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Medium effects on luminescence originating from UV-excited dicyanocuprate(I)–halide system

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Abstract

The nature of the dependence of the luminescence lifetime on the halide ion concentration is interpreted by a mechanism which involves an equilibrium reaction of excited dicyanocuprate(I) with the halide ion in the ground state, resulting in an emitting molecular entity assigned as an exciplex. A significant increase in the stepwise formation constant of $^*Cu(CN)_2^-\ldots I^-$ is obtained by increasing the ionic strength: $K_{EX}=16\pm4$ at $\mu=0.5$ M; $K_{EX}=72\pm14$ at $\mu=2.5$ M; $K_{EX}=320\pm60$ at $\mu=5$ M ($T=300$ K). The luminescence lifetimes obtained in various water–glycerol solvent mixtures at different ionic strengths clearly demonstrate the synergy of the two medium effects. The time-resolved absorption and emission measurements reveal three different species absorbing in the visible and near-UV range; the mechanism results in the formation of the following intermediates: solvated electron, luminescent exciplex ($^*Cu(CN)_2^-\ldots X^-$) and $^{\cdot}X_2^-$ radical.

Keywords: Luminescence; Quantum yield; Lifetime; Exciplex; Medium effects

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1. Introduction

Luminescence initiated by UV excitation of $Cu(CN)_2^-$–X^- systems ($X\equiv Cl, Br, I$) has been observed recently [1–4]. Steady state and time-resolved absorption and emission studies indicate that the luminescence lifetime and luminescence quantum yield depend on the concentration of halide ions which associate with both ground and excited dicyanocuprate(I). The stepwise formation constant is higher when the excited species is involved in the equilibrium reaction. The position of the maximum in the luminescence spectrum and the shape of the emission band are similar to those obtained in pure halocuprate(I) systems [5–7]. The luminescence spectrum shows a rather large Stokes shift, which is characteristic of other copper(I) complexes [8–18]. In this paper, we demonstrate that the effect of the medium on the luminescence dynamics can be used to confirm the assignment of the key processes in the photochemical system and to reveal the details of the mechanism involving an equilibrium reaction of the excited state molecule.

2. Experimental details

Samples at the desired bromide, iodide or chloride concentration and ionic strength were prepared from stock solutions of reagent grade NaBr, NaI, NaCl and $NaClO_4$ (Reanal). Glycerol–water mixtures ($X_{glycerol}=$ 0–0.3), prepared from double-distilled and deionized water and reagent grade glycerol (Reanal), were used as solvent. Weighed samples of crystalline potassium dicyanocuprate(I), synthesized by the method described elsewhere [1,19], were added to the samples, which were then deoxygenated by argon bubbling. The emisson spectra and time-resolved photochemical experiments were performed on reaction mixtures (3 cm^3) in a 1 cm quartz cuvette.

Luminescence excitation and emission spectra were recorded on a Perkin–Elmer LS50B spectrofluorophotometer. Luminescence quantum yields were determined by the quinine sulfate method [20].

Time-resolved spectra, luminescence lifetimes and transient absorbances were determined using a laser flash photolysis system described previously [6].

3. Results and discussion

The lifetime of the luminescence, appearing as a broad, structureless band between 400 and 600 nm on

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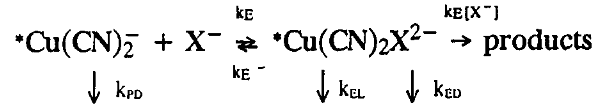
excitation of dicyanocuprate(I) in the presence of halide ions, exhibits a characteristic dependence on the concentration of halide ion [2–4]. The lifetime of the emission first increases with a different slope for chloride, bromide and iodide and then decreases with an increase in halide ion concentration (see fig. 4 in Ref. [3]). The value of τ_{max} is dependent on the nature of the halide ion, and occurs at nearly the same concentration for chloride and bromide ions (1.5–2.5 M), but at only 0.1 M iodide ion, in aqueous solutions at 5 M ionic strength. This behavior was interpreted by a mechanism involving an equilibrium reaction of the excited copper(I) species with the halide ion in the ground state, resulting in a luminescent molecular entity [3]. The mechanism is summarized in Scheme 1, where P is the precursor of the luminescent exciplex, E is the exciplex, D denotes decay, L denotes luminescent decay and R denotes reactive decay. The coordination of the second halide ligand to the excited copper complex quenches the emission. Since this process has a high efficiency only at rather high concentrations of chloride and bromide ion, it is expected that the effect of the ionic strength on the position of τ_{max} can only be investigated over a reasonably wide range for the $Cu(CN)_2^-$–I^- system.



