fig. 10, where values of $1/\Delta\Phi_{\text{ion}}^m$ calculated via eqn. (5) are

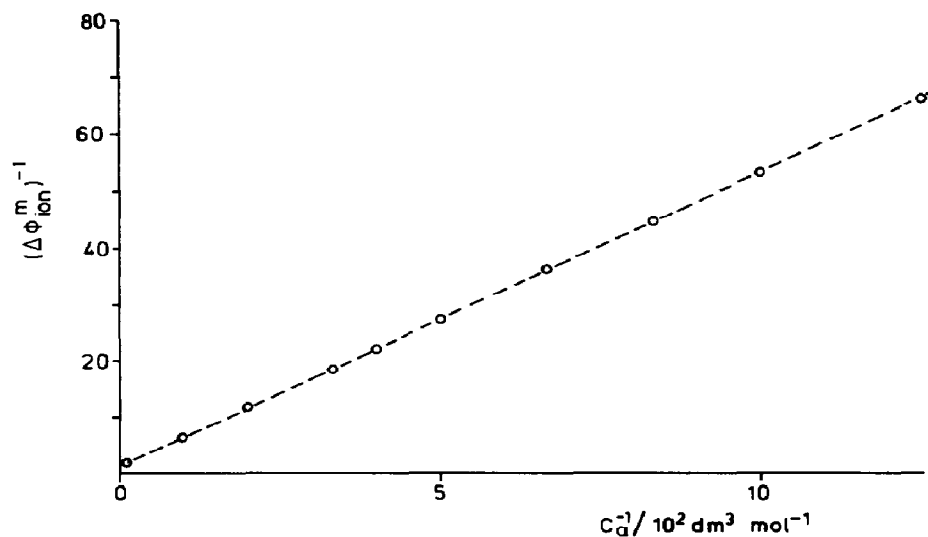


Fig. 10. Inverse of the increase $\Delta\Phi_{\text{ion}}^m$ in the quantum yield Φ_{ion}^m of the radical cations of DMABN in acetonitrile as a function of the reciprocal concentration $1/C_a$ of CCl_4 , calculated according to eqn. (5).

plotted *versus* $1/C_a$. From this we predict that plots of $\Delta j(0)^{-1}$ and of $\Delta OD_{\text{ion}}(500 \text{ nm})^{-1}$ *versus* $1/C_a$ are linear within the specified range of C_a , where $\Delta j(0)$ and $\Delta OD_{\text{ion}}(500 \text{ nm})$ are the enhancements in $j(0)$ and $OD_{\text{ion}}(500 \text{ nm})$ respectively, caused by EAs.

Figures 11 and 12 show that the predicted behaviour is found experimentally. The intercepts in these figures yield $\Delta j(0, C_a = \infty)^{-1}$ and $\Delta OD(500 \text{ nm}, C_a = \infty)^{-1}$ respectively. These results enable the determination of Φ_{ion}^m . Using Fig. 12 we may determine Φ_{ion}^m as

$$\frac{\Phi_{\text{ion}}^m}{\beta} = \frac{OD(500 \text{ nm}, C_a = 0)}{\Delta OD(500 \text{ nm}, C_a = \infty)} \quad (9)$$

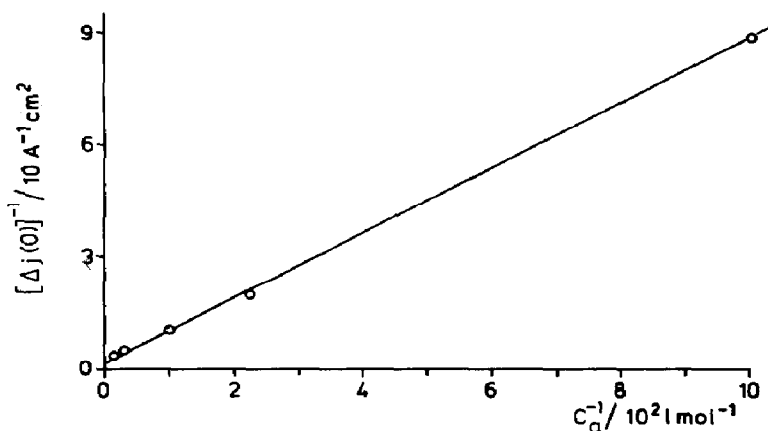


Fig. 11. Reciprocal value of the transient electrical conduction $\Delta j(0)^{-1}$ induced by a reaction of excited states of DMABN in acetonitrile with CCl_4 as a function of the reciprocal concentration $1/C_a$ of CCl_4 .

