

ELECTROGENERATED CHEMILUMINESCENCE. EFFECT OF A MAGNETIC FIELD ON THE DELAYED FLUORESCENCE AND ECL OF SEVERAL SYSTEMS INVOLVING EXCIMERS OR EXCIPLEXES

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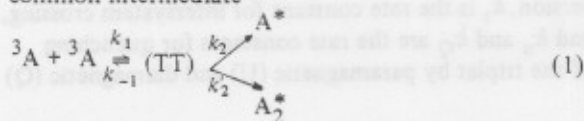
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The use of magnetic field effects in delayed fluorescence (DF) and electrogenerated chemiluminescence (ECL) studies to obtain information about the involvement of triplet state species in reactions leading to the production of monomeric and dimeric (excimer or exciplex) excited states is described. In the room temperature DF of pyrene and 1,2-benzanthracene, identical field effects are observed for monomer and excimer emission, in agreement with a mechanism involving a common intermediate produced on triplet-triplet annihilation (TTA), and different than previous DF results for 1,2-benzanthracene solutions at low temperatures. The ECL of the pyrene/*N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) system also shows monomer and excimer emissions identically affected by magnetic field and in agreement with an ECL mechanism involving TTA. In the ECL of the 9-methylanthracene (MA)/tri-*p*-tolylamine (TPTA) system, a field effect is observed for both the $^1\text{MA}^*$ and longer wavelength emission. In this case, however, a smaller effect is observed for the longer wavelength emission. A mechanism based on TTA to form $^1\text{MA}^*$ and some direct formation of exciplex on electron transfer is proposed.

1. Introduction

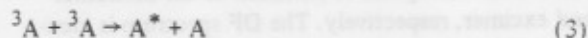
Previous investigations of the effect of an external magnetic field on delayed fluorescence (DF) in fluid solution [1-3] and on the emission resulting from electron transfer reactions of electrogenerated radical ions (ECL) [4-8] have been interpreted by a decrease in the rate of the reaction of two triplets to form an excited singlet (triplet-triplet annihilation or TTA) and in the rate of quenching of the triplet state by paramagnetic species (radical ions or oxygen) with increasing magnetic field. Several DF studies, especially those of pyrene [9-12], and several chemiluminescence and ECL investigations [13-18] have demonstrated the production of excited state dimeric species (excimers and exciplexes). In DF these species arise from TTA, but whether excimers arise via a common intermediate



or by a route in which the excimer dissociates to form an excited singlet state



which can also be formed by a long-range interaction process



has been the subject of some controversy. Recently Wyrsh and Labhart [19] studied the DF of 1,2-benzanthracene at low temperatures (-70 to -170°C) and reported that the effect of magnetic field on the DF of the monomer (excited singlet) (DFM) was different from that of the excimer (DFD). They concluded that a mechanism involving a common TTA process, such as (1), cannot be the main route at low temperatures. The effect of magnetic field on the relative emission of monomers and exciplexes in chemiluminescence studies has also been reported [17].

We report here studies of the effect of a magnetic field on the DF of pyrene (P) and 1,2-benzanthracene

(BA) and on the ECL of a P/N,N,N',N'-tetramethyl-*p*-phenylenediamine (TMPD) system at ambient temperatures in which identical effects on monomer and excimer emission are observed. We also describe some experiments on the effect of a magnetic field on the ECL of a 9-methylanthracene (MA)/tri-*p*-tolylamine (TPTA) system, where monomer and excimer emissions are found.

2. Experimental

The apparatus and techniques employed in the DF and ECL studies are the same as those previously described [3, 5-7]; a detailed description of the experimental methods is available [20]. Vacuum line techniques were used in preparation of all solutions and freeze-pump-thaw cycles were employed for deaeration.

3. Results and discussion

3.1. Delayed fluorescence of pyrene and 1,2-benzanthracene

Magnetic field effects on the DF of P in N,N-dimethylformamide (DMF) and acetonitrile (AN) solutions have previously been described [2]. In the study described here cyclohexane was employed as the solvent, because somewhat greater field effects are observed in it. The prompt fluorescence spectrum of P shows two major peaks at about 390 and 460 nm which correspond to emission of the monomer and excimer, respectively. The DF spectrum is identical to that for prompt fluorescence, except that the ratio of excimer to monomer emission is larger in the DF spectrum for 1 mM solutions at room temperature. The effect of a magnetic field on the monomer and excimer DF of pyrene is shown in fig. 1a. As observed in other DF studies in fluid solutions in the absence of paramagnetic quenchers, a monotonic decrease of intensity is observed with increasing field; in this case the relative DF monomer and excimer intensities are essentially the same, within experimental precision. BA shows similar behavior. The monomer and excimer DF of BA occur at 407 and 540 nm, respectively. Application of a magnetic field (fig. 1b)