3.1. Ionic strength effects

The shape of the τ vs. $[I^-]$ curves, depicted in Fig. 1, indicates the characteristic behavior of this type of system. The maximum value of the lifetime and the slope of the curve in the initial concentration range increase with ionic strength, which is consistent with a shift of the peak to the lower concentrations of iodide ion. Although the value of τ_{max} approximately doubles, the initial slope increases by a much higher value. These changes can be explained by an increase in the rates of the reactions occurring between molecular species possessing an electric charge of the same sign (characterized by the rate constants k_E and k_{ER}) and a decrease in the rate of dissociation (k_E^-), since there is a decline in the repulsion between particles encountered due to the shielding effects of the counterions. Hence a significant increase in the stepwise formation constant of the exciplex is obtained (Table 1). The other processes conforming to first-order kinetics, such as the decay of the precursor and luminescent species (k_{PD}, k_{ED}, k_{EL}), are only slightly influenced by the concentration of indifferent salts. Consequently, these experiments demonstrate the important role of the equilibrium reaction

$$*Cu(CN)_2^- + X^- \rightleftharpoons *Cu(CN)_2X^{2-} \qquad (1)$$

and the reactive decay of the luminescent complex, $*Cu(CN)_2X^{2-}$, assigned as an exciplex

$$*Cu(CN)_2X^{2-} + X^- \longrightarrow \text{non-radiative species} \qquad (2)$$

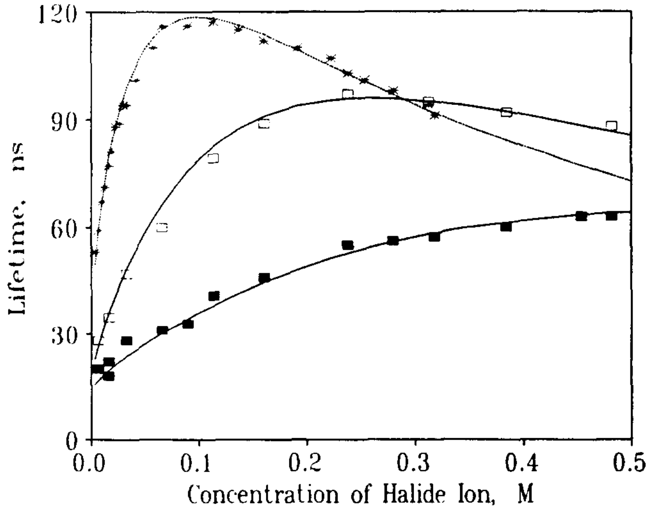


Fig. 1. Dependence of the luminescence lifetime detected at 480 nm on the iodide ion concentration in aqueous solutions of dicyanocuprate(I) at various ionic strengths: μ=0.5 M (■); μ=2.5 M (□); μ=5.0 M (*).

3.2. Solvent effects

Increasing the concentration of glycerol in the water–glycerol solvent mixture leads to a very effective growing-in of the luminescence lifetime. In the solvent mixture $X_{glycerol}=0.3$, a lifetime of 460 ns was obtained as a peak value at ambient temperature between 0.3 and 0.4 M concentration of iodide ion, which is about ten times higher than that obtained in water at 0.5 M ionic strength in the same concentration range of halide ion. Fig. 2 shows a more intense influence of the solvent composition on the lifetime observed in the presence of bromide ion (see also Table 2). This picture clearly demonstrates the synergy of two effects: an increase in the ionic strength leads to an increase in the formation constant of the luminescent exciplex, while an increase

Table 1
Rate constants and formation constant of the exciplex estimated from τ vs. $[I^-]$ data measured at 300 K in aqueous solutions of different ionic strength

Rate constant	μ=0.5 M	μ=2.5 M	μ=5.0 M
$k_{PD}\times10^{-7}$ (s^{-1})	7.2±1.2	7.2±1.4	7.2±1.4
$k_E\times10^{-9}$ (M^{-1} s^{-1})	1.9±0.2	4.3±0.4	7.1±0.6
$k_E^-\times10^{-7}$ (s^{-1})	11.8±1.2	6.0±0.6	2.2±0.2
$(k_{ED}+k_{EL})\times10^{-7}$ (s^{-1})	4.5±0.5	4.3±0.4	4.9±0.4
$k_{ER}\times10^{-7}$ (M^{-1} s^{-1})	0.9±0.2	1.2±0.2	1.7±0.2
$K_{EX}=k_E/K_E^-$ (M)	16±4	72±14	320±60

