# ELECTRON PHOTOEJECTION FROM DONOR–ARYL–ACCEPTOR MOLECULES IN AQUEOUS SOLUTION

GOTTFRIED KÖHLER and NIKOLA GETOFF

*Institute of Theoretical Chemistry and Radiation Chemistry, University of Vienna, and Ludwig Boltzmann Institute for Radiation Chemistry, Währingerstrasse 38, A-1090 Vienna (Austria)*

KRYSTYNA ROTKIEWICZ and ZBIGNIEW R. GRABOWSKI

*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44, 01-224 Warsaw (Poland)*

## Summary

The effects of the excitation wavelength on the quantum yields $Q(e_{aq}^-)$ and $Q_F$ of electron ejection and fluorescence respectively were measured for 4-cyano-$N,N$-dimethylaniline (CDMA) and related compounds in aqueous solutions. In the case of CDMA no electron ejection was found for excitation of the long-wavelength ($^1L_a$, $^1L_b$) band system. At shorter wavelengths ($\lambda_{exc} < 270$ nm) $Q(e_{aq}^-)$ increases gradually whereas $Q_F$ decreases. The quantum yields level off at excitation within the third absorption band. This shows that internal charge transfer (twisted intramolecular charge transfer formation) is not accompanied by charge transfer to the solvent. At higher excitation energies electron ejection competes with internal conversion.

## 1. Introduction

Molecules of the donor–acceptor type often undergo a relaxation from the excited singlet state to a highly polar state [1]. The dual fluorescence of 4-cyano-$N,N$-dimethylaniline (CDMA) and its derivatives in polar solvents [2] has led to the discovery of twisted intramolecular charge transfer (TICT) excited states [3]. A TICT state is characterized by a mutually perpendicular orientation of the donor and acceptor subsystems in the molecule and by full charge separation [4]. The high dipole moment of such states is demonstrated by the pronounced solvent effect. On increasing the polarity of the solvent, the quantum yield of the normal emission at short wavelengths (band b) decreases, whereas a new band at longer wavelengths (band a) is observed. Band a is assigned to the TICT state. In aqueous solutions of CDMA, however, the yield of both emissions is very low [5, 6].

Previous investigations of the nature of the TICT states of substituted $N,N$-dialkylanilines, in which the amino group attains a conformation

orthogonal to the benzene ring, led first to a hypothesis relating them to the Rydberg or "Rydberg-like" states of aliphatic amines [7 - 11]. However, there is now ample evidence demonstrating that the TICT states are not in general derived from the Rydberg states [4]. Nevertheless, in molecules like the benzoquinuclidine derivatives, with a cage amine built into the molecule, a Rydberg admixture to the excited state can be assumed. Rydberg states have been characterized as "stepping stones towards ionization" [12].

In contrast, photoejection of electrons in polar media and the formation of solvated electrons $e_{aq}^-$ and radical cations have been observed for benzene derivatives with an electron-donating substituent such as phenol or aniline [13 - 17]. Electrons are emitted from the relaxed lowest excited singlet states, but their yield increases at higher energies. Concomitant with this rise in the efficiency of photoelectron ejection the yield of fluorescence emission decreases for aqueous solutions of, for example, anilines [16, 18], phenols [19] and monophenyl phosphate [20] as well as of indole and its derivatives [21]. Apart from a recent report of photoconductivity in a methanol solution of CDMA irradiated with a 308 nm laser pulse [22], nothing is known about the formation of $e_{aq}^-$ from molecules with both electron-donating and electron-accepting subsystems. Hence this process has been investigated for CDMA and related compounds in aqueous solution as a function of the excitation energy and is related to the fluorescence yields.

## 2. Experimental details

CDMA (Fluka, pure) was crystallized from n-hexane. 3-Methyl-4-cyano-N,N-dimethylaniline (MCDMA) and 5-cyano-N-methylindoline (CMI) were prepared and purified as previously described [7]. 6-Methylbenzoquinuclidine (MBQ) was obtained as one of the intermediate stages in the synthesis of 6-cyanobenzoquinuclidine [23]. N,N-dimethylaniline (DMA) (Merck; pro analysi grade) was purified by distillation under reduced pressure. The solutions were prepared using water that had been distilled at least four times. The fluorescence facility has been described earlier [19].

