RELATIONSHIP BETWEEN THE QUANTUM YIELDS OF ELECTRON PHOTOEJECTION AND FLUORESCENCE OF AROMATIC CARBOXYLATE ANIONS IN AQUEOUS SOLUTION[†]

G. KÖHLER, S. SOLAR and N. GETOFF

Institut für theoretische Chemie und Strahlenchemie der Universität Wien, Währingerstrasse 38, A-1090 Vienna (Austria)

A. R. HOLZWARTH and K. SCHAFFNER

Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34 - 36, D-4330 Mülheim an der Ruhr (F.R.G.)

(Received July 3, 1984)

Summary

The quantum yield $\phi(e_{aq})$ of photoejected electrons from aromatic carboxylate anions in aqueous solutions (pH 9.5 - 12.3) appreciably increases with increasing excitation energy; for example, $\phi(e_{aq})$ for benzoate is 0.0025 for the S_1 state (excitation at 254 nm) and 0.0048 for the S_2 state (excitation at 214 nm). The $\phi(e_{aq})$ value also increases with the number of CH_2 groups separating the phenyl and carboxylate groups; for example, for phenylbutyrate $\phi(e_{aq})$ is 0.05 for the S_1 state and 0.010 for the S_2 state. Furthermore, increases of $\phi(e_{aq})$ are linked with decreases in the quantum yield of fluorescence. In order to evaluate a possible consumption of the photoejected electrons by the ground state carboxylates, the rate constants $k(e_{aq} + \text{substrate})$ for the reaction of solvated electrons with the corresponding substrates were determined.

1. Introduction

In previous qualitative flash photolysis experiments with various substituted aromatic compounds in aqueous solution the appearance of a strong absorption above 600 nm was attributed to the formation of solvated electrons (e_{aq}) [1 - 3]. These studies attracted considerable attention, particularly in view of the possibility of determining the quantum yield $\phi(e_{aq})$ of photoinduced electron ejection from phenols [4 - 8], anisole [9, 10], monophenylphosphate [11, 12], aromatic amines [13 - 15], β-naphthol [16, 17], indoles [18 - 24], formate anion [25], amino acids [26 - 30],

---

[†]Dedicated to Professor Dr. Dietrich Schulte-Frohlinde on the occasion of his 60th birthday.

flavines [31], thiazine [32] and acridine dyes [33]. For phenol and the aromatic amines it was shown that the electrons are emitted from the excited singlet manifold in a one-quantum process, and that the process is roughly inversely proportional to the fluorescence properties [8, 12, 14, 15, 24, 34]. It was established that temperature [35] and solvent polarity [36] have a strong effect on $\phi(e_{aq})$.

The present work is focused on the determination of e_{aq} formed by excitation to the first and second excited singlet states S_1 and S_2 of some simple aromatic carboxylate anions in aqueous solution. Moreover, the fluorescence quantum yields $\phi(F)$ of these substrates were studied as a function of the excitation energy λ_{exc} with respect to a possible relationship between $\phi(e_{aq})$ and $\phi(F)$. This study is of particular relevance to the photophysical and photochemical primary processes of aromatic amino acids.

2. Experimental details

2.1. Preparation of solutions

The aromatic carboxylic acids (reagent grade; Merck) were purified by repeated zone refining. Sodium acetate (reagent grade; Merck) was used as supplied. Benzene, after shaking with concentrated H_2SO_4, and toluene were distilled under argon and over metallic sodium in concentric-tube columns. tert-Butyl alcohol was purified by zone refining. The aqueous solutions were prepared with water which had been freshly distilled at least four times, and they were saturated with either argon or N_2O for about 1 h prior to irradiation. In order to remove traces of oxygen from the gases, they were first passed through columns containing Oxisorb (Messer-Griesheim G.m.b.H., Vienna).