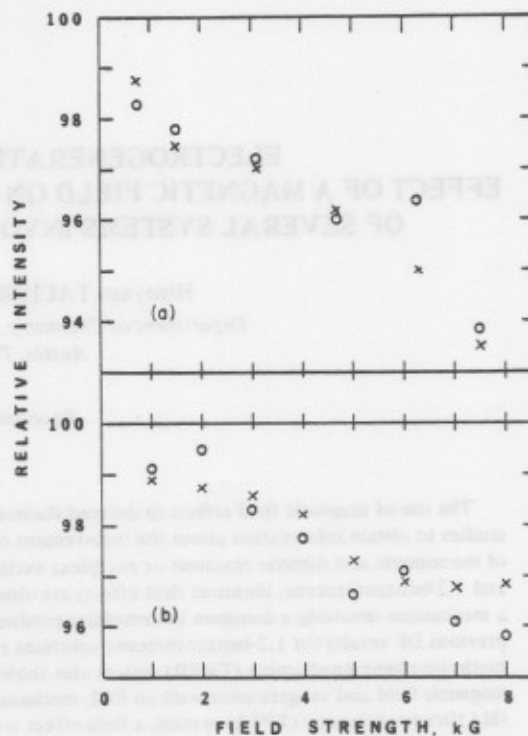
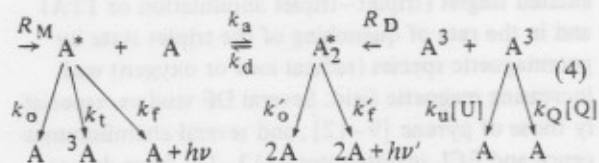


Fig. 1. Magnetic field effects on monomer and excimer DF from (a) 1 mM pyrene, in cyclohexane. \circ : monomer (393 nm), \times : excimer (470 nm). (b) 2.3×10^{-4} M 1,2-benzanthracene in cyclohexane. \circ : monomer (386 nm), \times : excimer (550 nm).

causes an identical decrease in relative intensity for both emissions.

The steady-state treatment of a system exhibiting monomer and excimer emission can be based on the following scheme [9-11, 14]:



where k_f and k'_f are the rate constants for the radiative transitions of the monomer and excimer, k_o and k'_o are the respective rate constants for radiationless conversion, k_t is the rate constant for intersystem crossing, and k_u and k_Q are the rate constants for quenching of the triplet by paramagnetic (U) and diamagnetic (Q)

quenchers. R_M and R_D are the rate of formation of the excited monomer (A^*) and excimer (A_2^*), respectively, by any route. The ratio of excimer to monomer emission ϕ_D/ϕ_M is given by

$$\frac{\phi_D}{\phi_M} = \frac{k_f'}{k_f} \frac{\tau_D}{1 + \alpha \tau_D k_d} \left[\frac{\alpha}{\tau_M} + (1 + \alpha) k_a [A] \right], \quad (5)$$

where $\tau_D^{-1} = k_f' + k_0' + k_d$, $\tau_M^{-1} = k_f + k_0 + k_t$, and $\alpha = R_D/R_M$. Within the theory of magnetic field effects on DF [3, 21] only rate constants for energy transfer processes involving a change of multiplicity are affected by a magnetic field. Thus, only α and k_u in the above scheme can be field dependent (Faulkner and Bard [1] showed that k_t is probably not field dependent by observing identical behavior in the normal and sensitized DF of anthracene). For the scheme of eq. (1) and assuming that only pair states with singlet character can form A^* or A_2^* , the overall annihilation rate constants producing A^* and A_2^* , $\gamma(H)$ and $\gamma'(H)$, respectively are