Steady state irradiations were carried out at 254 nm using a low pressure mercury lamp (Osram HNS 10 ozone free), at 229 nm using a cadmium lamp (Philips 93107) and at 214 nm using a zinc lamp (Philips 93106). Details of the experimental set-up have been reported earlier [16, 19]. Irradiations were also performed using a 450 W xenon arc lamp in combination with a high intensity grating monochromator (Schoeffel Kratos) and a 50 ml irradiation quartz cell. During all experiments the solutions were stirred and kept at the desired temperature.

Actinometry was carried out using the potassium ferrioxalate system [24, 25]. The intensity of the light entering the cell was measured as a function of the wavelength using a calibrated radiometer (model 65A, Yellow Springs Inc., U.S.A.). No change in the quantum yield of $Fe^{2+}$ was observed in the range 215 - 300 nm, and hence $Q(Fe^{2+}) = 1.25$ was used for the

calculations of the yields. The quantum yield $Q(e_{aq}^-)$ of the solvated electrons formed under illumination was determined by scavenging $e_{aq}^-$ either with $N_2O$ ($k(e_{aq}^- + N_2O) = 6 \times 10^9 \, M^{-1} \, s^{-1}$ [26]) or with 2-chloroethanol ($k(e_{aq}^- + \text{2-chloroethanol}) = 5.6 \times 10^8 \, M^{-1} \, s^{-1}$ [27]). In the first case methanol ($k(OH + \text{methanol}) = 9 \times 10^8 \, M^{-1} \, s^{-1}$ [28]) or propan-2-ol ($k(OH + \text{propan-2-ol}) = 2 \times 10^9 \, M^{-1} \, s^{-1}$ [28]) was added to scavenge the OH radicals, which otherwise would have interfered with the measurements. The nitrogen produced was quantitatively measured using gas chromatography and the $Cl^-$ yield was determined by a spectrophotometric mercury thiocyanate method [29]. In solutions of DMA the amine was removed prior to $Cl^-$ determination by extraction with diethyl ether. Neither $N_2O$ nor 2-chloroethanol influence the fluorescence in the concentration range used. In view of the value of $1 \times 10^{10} \, M^{-1} \, s^{-1}$ obtained for the rate constant $k(e_{aq}^- + \text{benzonitrile})$ [30] CDMA was expected to react efficiently with $e_{aq}^-$. To prevent this a higher scavenger concentration (0.1 M 2-chloroethanol) was applied in the presence of $3 \times 10^{-4}$ M CDMA; only 0.02 M 2-chloroethanol was used in the case of DMA. Under these conditions less than 10% of the solvated electrons are expected to react with CDMA. The final $Cl^-$ concentration was kept below $2 \times 10^{-5}$ M with an accuracy of determination better than $\pm 5\%$.

## 3. Results

The absorption spectra of CDMA and MCDMA in aqueous solutions are shown in Figs. 1 and 2. The emission spectra of CDMA and MCDMA were measured for various excitation wavelengths and no effect of the excitation energy on the form of the spectrum was detected. These findings contrast with those reported by Visser and Varma [31] for methanolic solutions of CDMA. For solutions of CDMA in ethanol the ratio $r$ of long-wavelength to short-wavelength emission remained constant within $\pm 5\%$ throughout the excitation range from 225 to 320 nm. In aqueous solutions such measurements could only be performed between $\lambda_{exc} = 260$ nm and $\lambda_{exc} = 320$ nm because of the low emission yield at the short wavelengths, and $r$ was again found to be constant.