2.2. Light sources and actinometry for steady state experiments

All solutions were irradiated in a double-walled immersion well vessel (volume, 150 ml) at 30 ± 0.5 °C [18, 37, 38]. The light source for 254 nm radiation was a low pressure mercury lamp (Osram HNS 10 W ozone-free) incorporating a Vycor filter to remove the 185 nm line. Deoxygenated 1 M aqueous $ClCH_2CO_2H$ at 30 °C with $\phi(Cl^-) = 0.34$ [39] was used as an actinometer. A light intensity I_0^{254} of 6.2×10^{17} quanta ml^{-1} min^{-1} was measured. Zinc and cadmium lamps (Philips) provided light of wavelengths 214 nm and 228 nm respectively. The potassium ferrioxalate system [40] was used for the actinometry of these lamps, giving $I_0^{214} = 2 \times 10^{16}$ quanta ml^{-1} min^{-1} and $I_0^{228} = 1 \times 10^{16}$ quanta ml^{-1} min^{-1} respectively. The intensity of each lamp was periodically checked.

2.3. Determination of $\phi(e_{aq})$

In the first series of experiments, the quantum yields $\phi(e_{aq})$ of solvated electrons photoejected from the aromatic carboxylates (2×10^{-3} - 2×10^{-2}

M; pH 9.5 - 12.3) were determined with N_2O (2.3×10^{-2} M at 30 °C), which is transparent to light of the wavelengths used, as an electron scavenger.

$$N_2O + e_{aq} \longrightarrow N_2 + OH + OH^- \qquad (1)$$

with $k = 0.91 \times 10^{10}$ l mol^{-1} s^{-1} [41].

In order to prevent an attack by OH on the substrate, 10^{-2} - 1 M *tert*-butyl alcohol was added to the solutions (k(OH + *tert*-C$_4$H$_9$OH) = 5.5×10^8 l mol^{-1} s^{-1} [42]).

The $\phi(e_{aq})$ (= $\phi(N_2)$) and $\phi(H_2)$ values of each aromatic carboxylate were determined from the yields of molecular nitrogen and hydrogen (measured using a Perkin–Elmer Fraktometer 116E with molecular sieves) at various UV doses. They were derived from the slopes of the straight lines in the quantum yield *versus* UV dose plots. The following corrections were made: (a) the quantum yields of molecular nitrogen and hydrogen obtained in parallel runs (blank solutions without the substrate but otherwise identical) were subtracted from the corresponding yields obtained in the presence of the substrate; (b) corrections for incomplete light absorption.

In a second series of experiments $\phi(e_{aq})$ was determined by measuring the Cl$^-$ ions produced by the reaction of e_{aq} with 2-chloroethanol:

$$ClCH_2CH_2OH + e_{aq} \longrightarrow Cl^- + \cdot CH_2CH_2OH \qquad (2)$$

where $k = (2.0 \pm 0.2) \times 10^8$ l mol^{-1} s^{-1} [29, 36]. In these cases solutions containing 5×10^{-3} M substrate and 5×10^{-2} M 2-chloroethanol were used [29, 30, 36].

2.4. Determination of k(e_{aq} + carboxylate)

In principle, reaction of the ejected electrons with the aromatic carboxylate may compete with the reaction with the electron scavenger (N_2O or $ClCH_2CH_2OH$), which would result in a decrease of $\phi(e_{aq})$. In order to evaluate this possible effect, the absolute rate constants k(e_{aq} + carboxylate) were determined by pulse radiolysis using a 3 MeV Van de Graaff electron accelerator. The dose varied from 5 to 10 J kg^{-1} (0.5 - 1 krad) per 0.4 μs electron pulse depending on the substrate concentration. The solutions containing 10^{-4} - 10^{-2} M carboxylate and 0.1 M *tert*-butyl alcohol as an OH scavenger (pH 9 - 11.5) were purged with high purity argon for about 1 h prior to irradiation. Details of the pulse radiolysis facility and the dosimetry are given in ref. 43. The rate constants for the e_{aq} attack on the carboxylates were determined by following the pseudo-first-order decay of e_{aq} at 720 nm (λ_{max} of e_{aq}) and correcting for the reactivity of e_{aq} with *tert*-butyl alcohol.