$$\gamma(H) = \frac{1}{3} k_1 k_2 f(H), \quad (6)$$

$$\gamma'(H) = \frac{1}{3} k_1 k_2' f(H), \quad (7)$$

where the field dependent term $f(H)$ is given by

$$f(H) = \sum_{l=1}^9 \frac{S_l^2}{k_{-1} + (k_2 + k_2') S_l^2} \quad (8)$$

(S_l is the amplitude of the singlet component of the l th pair state, $1 \leq l \leq 9$). Thus, since $R_M = \lambda T^2$ and $R_D = \lambda' T^2$, $\alpha = k_2'/k_2$, independent of field. The mechanism shown by eqs. (2) and (3) would show identical field effects only if the nature of the triplet-triplet interaction in (2) and (3) were very similar. Since (3) is assumed to be a long-range interaction, a different dependency might be expected. Recently Wyrsh and Labhart [22] found no evidence for a long-range, viscosity independent, mechanism leading to TTA in a study of the BA system. Note that if (2) were the only path to emission by A^* and A_2^* , no magnetic field dependence on ϕ_D/ϕ_M would be expected, since α would approach infinity and ϕ_D/ϕ_M would become independent of α . This last possibility is not likely, however, since finite α -values (e.g., $\alpha = 2$ for pyrene DF at room temperature [11]) are usually found.

3.2. ECL of the pyrene-TMPD system

The ECL of mixtures of P and TMPD, resulting from the electron transfer reaction between P^- and TMPD^{\ddagger} to produce triplet P, followed by TTA and leading to emission from monomer and excimer has previously been described [14]. The relevant electrochemical and spectroscopic data for this system are E_{pc} (peak potential for reduction of P to P^-) = -2.07 V versus S.C.E., E_{pa} (peak potential for oxidation of TMPD to TMPD^{\ddagger}) = +0.22 V versus S.C.E., E_s (energy level of P first excited singlet) = 3.34 eV, E_T (P triplet energy level) = 2.095 eV [23]. Thus the enthalpy of the radical ion electron transfer reaction (ΔH^0), -2.13 eV [5], is sufficient to produce the triplet level of P, but not the excited singlet, and the reaction proceeds via the TTA (the T-route), as previously deduced from rotating ring-disc electrode measurements [14]:



The effect of a magnetic field on monomer and excimer ECL (fig. 2) shows the enhancement of ECL intensity with field usually observed. Moreover, the behavior of the monomer and excimer emission is the same, within the experimental uncertainty. The following equation has been proposed [3] for the variation of ECL intensity (in the limit of strong triplet quenching) with magnetic field:

$$\frac{I(H)}{I(0)} = r_\gamma(H) \left[\frac{[U] + q}{r_u(H)[U] + q} \right]^2, \quad (11)$$

where $r_\gamma(H) = \gamma(H)/\gamma(0)$, $r_u(H) = k_u(H)/k_u(0)$, and $q = k_Q Q/k_u(0)$ [see eq. (4)]. The larger field effect observed for the 1:1 P to TMPD mixture (fig. 2a) compared with the 5:1 mixture (fig. 2b) probably reflects a greater concentration of the paramagnetic quencher, $[u]$, (TMPD^{\ddagger}) in the ECL reaction layer in the former case; in the 5:1 mixture case the excess of P^- is more effective in removing TMPD^{\ddagger} . This argument supposes, however, that TMPD^{\ddagger} is a more effective quencher of triplets than P^- . As concerns the relative emission from monomer and excimer, eq. (5) still applies, and hence the constancy of I_D/I_M with field is consistent

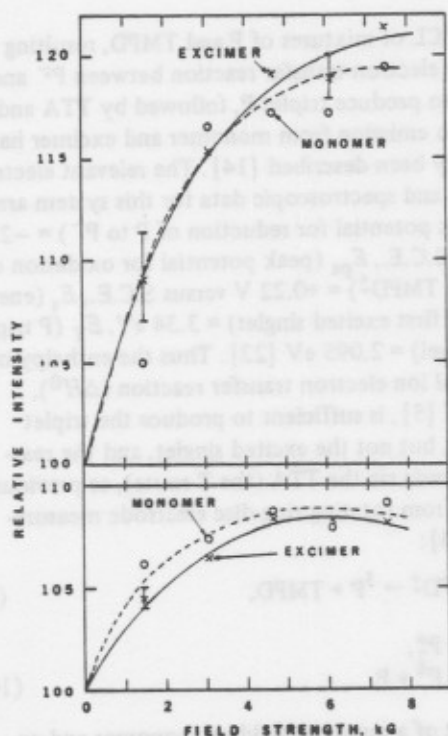


Fig. 2. Magnetic field effects on monomer and excimer ECL from (a) 1 mM pyrene, 1 mM TMPD and 0.1 M TBAP in DMF. (b) 5 mM pyrene, 1 mM TMPD and 0.1 M TBAP in DMF.

with the DF results and demonstrates that there is no route to production of excimer other than TTA.