To measure the effect of the excitation wavelength on the fluorescence yield, the emission was monitored near 530 nm for CDMA and near 570 nm for MCDMA at various concentrations ($5 \times 10^{-6} - 4 \times 10^{-3}$ M) in aqueous solutions. The fluorescence quantum yields $Q_F$ are normalized to that for the long wavelength excitation. The $Q_F$ yields remain constant throughout the first absorbing system, but decrease below 270 nm. Methyl substitution (MCDMA, Fig. 2), alcohol concentrations up to 25% and the concentration of the solute have little effect on the observed behaviour. However, in pure ethanolic solutions $Q_F$ remained constant throughout the excitation range ($\lambda_{exc} = 225 - 320$ nm). Similar behaviour has been observed for aniline [20].
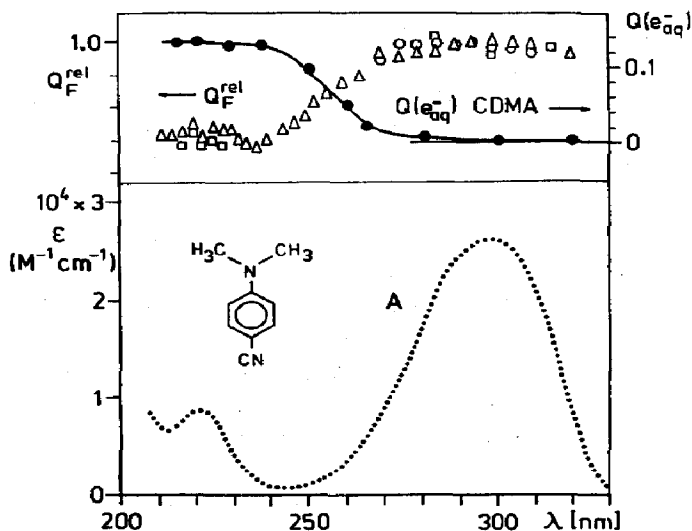
Fig. 1. Relative fluorescence quantum yield $Q_F^{rel}$ of aqueous CDMA ($\square$, $4 \times 10^{-3}$ M CDMA in 30 vol.% propan-2-ol; $\circ$, $8 \times 10^{-4}$ M CDMA in 10% vol.% propan-2-ol; $\triangle$, $5 \times 10^{-6}$ M CDMA in water) at pH 8 and 25 °C and quantum yield $Q(e_{aq}^-)$ of $e_{aq}^-$ for $3 \times 10^{-4}$ M CDMA in deoxygenated aqueous solutions (pH 8; 30 °C; 0.1 M 2-chloroethanol as electron scavenger) ($\bullet$) as functions of the excitation wavelength; curve A, absorption spectrum of aqueous CDMA in water (pH 8).
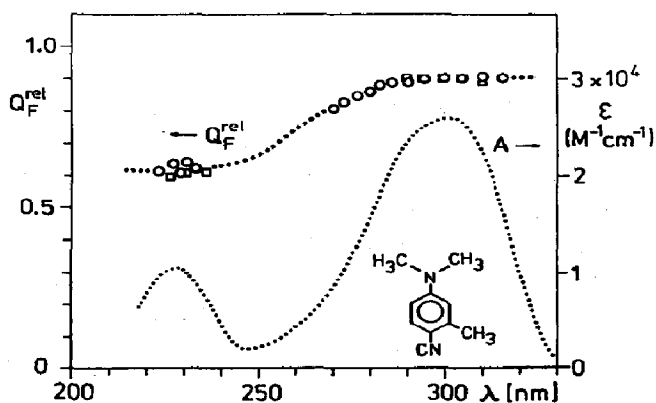


Fig. 2. Relative fluorescence quantum yield $Q_F^{rel}$ of $1.5 \times 10^{-3}$ M ($\circ$) and $5 \times 10^{-6}$ M ($\square$) MCDMA in aqueous solutions in the presence of 20 vol.% propan-2-ol (pH 8; 25 °C) as a function of the excitation wavelength; curve A, absorption spectrum of MCDMA in water (pH 8).