2.5. Fluorescence

The fluorometer facility used in most of the experiments is described in ref. 7. The relative intensity $I(\lambda_{exc})$ of the exciting light was monitored by means of a deaerated 10^{-2} M solution of 2,5-diphenyloxazole (Merck) in cyclohexane. In order to obtain corrected fluorescence spectra directly some measurements were performed using a computerized Spex Fluorolog instru-

ment [44]. The carboxylates (aqueous $2 \times 10^{-5} - 10^{-3}$ M solutions; pH around 9) were excited to the first and second excited singlet states S_1 and S_2.

3. Results and discussions

3.1. The reactivity of e_{aq} with some aromatic carboxylate anions

The absolute rate constants $k(e_{aq} + RCOO^-)$ for the reaction of e_{aq} with each aromatic carboxylate anion are mean values of at least 10 separate determinations and are given in Table 1. The k values of some related substances are also given for comparison.

With the exception of *tert*-butyl alcohol[†] our values are in good agreement with literature data where available. Furthermore, the k values of benzene, toluene and all carboxylates except benzoate are of the same order of magnitude.

TABLE 1

Absolute rate constants k for the reaction of e_{aq} with aromatic carboxylates and with some model compounds (pH 9 - 11.5) in aqueous solution

Substrate (S)	$k(e_{aq} + S)$ (l mol^{-1} s^{-1})	
	This work	Literature data
Benzoate ion	$(3.0 \pm 0.1) \times 10^9$	3.1×10^9 (pH 11) [45]
Phenylacetate ion	$(1.6 \pm 0.1) \times 10^7$	5.1×10^7 (pH 5.43) [46]
Phenylpropionate ion	$(1.4 \pm 0.1) \times 10^7$	—
Phenylbutyrate ion	$(1.3 \pm 0.1) \times 10^7$	—
tert-Butyl alcohol	$(4 \pm 1) \times 10^5$	10^8 (pH 6 - 12) [47]
Benzene	$(0.9 \pm 0.2) \times 10^7$	1.4×10^7 (pH 11) [48]
Toluene	$(1.45 \pm 0.1) \times 10^7$	1.2×10^7 (pH 11) [48]
Acetate ion	$(1.1 \pm 0.2) \times 10^6$	1.2×10^6 (pH 10.5) [49]
2-Chloroethanol	$(2.0 \pm 0.2) \times 10^8$	2.0×10^8 [29, 36]

Calculations using the concentrations employed (less than 10^{-2} M), the measured $k(e_{aq} + RCOO^-)$ values (Table 1), and the known $k(e_{aq} + N_2O)$ and $k(e_{aq} + ClCH_2CH_2OH)$ data show that the electrons photochemically ejected from the carboxylates will be quantitatively scavenged by N_2O and $ClCH_2CH_2OH$. Hence, the measured N_2 and Cl^- yields should equal those of e_{aq}, *i.e.* $\phi(N_2) = \phi(Cl^-) = \phi(e_{aq})$. The H_2 yields were negligible throughout ($\phi \leqslant 10^{-3}$).

[†]We believe that the high k value which has previously been reported [47] for *tert*-butyl alcohol (Table 1) should be attributed to insufficient purification of the sample.

3.2. Photoejection of electrons from the S_1 and S_2 states

The $\phi(e_{aq})$ values obtained in aqueous solution for the aromatic carboxylate anions (pH $\approx$ 7 - 12.3; 30 °C) on excitation to the S_1 (λ_{exc} = 254 nm) and S_2 (228 and 214 nm) states are given in Table 2 as mean values of five to ten determinations, using either of the two electron scavengers.