3.3. ECL of the MA-TPTA system

The chemiluminescence resulting upon reaction of 9-methylanthracene (MA) radical anion and tri-*p*-tolylamine (TPTA) radical cation (in the form of the solid $\text{TPTA}^+ \text{ClO}_4^-$) in a tetrahydrofuran (THF) medium, described by Weller and Zachariasse [16, 17], shows emission both from the excited singlet state of MA and from an exciplex (or hetero-excimer) of MA and TPTA. The authors concluded from a study of the relative emission from exciplex to monomer as a function of solvent and temperature that the exciplex is formed mainly by the direct reaction of MA^- and TPTA^+ and $^1\text{MA}^*$ is formed by thermal dissociation of the exciplex

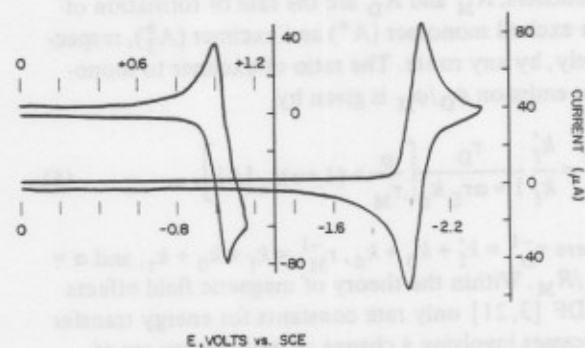
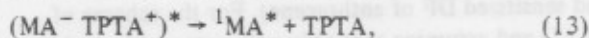
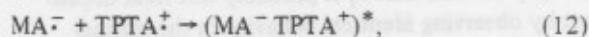


Fig. 3. Cyclic voltammogram of 1 mM MA, 1 mM TPTA and 0.1 M TBAP in THF.



with TTA processes playing only a negligible role at room temperature. In a preliminary experiment, Zachariasse [17] reported that the relative intensities of monomer and exciplex emission were unchanged by a magnetic field of 1.4 kG (absolute intensities could not be determined), in agreement with this mechanism. We report here ECL studies of this system in THF solutions, where magnetic field effects are observed.

Electrochemical data, collected from cyclic voltammetry of the MA/TPTA system in THF containing 0.2 M TBAP (fig. 3), and energy levels of MA and TPTA are shown in table 1. The ECL spectrum obtained from this solution, obtained by repetitive stepping between -2.34 and $+1.05$ V versus S.C.E., with a step duration of 50 msec, is identical to the prompt fluo-

Table 1
Electrochemical and spectroscopic data ^{a)}

Substance	E_p (V versus S.C.E.)	ΔE_p (mV)	Energy levels	
			E_s (eV)	E_t (eV)
MA	-1.97 (MA/MA ⁻)	60	3.20 ^{b)}	1.81 ^{c)}
TPTA	+1.01 (TPTA/TPTA ⁺)	60	3.51 ^{c)}	2.96 ^{c)}

^{a)} Electrochemical data for a solution containing 1 mM each MA and TPTA in THF - 0.2 M TBAP.

^{b)} Obtained by averaging the 0-0 band of the absorption and emission spectrum of 0.1 mM MA in hexane.

^{c)} From ref. [17].