It is of particular interest that the onset of this effect is at the same energy ($\lambda = 275$ nm) for CDMA and DMA [16]. In addition the value of $\beta$ for excitation into the third band is comparable for the two systems ($\beta = 0.65$ for DMA at $\lambda_{exc} = 215$ nm [16]). ($\beta$ is defined by $\beta(\lambda_{exc}) = Q(F)/Q_0(F)$ where $Q_0(F)$ is the constant value of $Q(F)$ obtained on excitation to the $S_1$ state.) Furthermore, this decrease in the emission yield is accompanied by an increase in the efficiency of $e_{aq}^-$ formation for DMA in aqueous solutions [16, 18]. The same effect was observed in this work for CDMA (Fig. 1) with
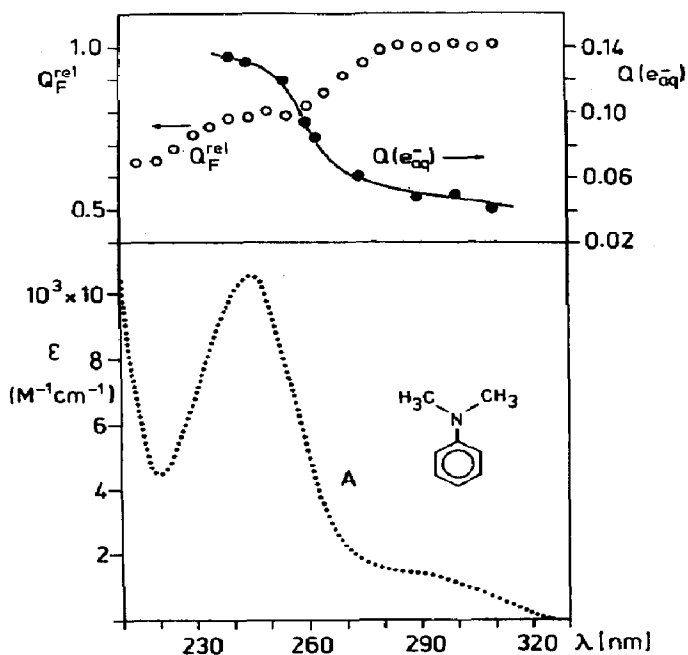
Fig. 3. Relative fluorescence quantum yield $Q_F^{rel}$ (○) and quantum yield $Q(e_{aq}^-)$ of $e_{aq}^-$ (●) as functions of the excitation wavelengths for $10^{-5}$ M DMA in water (pH 8; $T = 30$ °C; 0.02 M 2-chloroethanol as electron scavenger); curve A, absorption spectrum of aqueous DMA (pH 8).

2-chloroethanol as the electron scavenger. The results obtained for DMA with the same scavenger are given in Fig. 3. No dependence of $Q(Cl^-)$ on the scavenger concentration (0.07 - 0.25 M 2-chloroethanol) was observed. The values of $Q(e_{aq}^-)$ obtained by scavenging $e_{aq}^-$ with $N_2O$ (Table 1) and with 2-chloroethanol are almost identical.
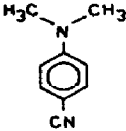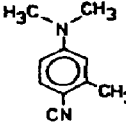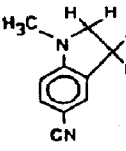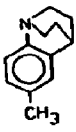
The results for aqueous DMA are in good agreement with the yields obtained previously by scavenging with $N_2O$ at certain wavelengths [16]. In this case electron ejection is also found for excitation into the lowest absorption band and the yield increases only slightly throughout its absorption range. Electron ejection is negligible at excitation into the first band of CDMA. $Q(e_{aq}^-)$ also increases markedly below 280 nm for aqueous DMA. The data for $Q(e_{aq}^-)$ in aqueous CMI and MBQ are included in Table 1. The yields are independent of the 2-chloroethanol concentration and of the scavenger used (the scavenging efficiencies of $N_2O$ and 2-chloroethanol differ considerably).