TABLE 2

Quantum yields $\phi(e_{aq})$ of photoejected electrons obtained from aromatic carboxylates in aqueous solution on excitation to the first (S_1 at 254 nm) and second absorption (S_2 at 228 and 214 nm) bands at 30 °C

Substrate	pH	λ_{exc} (nm)	$\phi(N_2) = \phi(e_{aq})^a$
Benzoate ion	12.3	254	0.0025
Benzoate ion	$\approx$ 7	228	0.0030
Benzoate ion	9.5	214	0.0048
Phenylacetate ion	9.5	254	0.0030
Phenylacetate ion	$\approx$ 7	228	0.0050
Phenylacetate ion	9.5	214	0.0064
Phenylpropionate ion	12.3	254	0.0080
Phenylpropionate ion	$\approx$ 7	228	0.0110
Phenylpropionate ion	12.3	214	0.0250
Phenylbutyrate ion	11.7	254	0.0100
Phenylbutyrate ion	11.7	214	0.0290
Formate ion	> 7	185 (S_1)	0.060 [25]

[a]The error limits are less than 10%. The values at pH $\approx$ 7 were obtained using 2-chloroethanol only.

Two pronounced effects are observed: (a) the $\phi(e_{aq})$ values are higher at higher excitation energies; (b) with the lengthening of the side chain $\phi(e_{aq})$ increases and approaches the value for formate (Table 2). When 2-chloroethanol was used as an electron scavenger, the $\phi(e_{aq})$ values for phenylbutyrate ion were significantly lower (0.005 at 254 nm and 0.01 at 228 nm) than those obtained with N_2O. This can be explained by the fact that $k(e_{aq} + ClCH_2CH_2OH)$ is much lower than $k(e_{aq} + N_2O)$. As a consequence, 2-chloroethanol can be expected to react exclusively with e_{aq}, whereas N_2O may occasionally also abstract small amounts of electrons from excited substrate molecules. Furthermore, the UV dose was considerably higher using N_2O as an electron scavenger. Hence electron ejection from photolytical products could also contribute to the yields in this case.

3.3. $\phi(F)$ dependence on excitation energy

The carboxylic group of aromatic acids is known to have a strong effect on the fluorescence quantum yield [50 - 53]. Benzoic acid has been widely reported to be non-fluorescent [52, 54, 55]. However, fluorescence of the monomeric form at room temperature in aqueous (pH < 6) and ethanolic

solutions has been reported more recently [53]. The emission is strongly influenced by pH, buffer, solute concentration and solvent nature. Differences in the behaviour of the dissociated and acid forms have been attributed to the inversion of the $^1(\pi,\pi^*)$ and $^3(n,\pi^*)$ states. With the lengthening of the $(CH_2)_n$ chain separating the two chromophores, $\phi(F)$ increases in ethanol and in acidic aqueous solutions, and for $n = 4$ it is about equal to the value for toluene [52]. The fluorescence yield has also been claimed [51] to increase on dissociation and to reach a maximum value for the carboxylate anion at pH $\geqslant$ 7. For phenylacetate it was found to be about equal to that of toluene [51].

In the present work the fluorescence quantum yields were measured at various excitation energies $\phi(F; \lambda_{exc})$ and were normalized to the fluorescence efficiencies $\phi(F)$ for excitation to the S_1 state. These relative yields are expressed [6, 7] as

$$\phi^{rel}(\lambda_{max}) = \frac{\phi(F; \lambda_{exc})}{\phi(F)} \qquad (3)$$

The $\phi^{rel}(\lambda_{max})$ values obtained for the phenylacetate and phenylpropionate anions are shown in Figs. 1 and 2 respectively; the fluorescence of the benzoate anion in aqueous solution (pH $\geqslant$ 7) was too weak for a meaningful study. The $\phi(F)$ values in the two figures are quite constant within the first and second absorption bands S_1 and S_2, but in the S_1-S_2 overlap region they decrease with increasing excitation energy by 20% for phenylacetate and by 30% for phenylpropionate and phenylbutyrate. The $\phi(F)$ values for S_2 of phenylpropionate and phenylbutyrate are quite close to those of phenylalanine [19] and toluene [14].