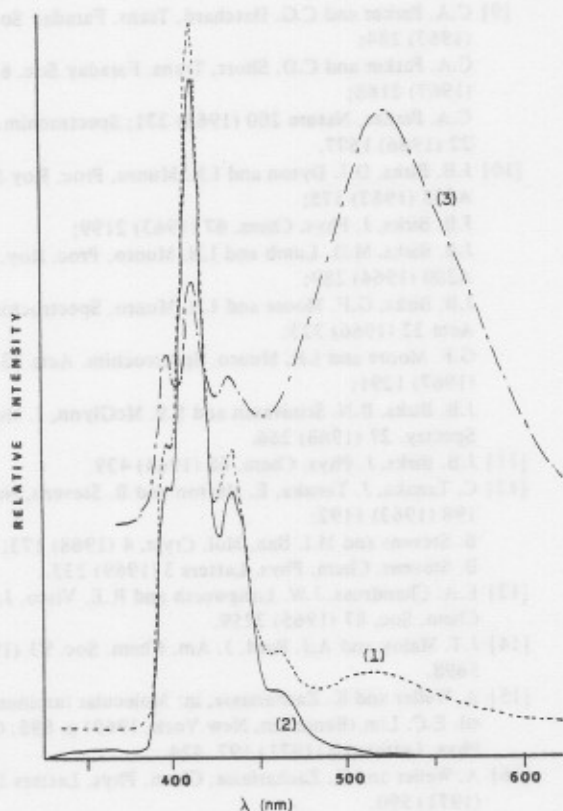


Fig. 4. (1) ECL spectrum of 1 mM MA, 1 mM TPTA and 0.1 M TBAP in THF. (2) Fluorescence spectrum of 1 mM MA, 1 mM TPTA and 0.1 M TBAP in THF. (3) Chemiluminescence spectrum from the reaction of MA^- in THF with solid TPTA^+Cl^- at 20°C obtained by Weller and Zachariasse [16].

rescence spectrum obtained with the same solution, except that the ECL spectrum also shows a broad peak with a maximum at about 520 nm (fig. 4). This peak occurs at the same wavelength, as the exciplex peak observed in the CL experiment of Weller and Zachariasse [16], but is of lower intensity compared to the monomer peak. The effect of magnetic fields up to 7.5 kG on both the 415 nm and 520 nm peaks in the ECL spectrum is shown in fig. 5. The intensities of both peaks are increased with increasing fields, however, the maximum relative intensity of the 415 nm (monomer) peak is about 10% while that of the 520 nm (exciplex) peak is only 5 to 6%.

Since the reaction enthalpy of the $\text{MA}^-/\text{TPTA}^+$ system is about -2.82 eV, the electron transfer reaction

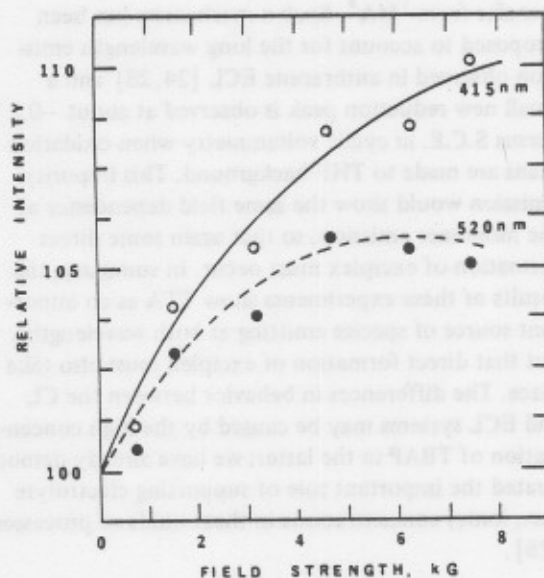
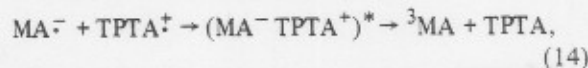


Fig. 5. Magnetic field effects on (○) 415 nm and (●) 520 nm ECL emission from 1 mM MA, 1 mM TPTA and 0.2 M TBAP in THF.

does not have sufficient energy to form $^1\text{DMA}^*$ directly, but can form ^3DMA . The field effect shown by the monomer peak suggests a large contribution to emission at this wavelength by the T-route:



However, the magnetic field effect shown for the 520 nm peak also implicates triplets in the reactions leading to this emission. One possibility is that some of the emission observed at 520 nm results from excimers of MA [i.e., $(\text{MA})_2^*$] formed on TTA; the smaller magnetic field effect observed for this peak is then accounted for by the combined emission of directly-formed exciplex [eq. (12)] (not field dependent) and excimer (field dependent). One could also invoke some contribution of mixed TTA to the formation of an exciplex, however, this appears unlikely, since the electron-transfer reaction has insufficient energy to produce $^3\text{TPTA}$, and the lifetime of this species is probably very small in this solution. Another possibility is that there is a contribution to the long wavelength peak from a decomposition product of either TPTA^+ or THF oxidation which is excited by energy

transfer from $^1MA^*$. Such a mechanism has been proposed to account for the long wavelength emission observed in anthracene ECL [24, 25] and a small new reduction peak is observed at about -0.2 V versus S.C.E. in cyclic voltammetry when oxidation scans are made to THF background. This impurity emission would show the same field dependence as the monomer emission, so that again some direct formation of exciplex must occur. In summary, the results of these experiments show TTA as an important source of species emitting at both wavelengths, but that direct formation of exciplex must also take place. The differences in behavior between the CL and ECL systems may be caused by the high concentration of TBAP in the latter; we have already demonstrated the important role of supporting electrolyte (i.e., ionic) concentrations in these kinds of processes [26].