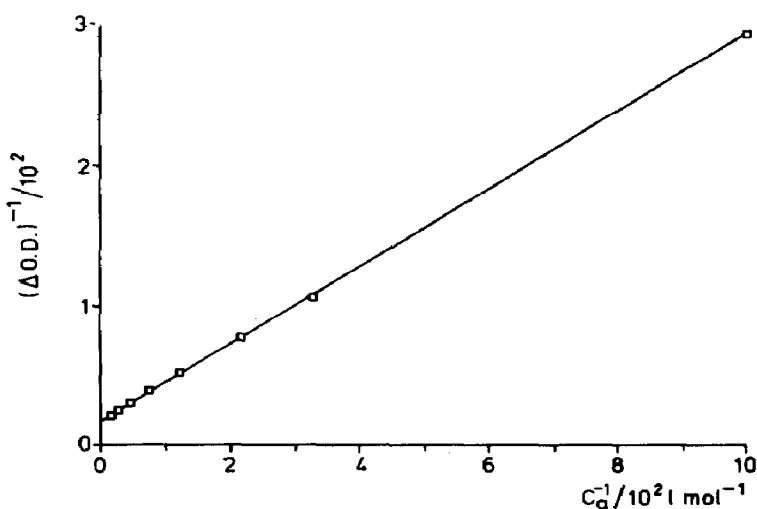


Fig. 12. Reciprocal value ΔOD^{-1} of the absorption of the radical cation of DMABN in acetonitrile at 500 nm produced by a reaction of excited states with CCl_4 as a function of the reciprocal concentration $1/C_a$ of CCl_4 .

In this manner we get $\Phi_{\text{ion}}^{\text{m}} = 5 \times 10^{-2}$ when $\beta = 1$. Using Fig. 11 we may determine $\Phi_{\text{ion}}^{\text{m}}$ via

$$\frac{j(0, C_a = 0)}{\Delta j(0, C_a = \infty)} = \frac{\alpha \Phi_{\text{ion}}^{\text{m}}}{\beta} \quad (10)$$

where α is defined by

$$\alpha \equiv \frac{\mu(\text{DMABN}^+) + \mu(\text{O}_2^-)}{\mu(\text{DMABN}^+) + \mu(\text{Cl}^-)} \quad (11)$$

The values of the mobilities in eqn. (11) are given above except for $\mu(\text{Cl}^-)$ which has the experimental value $9.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [13]. It turns out that the factor α is equal to unity and eqn. (10) yields $\Phi_{\text{ion}}^{\text{m}} = 7 \times 10^{-2}$ when $\beta = 1$. The values of $\Phi_{\text{ion}}^{\text{m}}$ obtained via eqn. (9) and via eqn. (10) should be compared with its value of 1.3×10^{-2} derived earlier. This comparison shows that the efficiency parameter β has to have a value of 0.2 rather than unity to obtain agreement between the results from the three different methods of estimating $\Phi_{\text{ion}}^{\text{m}}$.