As already pointed out, wavelength effects have previously been observed for the fluorescence quantum yields of phenols, aromatic amines, indoles etc. [8, 12, 14, 24, 34]. The yields of some of these compounds
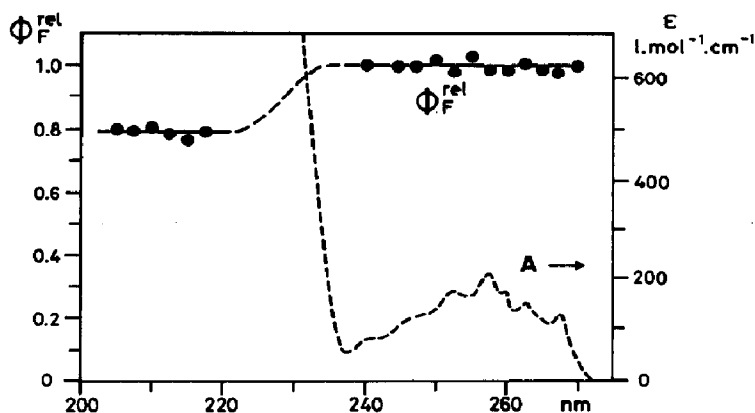

Fig. 1. Fluorescence quantum yield ϕ_F^{rel} of phenylacetate anion (PAA) in aqueous solution as a function of the excitation wavelength for excitation from 240 to 270 nm (7.6×10^{-4} M PAA (pH 8.7)) and for 205 to 217 nm (2.3×10^{-5} M PAA) (fluorescence emission, λ_{em} = 285 nm): A, absorption spectrum of PAA in water (pH 8.7).
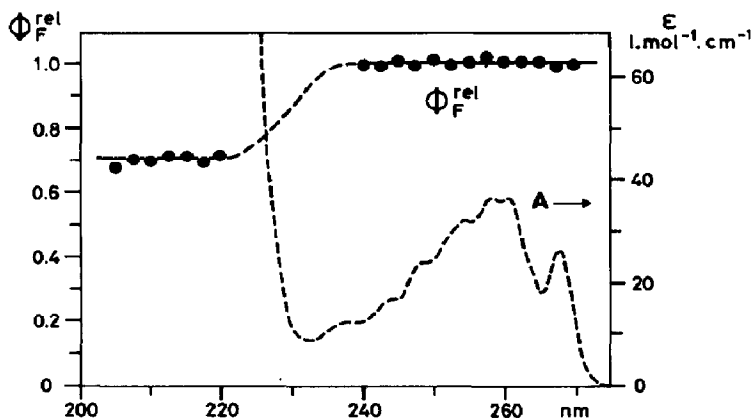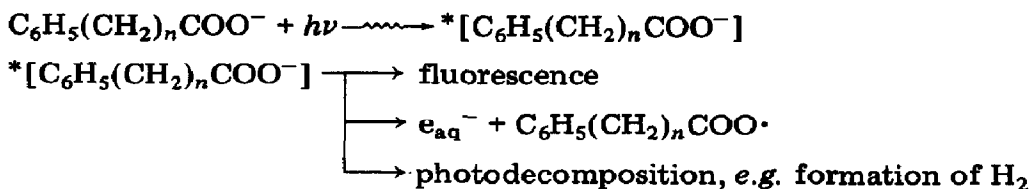
Fig. 2. Fluorescence quantum yield ϕ_F^{rel} of phenylpropionate anion (PPA) in aqueous solution as a function of the excitation wavelength for excitation from 240 to 270 nm (6×10^{-4} M PAA (pH 9)) and for 205 to 220 nm (2×10^{-5} M PPA) (fluorescence emission, λ_{em} = 283 nm): A, absorption spectrum of PPA in water (pH 9).

appear to be independent of excitation wavelength within a given absorption band but to differ for the corresponding excited states, *i.e.* $\phi(F; S_1)$ is greater than $\phi(F; S_2)$. The electron ejection efficiency of the same substances was found to behave in an approximately inverse fashion, increasing with excitation energy between the S_1 and S_2 absorptions and compensating at least partly for the fluorescence decrease in the same energy range.