## 4. Discussion

The fluorescence yields of $p$-cyano-substituted anilines (CDMA and MCDMA) in aqueous solution depend on the excitation energy when it exceeds 4.5 eV (275 nm) (Figs. 1 and 2). The yield is independent of the

TABLE 1

Quantum yield of solvated electrons formed photochemically from various aromatic amines excited at several wavelengths in aqueous solutions at 30 °C

| Solution | Substrate | $\lambda_{exc}$ (nm) | $Q(N_2) = Q(e_{aq}^-)$ |
|---|---|---|---|
| $10^{-3}$ M CDMA<br>1 M propan-2-ol<br>(pH 8) | | 300<br>275<br>229 | < 0.001<br>< 0.001<br>0.12 ± 0.02 |
| $10^{-3}$ M MCDMA<br>1 M propan-2-ol<br>(pH 8) | | 275<br>229 | < 0.001<br>0.12 ± 0.02 |
| $10^{-3}$ M CMI<br>1 M methanol<br>(pH 8) | | 229 | 0.12 ± 0.02 |
| $5 \times 10^{-3}$ M MBQ<br>1 M methanol<br>(pH 9) | | 260<br>214 | 0.04 ± 0.01<br>0.14 ± 0.02 |

excitation energy in the long-wavelength region of the absorption spectrum. Below 240 nm (approximately 0.5 eV above this onset) it again becomes constant and is about 28% less than its value in the long-wavelength region.

The first absorption system of these compounds, around 300 nm, is composed of the $^1L_b$ and $^1L_a$ bands (transitions to $^1B_2$ and $^1A_1$ respectively in $C_{2v}$ symmetry) which overlap strongly and are sometimes vibronically coupled [32, 33]. This is confirmed by complete neglect of differential overlap (CNDO) [34] and intermediate neglect of differential overlap (INDO) [35] calculations, which also support the much higher oscillator strength for the $^1A \rightarrow {}^1L_a$ transition compared with that for the $^1A \rightarrow {}^1L_b$ transition. It shows that the orbital character of the primary absorbing state does not influence the quantum yield $Q_F$. This contrasts with dimethylaniline, where a decrease in $Q_F$ is observed just as the $^1L_a$ absorption rises [16]. In this latter

case the transitions to the $^1L_b$ (lower) and $^1L_a$ (upper) states are well separated, and both states may be less strongly coupled than in CDMA.

Whereas the decrease of the fluorescence yield in DMA appears to be related to the appearance of a new absorption, this is not so obvious for CDMA. The third transition in CDMA, whose orbital origin is not yet established, occurs just below 240 nm when $Q_F$ has already levelled off. In these compounds the decrease in $Q_F$ therefore seems to be unrelated to the onset of $S_3$ absorption. The process, which competes efficiently with relaxation to the fluorescing state, probably originates from higher vibrational levels of the dominant $^1L_a$ band. However, the onset of the fluorescence decrease is at the same energy for all three compounds (DMA, CDMA and MCDMA).

These observations should be related to the effects of the excitation wavelength on the yield of solvated electrons in aqueous solution (electron ejection to the solvent) given in Fig. 1. It is obvious that $Q(e_{aq}^-)$ exhibits a mirror image relationship with $Q_F$ when the excitation energy increases. Whereas electron ejection from $p$-cyano compounds occurs only above the onset around 275 nm, DMA releases electrons at lower energies also. In this excitation range $Q(e_{aq}^-)$ is almost independent of the wavelength (the observed small increase may be due to the bandwidth of 10 nm of the photochemical experiments) and therefore probably originates from the relaxed singlet in competition with the fluorescence. The same behaviour was found for phenol [14, 19], aromatic amines [16, 18], monophenyl phosphate [20] etc. where at least two channels are available for electron ejection. One originates from the relaxed fluorescent state and the other originates from the upper excited levels in competition with the relaxation. This is demonstrated for DMA in Fig. 3.

The fluorescent state b* is the precursor of TICT formation in CDMA and related compounds [3, 4]. The intramolecular charge transfer state is, however, not a precursor of $e_{aq}^-$ formation since no electrons are found for CDMA at long-wavelength excitation.

Charge transfer to the solvent was postulated for excited CDMA in polar solvents in a hypothesis which ascribes the long-wavelength emission to a solute–solvent exciplex state [22]. Conductivity was also found in the methanolic solution following laser excitation [22]. Our results show, however, that at least in aqueous solutions no charge transfer to the solvent from this state is observable at low excitation intensities.