3.2. Solutions of DMABN and 1M6CTHQ in mixtures of 1,4-dioxane and water

Previously we have suggested that the low quantum yield of the anomalous fluorescence of DMABN in mixtures of water and 1,4-dioxane (which has a dielectric constant larger than 30) might be the consequence of competition between anomalous fluorescence and photoinduced formation of ions [1]. Here we provide evidence against this suggestion. In Table 2 we give the quantum yields $\Phi_{\text{F}}(\text{N})$ and $\Phi_{\text{F}}(^1\text{E}_2)$ of the normal and exciplex fluorescence respectively, the lifetime $\tau_{\text{F}}(^1\text{E}_2)$ of the exciplex fluorescence and the radiationless and radiative decay rate constants $k_{\text{d}}(^1\text{E}_2)$ and $k_{\text{F}}(^1\text{E}_2)$

TABLE 2

Quantum yield $\Phi_{\text{F}}(\text{N})$ of the normal fluorescence, quantum yield $\Phi_{\text{F}}(^1\text{E}_2)$, lifetime $\tau_{\text{F}}(^1\text{E}_2)$, radiative rate constant $k_{\text{F}}(^1\text{E}_2)$ and non-radiative rate constant $k_{\text{d}}(^1\text{E}_2)$ of the solute-solvent exciplex $^1\text{E}_2$ of DMABN (I) in a solvent mixture of 1,4-dioxane and water

[H ₂ O] (vol.%)	$\Phi_{\text{F}}(\text{N})$	$\Phi_{\text{F}}(^1\text{E}_2)$	$\tau_{\text{F}}(^1\text{E}_2)$ (ns)	$k_{\text{F}}(^1\text{E}_2)$ (s ⁻¹)	$k_{\text{d}}(^1\text{E}_2)$ (s ⁻¹)
0	0.035	0.034	4.0	1×10^7	2.4×10^8
4.75	7×10^{-3}	0.025	3.9	6.4×10^6	2.5×10^8
9.1	3×10^{-3}	0.021	3.8	5.5×10^6	2.6×10^8
20	1.3×10^{-3}	0.0136	2.5	5.4×10^6	4.0×10^8
33	8×10^{-4}	0.089	2.0	4.5×10^6	5.0×10^8
50	4×10^{-4}	0.0040	1.5	2.7×10^6	6.6×10^8
67	2.4×10^{-4}	0.0022	1.2	1.8×10^6	8.3×10^8
80	1.9×10^{-4}	0.0011	0.8	1.4×10^6	1.2×10^9
100	1.5×10^{-4}	0.0004	0.3	1.3×10^6	3.3×10^9

respectively of 1E_2 , in solutions of DMABN in mixtures of 1,4-dioxane and water. The table shows that a decrease in $k_F({}^1E_2)$ occurs with increasing polarity of the solvent mixture. This effect of solvent polarity has also been noted in the case of solutions of DMABN in mixtures of cyclohexane and propionitrile [3]. The rate constant $k_d({}^1E_2)$ of DMABN increases rapidly with the increasing concentration C_{H_2O} of water in the solvent mixture. The increase in k_d with C_{H_2O} is much larger in the case of 1M6CTHQ, as is evident from Table 3 and Fig. 13.

The transient optical absorptions of degassed solutions of the two compounds in water reveal two different transient species in each case, namely one with a lifetime of about 1 μ s and another with a lifetime of more than

TABLE 3

Quantum yield $\Phi_F(N)$ of the normal fluorescence, quantum yield $\Phi_F({}^1E_1)$, lifetime $\tau_F({}^1E_1)$, radiative rate constant $k_F({}^1E_1)$ and non-radiative rate constant $k_d({}^1E_1)$ of the solute-solvent exciplex 1E_1 of 1M6CTHQ (IV) in a solvent mixture of 1,4-dioxane and water

[H ₂ O] (vol.%)	$\Phi_F({}^1E_1)$	$\tau_F({}^1E_1)$ (ns)	$k_F({}^1E_1)$ (s ⁻¹)	$k_d({}^1E_1)$ (s ⁻¹)
0	0.36	2.9	1.24×10^8	2.2×10^8
4.75	0.30	2.4	1.25×10^8	2.9×10^8
9.1	0.22	2.0	1.11×10^8	3.9×10^8
16.7	0.13	1.0	1.3×10^8	8.7×10^8
28.5	0.062	0.5	1.2×10^8	1.9×10^9
50	0.022	0.18 ^a		5.4×10^9 ^a
67	0.008	0.067 ^a		1.5×10^{10} ^a
83	0.004	0.033 ^a		3×10^{10} ^a
100	0.002	0.016 ^a		6×10^{10} ^a

^aCalculated assuming $k_F({}^1E_1) = 1.25 \times 10^8$ s⁻¹.