The wavelength dependence of the emission efficiency observed here for phenylacetate and phenylpropionate seems to follow a similar pattern. Figures 1 and 2 clearly indicate that the fluorescence quantum yields are again independent of excitation wavelength within a given excited state, but differ for the excited state configurations ($\phi(F; S_{1(n,\pi*)})$ is greater than $\phi(F; S_{2(\pi,\pi*)})$). The quantum yields of the electron photoejection may follow a parallel trend, with ample precedent for selective photoprocesses from the upper excited states [56]. However, the data available at present for λ_{exc} values of 254, 228 and 214 nm, although compatible, are not as yet conclusive on this point.

Since the electron ejection efficiency is generally smaller than the difference between the $\phi(F)$ values of the two excited states, additional processes must compete with the relaxation of the initially excited state level to the lowest-lying fluorescent level. These may be photoreactions which selectively occur from the higher excited state [56], for example the formation of hydrogen in the present case:

$$C_6H_5(CH_2)_n COO^- + h\nu \longrightarrow {}^*[C_6H_5(CH_2)_n COO^-]$$

$${}^*[C_6H_5(CH_2)_n COO^-] \begin{cases} \longrightarrow \text{fluorescence} \\ \longrightarrow e_{aq}^- + C_6H_5(CH_2)_n COO \cdot \\ \longrightarrow \text{photodecomposition, } e.g. \text{ formation of } H_2 \end{cases}$$

Acknowledgments

References

1 G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, *61* (1965) 708.
2 L. I. Grossweiner and H.-I. Joschek, *Adv. Chem. Ser.*, *50* (1965) 279.
3 H.-I. Joschek and L. I. Grossweiner, *J. Am. Chem. Soc.*, *88* (1966) 3261.
4 R. Leschlaux and J. Joussot-Dubien, in J. B. Birks (ed.), *Organic Molecular Photophysics*, Wiley, New York, 1973, p. 457.
5 J. Feitelson, E. Hayon and A. Teinin, *J. Am. Chem. Soc.*, *95* (1973) 1025.
6 G. Köhler and N. Getoff, *Chem. Phys. Lett.*, *26* (1974) 525.
7 G. Köhler and N. Getoff, *J. Chem. Soc., Faraday Trans. I*, *72* (1976) 2101.
8 G. Grabner, G. Köhler, J. Zechner and N. Getoff, *Photochem. Photobiol.*, *26* (1977) 449.
9 H.-I. Joschek and L. I. Grossweiner, *Z. Naturforsch.*, *24b* (1969) 562.
10 G. Grabner, W. Rauscher, J. Zechner and N. Getoff, *J. Chem. Soc., Chem. Commun.*, (1980) 222.
11 N. Getoff and S. Solar, *Monatsh. Chem.*, *105* (1974) 241.
12 G. Köhler and N. Getoff, *J. Chem. Soc., Faraday Trans. I*, *74* (1978) 1029.
13 J. Zechner, L. S. Prangova, G. I. Grabner and N. Getoff, *Z. Phys. Chem. N.F.*, *102* (1976) 137.
14 G. Köhler, C. Rosicky and N. Getoff, in B. Pullman and N. Goldblum (eds.), *Excited States in Organic Chemistry and Biochemistry*, Reidl, Dordrecht, 1977, p. 303.
15 G. Köhler and N. Getoff, *J. Chem. Soc., Faraday Trans. I*, *76* (1980) 1576.
16 M. Ottolenghi, *J. Am. Chem. Soc.*, *85* (1963) 3557.
17 C. R. Goldschmidt and G. Stein, *Chem. Phys. Lett.*, *6* (1970) 299.
18 H. B. Steen, *J. Chem. Phys.*, *61* (1974) 3997.
19 I. Tatischeff and R. Klein, in J. B. Birks (ed.), *Excited States of Biological Molecules*, Wiley, New York, 1974, p. 375.
20 I. Tatischeff and R. Klein, *Photochem. Photobiol.*, *22* (1975) 221.
21 J. Zechner, G. Köhler, N. Getoff, I. Tatischeff and R. Klein, *J. Photochem.*, *9* (1978) 304.
22 D. Grand, A. Bernas and E. Amouyal, *Chem. Phys.*, *44* (1979) 73.
23 A. Bernas, D. Grand and E. Amouyal, *J. Phys. Chem.*, *84* (1980) 1259.
24 J. Zechner, G. Köhler, N. Getoff, I. Tatischeff and R. Klein, *Photochem. Photobiol.*, *34* (1981) 163.
25 J. Zechner and N. Getoff, *Radiat. Phys. Chem.*, *6* (1974) 215.
26 V. D. Bent and E. Hayon, *J. Am. Chem. Soc.*, *97* (1975) 2599.
27 U. Lachish, A. Schaffermann and G. Stein, *J. Chem. Phys.*, *64* (1976) 4205.
28 G. Köhler, J. Zechner, G. Grabner and N. Getoff, *Proc. 7th Int. Congr. on Photobiology, Rome, 1976*, p. 11.
29 G. Köhler, G. Grabner, J. Zechner and N. Getoff, *J. Photochem.*, *17* (1981) 21.
30 G. Grabner and N. Getoff, *Proc. 9th IUPAC Symp. on Photochemistry, Pau, 1982*.
31 N. Getoff, S. Solar and D. B. McCormick, *Science*, *201* (1978) 616.
32 W. Vonach and N. Getoff, *J. Photochem.*, *23* (1983) 233.
33 W. Vonach and N. Getoff, to be published.
34 J. Zechner, G. Köhler, G. Grabner and N. Getoff, *Can. J. Chem.*, *58* (1980) 2006.