The first channel for electron ejection seems, however, to be operative in MBQ with a quantum yield similar to that of DMA, although the geometries of the two molecules are quite different. Whereas in DMA the amino group can rotate freely, in MBQ the nitrogen lone pair is fixed coplanar to the toluene ring. Because of these geometrical restrictions, the aromatic $\pi$ system and the nitrogen lone-pair orbital are decoupled, whereas the strongly red-shifted fluorescence of MBQ fits energetically to what is expected for an intramolecular charge transfer state [1]. Since no electron ejection was observed for toluene [18], electron release from MBQ probably originates from the orbitals of the excited amino group.

The second channel for the photoejection of electrons, which is a hot process originating from higher levels, is operative in all molecules investigated (see Table 1) and the yield of solvated electrons is the same for all of them within the limits of experimental error. However, this yield is equivalent to only about 40% of the decrease in $Q_F$ (in Fig. 1 a mirror image relationship between $\beta$ and $Q(e_{aq}^-)$ was obtained by suitable scale fitting). Only about every second process bypassing the relaxation to $S_1$ produced an ejected electron counted by the scavenger. The triplet or ground state of the molecule is probably produced by a back reaction (germinal recombination) which competes with the formation of freely diffusing solvated electrons.

The second channel is not significantly influenced by structures able to form an intramolecular charge transfer state. It is related to a definite onset energy. The photoionization mechanism can be explained in two ways.

(i) The mechanism proposed by Grand et al. [36] for indolic compounds may be appropriate. However, some data do not agree with the treatment of electron ejection in aqueous solution as the transfer of an electron to the conduction band of the solvent. In such a model a well-defined threshold, strongly dependent on the solvent and on the ionization potential of the solute, is assumed. However, the onset of the fluorescence decrease for DMA and CDMA occurs at almost the same excitation energy, and the influence of the solvent is found to be negligible for anilines [18]. No electrons were observed by scavenger methods in non-aqueous aniline solutions [16]. There is an apparent difference between the experimental results reported by Grand et al. [36] and our data: their $Q(e_{aq}^-)$ and photoconductivity measurements do not show any saturation at higher excitation energies.

(ii) Rather, in accordance with previous publications [15, 19], it is suggested that the electron is transferred to a solvent trap adjacent to the solute. Such a cluster state could dissociate, resulting in the formation of $e_{aq}^-$, or relax to the neutral molecular ground state. The parent amines of the compounds studied have low-lying Rydberg states [37]. Electron release from molecules such as MBQ indicates the possible participation of the Rydberg excited states in the electron ejection process. Model calculations have shown that these spatially extended excited states do not lose their predominant Rydberg character when interacting with perturbing molecules [38, 39]. Such states could act efficiently as intermediates in a charge transfer process to the solvent.

Thus in the donor—acceptor molecule CDMA intramolecular charge transfer dominates the decay of the two lowest excited states, whereas at higher excitations photoejection of electrons to the solvent becomes significant. The latter process is very similar to that in other aniline derivatives and is not markedly modified by the acceptor substituent.