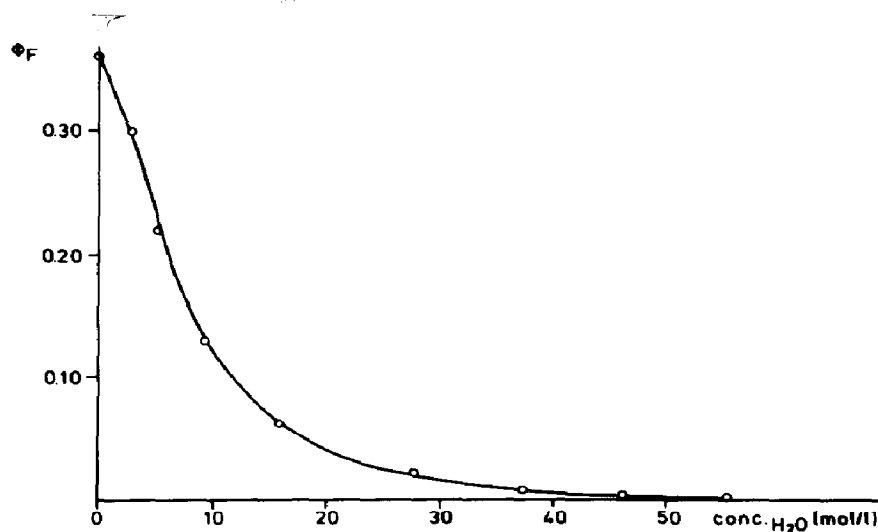


Fig. 13. Quantum yield of fluorescence of solutions of compound IV in mixtures of 1,4-dioxane and water as a function of the water concentration.

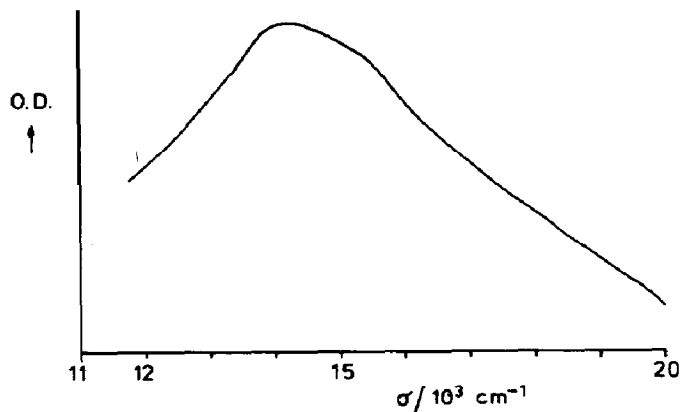


Fig. 14. Spectrum of the solvated electron in water produced by laser excitation of a solution of DMABN in water.

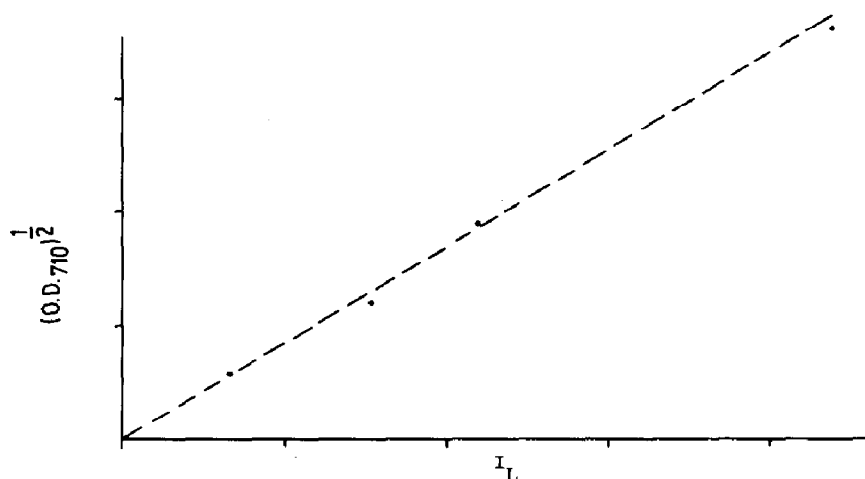


Fig. 15. Square root of the transient absorption of the solvated electron at 710 nm of a solution of DMABN in water as a function of the intensity of the laser.