35 J. Zechner, G. Köhler, G. Grabner and N. Getoff, *Chem. Phys. Lett.*, *37* (1976) 297.
36 G. Grabner, G. Köhler, J. Zechner and N. Getoff, *J. Phys. Chem.*, *84* (1980) 3000.
37 N. Getoff, *Monatsh. Chem.*, *99* (1968) 136.
38 N. Getoff and G. O. Schenck, *Photochem. Photobiol.*, *8* (1968) 167.
39 M. Neumann-Spallart and N. Getoff, *Monatsh. Chem.*, *106* (1975) 1359.
40 G. G. Hatchard and G. A. Parker, *Proc. R. Soc. London, Ser. A*, *235* (1956) 518.
41 E. Janata and R. H. Schuler, *J. Phys. Chem.*, *86* (1977) 2078.
42 M. Gohn and N. Getoff, *J. Chem. Soc., Faraday Trans. I*, *73* (1977) 1207.
43 N. Getoff and F. Schwörer, *Radiat. Res.*, *41* (1970) 1.
44 A. R. Holzwarth, H. Lehner, S. E. Braslavsky and K. Schaffner, *Justus Liebigs Ann. Chem.*, (1978) 2002.
    S. E. Braslavsky, A. R. Holzwarth, E. Langer, H. Lehner, J. I. Matthews and K. Schaffner, *Isr. J. Chem.*, *20* (1980) 196.
45 M. Anbar and E. J. Hart, *J. Phys. Chem.*, *69* (1965) 973.
46 A. Szutka, J. K. Thomas, S. Gordon and E. J. Hart, *J. Phys. Chem.*, *69* (1965) 289.
47 V. Gold and J. H. Rolston, *J. Chem. Soc., Chem. Commun.*, (1970) 208.
48 M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, *86* (1964) 5633.
49 M. Anbar and E. J. Hart, *J. Phys. Chem.*, *69* (1965) 271.
50 A. White, *Biochem. J.*, *71* (1959) 217.
51 J. Tournon and M. A. El-Bayoumi, *J. Am. Chem. Soc.*, *93* (1971) 6396.
52 J. Tournon and M. A. El-Bayoumi, *J. Chem. Phys.*, *56* (1972) 5128.
53 R. Martin and G. A. Clarke, *J. Phys. Chem.*, *82* (1978) 81.
54 S. K. Lower and M. A. El-Sayed, *Chem. Rev.*, *66* (1966) 199.
55 R. S. Becker, *Theory and Interpretation of Fluorescence and Phosphorescence*, Wiley-Interscience, New York, 1969, p. 156.
56 N. J. Turro, V. Ramamurthy, W. Cherry and W. Farneth, *Chem. Rev.*, *78* (1978) 125.