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References

- [1] L.R. Faulkner and A.J. Bard, *J. Am. Chem. Soc.* 91 (1969) 6495, 6497.
- [2] H. Tachikawa and A.J. Bard, *J. Am. Chem. Soc.* 95 (1973) 1672.
- [3] H. Tachikawa and A.J. Bard, *Chem. Phys. Letters* 26 (1974) 10.
- [4] L.R. Faulkner and A.J. Bard, *J. Am. Chem. Soc.* 91 (1969) 209.
- [5] L.R. Faulkner, H. Tachikawa and A.J. Bard, *J. Am. Chem. Soc.* 94 (1972) 691.
- [6] H. Tachikawa and A.J. Bard, *Chem. Phys. Letters* 19 (1973) 287.
- [7] H. Tachikawa and A.J. Bard, *Chem. Phys. Letters* 26 (1974) 246.
- [8] N. Periasamy, S.J. Shah and K.S.V. Santhanam, *J. Chem. Phys.* 58 (1973) 821.
- [9] C.A. Parker and C.G. Hatchard, *Trans. Faraday Soc.* 59 (1963) 284; C.A. Parker and C.D. Short, *Trans. Faraday Soc.* 63 (1967) 2168; C.A. Parker, *Nature* 200 (1963) 231; *Spectrochim. Acta* 22 (1966) 1677.
- [10] J.B. Birks, D.J. Dyson and I.H. Munro, *Proc. Roy. Soc. A* 725 (1963) 575; J.B. Birks, *J. Phys. Chem.* 67 (1963) 2199; J.B. Birks, M.D. Lumb and I.H. Munro, *Proc. Roy. Soc. A* 280 (1964) 289; J.B. Birks, G.F. Moore and I.H. Munro, *Spectrochim. Acta* 22 (1966) 323; G.F. Moore and I.H. Munro, *Spectrochim. Acta* 23A (1967) 1291; J.B. Birks, B.N. Srinivasan and S.P. McGlynn, *J. Mol. Spectry.* 27 (1968) 266.
- [11] J.B. Birks, *J. Phys. Chem.* 68 (1964) 439.
- [12] C. Tanaka, J. Tanaka, E. Hutton and B. Stevens, *Nature* 198 (1963) 1192; B. Stevens and M.I. Ban, *Mol. Cryst.* 4 (1968) 173; B. Stevens, *Chem. Phys. Letters* 3 (1969) 233.
- [13] E.A. Chandross, J.W. Longworth and R.E. Visco, *J. Am. Chem. Soc.* 87 (1965) 3259.
- [14] J.T. Maloy and A.J. Bard, *J. Am. Chem. Soc.* 93 (1971) 5698.
- [15] A. Weller and K. Zachariasse, in: *Molecular luminescence*, ed. E.C. Lim (Benjamin, New York, 1969) p. 895; *Chem. Phys. Letters* 10 (1971) 197, 424.
- [16] A. Weller and K. Zachariasse, *Chem. Phys. Letters* 10 (1971) 590.
- [17] K. Zachariasse, Ph.D. Thesis, Free University, Amsterdam (1972).
- [18] C.P. Keszthelyi and A.J. Bard, *Chem. Phys. Letters* 24 (1974) 300.
- [19] D. Wyrsh and H. Labhart, *Chem. Phys. Letters* 8 (1971) 217.
- [20] H. Tachikawa, Ph.D. Dissertation, The University of Texas (1973).
- [21] R.E. Merrifield, *J. Chem. Phys.* 48 (1968) 4318; V. Ern and R.E. Merrifield, *Phys. Rev. Letters* 19 (1967) 285.
- [22] D. Wyrsh and H. Labhart, *Chem. Phys. Letters* 10 (1971) 197.
- [23] M. Zander, *Phosphorimetry* (Academic Press, New York, 1969).
- [24] L.R. Faulkner and A.J. Bard, *J. Am. Chem. Soc.* 90 (1968) 6284.
- [25] T.C. Werner, J. Chang and D.M. Hercules, *J. Am. Chem. Soc.* 92 (1970) 763.
- [26] C.P. Keszthelyi, N.E. Tokel-Takvorian, H. Tachikawa and A.J. Bard, *Chem. Phys. Letters* 23 (1973) 219.