20 μ s. The spectrum of the short-lived component of the transient absorption of a solution of DMABN in water is shown in Fig. 14. Based on its absorption spectrum, the short-lived component may be assigned to the solvated electron. The long-lived component of the spectrum is the same as the absorption spectrum of the solute in its triplet state T_0 in acetonitrile. The absorption of solvated electrons is very strong in the case of DMABN in water and the absorbance is proportional to I_L^2 as illustrated in Fig. 15. From this we infer that the solvated electrons are formed by absorption of two photons per molecule. Solutions of 1M6CTHQ in water reveal a transient absorption by solvated electrons and a transient conduction signal which are much weaker than in the case of DMABN in water and consequently they cannot be studied as a function of I_L over a large range. However, we could observe a reduction in the transient absorption of the solvated

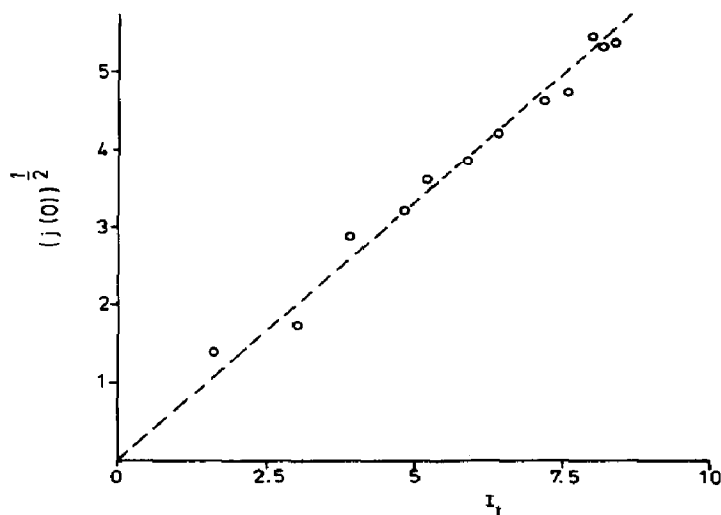


Fig. 16. Square root of the initial transient conduction $j(0)$ of a solution of DMABN in water as a function of the intensity I_L of the laser pulse.

electrons by a factor of 4 when I_L was reduced by a factor of 2. This suggests that a two-photon process is also involved in the generation of the ions in the case of 1M6CTHQ in water.

The observed proportionality between $j(0)$ and I_L^2 for solutions of DMABN in water does not exclude the possibility that single-photon ionization also takes place in this case. The contribution of the single-photon process to $j(0)$ at our largest value of I_L is estimated at most to be 10%, based on the experimental inaccuracy in $j(0)$ and I_L used to obtain Fig. 16. Since the values of $j(0)$ for the solutions of DMABN in water and in acetonitrile are nearly equal at our largest value of I_L we conclude that the contribution to Φ_{ion}^m from the single-photon process is at most of the order of 10^{-3} in the case of DMABN in water. Therefore the large value of $k_d(^1E_2)$ found for DMABN in water does not arise from efficient single-photon ionization. However the rate constant k_i^m may have the same value in both the case of water and acetonitrile solutions.

From the estimated contribution of the single-photon ionization process we may obtain an upper limit for the value of k_i^m for the solution of DMABN in water, by using a value of 300 ps for the lifetime $\tau_F(^1E_2)$ of the exciplex 1E_2 . Since the single-photon contribution to ionization is equal to the product of k_i^m and $\tau_f(^1E_2)$ according to mechanism (II), we obtain $k_i^m \leq 3 \times 10^6 \text{ s}^{-1}$. Note that $k_i^m = 3 \times 10^6 \text{ s}^{-1}$ is found for the solution of DMABN in acetonitrile.

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