## References

1   Z. R. Grabowski and J. Dobkowski, *Pure Appl. Chem.*, *55* (1983) 245.
2   E. Lippert, W. Lüder and H. Boos, in A. Mangini (ed.), *Advances in Molecular Spectroscopy*, Pergamon, Oxford, 1962, p. 443.
3   K. Rotkiewicz, K. H. Grellmann and Z. R. Grabowski, *Chem. Phys. Lett.*, *40* (1973) 315.
4   Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley and W. Baumann, *Nouv. J. Chim.*, *3* (1979) 443.
5   K. Rotkiewicz and K. H. Grellmann, unpublished results.
6   R. Kolos and Z. R. Grabowski, *J. Mol. Struct.*, *84* (1982) 251.
7   K. Rotkiewicz, Z. R. Grabowski, A. Krowczynski and W. Kühnle, *J. Lumin.*, *12/13* (1976) 877.
8   Y. Nakato and H. Tsubomura, *J. Phys. Chem.*, *79* (1975) 2135.
9   A. M. Halpern and T. Gartman, *J. Am. Chem. Soc.*, *96* (1974) 1393.
     A. M. Halpern, *J. Am. Chem. Soc.*, *96* (1974) 7655.
10  Y. Muto, Y. Nakato and H. Tsubomura, *Chem. Phys. Lett.*, *9* (1971) 597.
11  A. M. Halpern, *J. Phys. Chem.*, *85* (1981) 1682.
12  R. S. Mulliken, *Acc. Chem. Res.*, *9* (1976) 7.
13  G. Dobson and L. Grossweiner, *Trans. Faraday Soc.*, *61* (1965) 701.
14  J. Zechner, G. Köhler, G. Grabner and N. Getoff, *Chem. Phys. Lett.*, *37* (1976) 297.
15  G. Grabner, G. Köhler, J. Zechner and N. Getoff, *Photochem. Photobiol.*, *26* (1977) 449.
16  G. Köhler and N. Getoff, *J. Chem. Soc., Faraday Trans. I*, *76* (1980) 1576.
17  G. Grabner, W. Rauscher, J. Zechner and N. Getoff, *J. Chem. Soc., Chem. Commun.*, (1980) 222.
18  G. Köhler, C. Rosicky and N. Getoff, in B. Pullman and N. Goldblum (eds.), *Excited States in Organic Chemistry and Biochemistry*, Reidel, Dordrecht, 1977, p. 303.
19  G. Köhler and N. Getoff, *J. Chem. Soc., Faraday Trans. I*, *72* (1976) 2101.
20  G. Köhler and N. Getoff, *J. Chem. Soc., Faraday Trans. I*, *74* (1978) 1029.
21  J. Zechner, G. Köhler, N. Getoff, I. Tatischeff and R. Klein, *Photochem. Photobiol.*, *34* (1981) 163.
22  R. J. Visser, C. A. G. O. Varma, J. Konijnenberg and P. Bergwerf, *J. Chem. Soc., Faraday Trans. II*, *79* (1983) 347.
23  K. Rotkiewicz and W. Rubaszewska, *Chem. Phys. Lett.*, *70* (1980) 444.
24  C. G. Hatchard and G. A. Parker, *Proc. Soc. London, Ser. A*, *235* (1956) 518.
25  J. Lee and H. M. Selinger, *J. Chem. Phys.*, *40* (1964) 519.
26  J. P. Keene, *Radiat. Res.*, *22* (1964) 1.
27  M. Anbar and E. J. Hart, *J. Phys. Chem.*, *71* (1967) 3700.
28  L. M. Dorfman and G. E. Adams, *Reactivity of the Hydroxyl Radical in Aqueous Solutions*, National Bureau of Standards, Washington, DC, 1973.
29  A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, Longmans, Harlow, 3rd edn., 1961, p. 809.
30  B. Chunty and A. J. Swallow, *Trans. Faraday Soc.*, *66* (1970) 2847.
31  R. J. Visser and C. A. G. O. Varma, *J. Chem. Soc., Faraday Trans. II*, *76* (1980) 453.
32  Z. R. Grabowski, K. Rotkiewicz, W. Rubaszewska and E. Kirkor-Kaminska, *Acta Phys. Pol. A*, *54* (1978) 768.
33  W. Rettig, G. Wermuth and E. Lippert, *Ber. Bunsenges. Phys. Chem.*, *83* (1979) 692.

34 O. S. Khalil, J. L. Meeks and S. P. McGlynn, *Chem. Phys. Lett.*, *39* (1976) 457.

35 J. Lipinski, H. Chojnacki, Z. R. Grabowski and K. Rotkiewicz, *Chem. Phys. Lett.*, *70* (1980) 449.

36 D. Grand, A. Bernas and E. Amouyal, *Chem. Phys.*, *44* (1979) 73.

37 K. Fuke and S. Nagakura, *J. Mol. Spectrosc.*, *64* (1977) 139.

38 G. Köhler, N. Getoff, R. Janoschek, J. Kalcher and A. Sax, in N. Trinajstić (ed.), *Proc. IUPAC Int. Symp. on Theoretical Organic Chemistry, Dubrovnik, 1982.*

39 G. Köhler, *J. Mol. Struct.*, *114* (1984) 191.