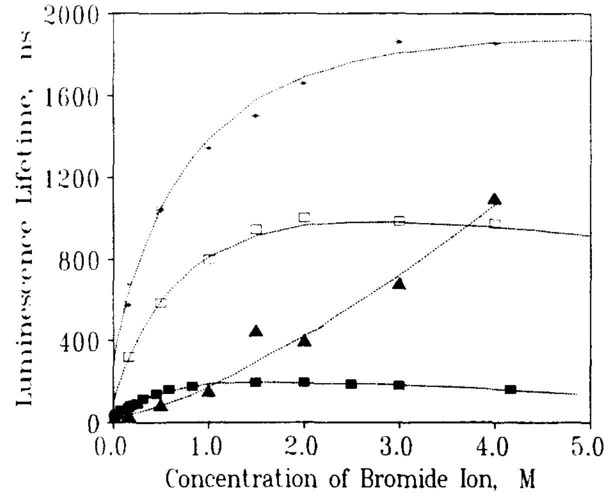


Fig. 2. Dependence of the luminescence lifetime detected at 480 nm on the bromide ion concentration at various ionic strengths and in different solvent mixtures: $\mu = 5$ M and $X_{glycerol} = 0$ (■); $\mu = 5$ M and $X_{glycerol} = 0.15$ (□); $\mu = 5$ M and $X_{glycerol} = 0.3$ (•), $X_{glycerol} = 0.15$ (▲).

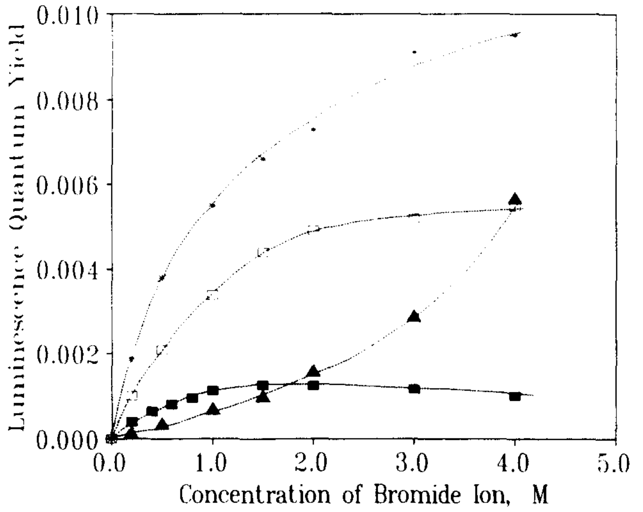


Fig. 3. Dependence of the luminescence quantum yield detected at 480 nm on the bromide ion concentration at various ionic strengths and in different solvent mixtures: $\mu = 5$ M and $X_{glycerol} = 0$ (■); $\mu = 5$ M and $X_{glycerol} = 0.15$ (□); $\mu = 5$ M and $X_{glycerol} = 0.3$ (•), $X_{glycerol} = 0.15$ (▲).

Table 2
Rate constants and formation constant of the exciplex estimated from τ vs. $[Br^-]$ data measured at 298 K in different solvent mixtures at 5 M ionic strength

Rate constant	$X_{glycerol} = 0$	$X_{glycerol} = 0.15$	$X_{glycerol} = 0.3$
$k_{PD} \times 10^{-7}$ (s^{-1})	7.0 ± 1.2	6.0 ± 0.9	5.0 ± 0.8
$k_E \times 10^{-9}$ (M^{-1} s^{-1})	1.4 ± 0.2	1.1 ± 0.2	0.44 ± 0.05
$k_E^- \times 10^{-7}$ (s^{-1})	5.0 ± 0.2	1.1 ± 0.1	0.30 ± 0.03
$(k_{ED} + k_{EL}) \times 10^{-6}$ (s^{-1})	2.7 ± 0.1	0.6 ± 0.1	0.40 ± 0.08
$k_{ER} \times 10^{-5}$ (M^{-1} s^{-1})	7.2 ± 0.2	0.8 ± 0.2	0.12 ± 0.02
$K_{EX} = k_E/k_E^-$ (M)	28 ± 4	100 ± 15	150 ± 26

in the viscosity and the relaxation time of the solvent results in a decrease in both the radiative and non-radiative decay of the emitting species. In the solvent mixture $X_{glycerol} = 0.15$, in which the ionic strength was not kept constant, the lifetime increases moderately with the concentration of bromide ion in the region $[Br^-] < 2$ M. Above 2 M, the curve becomes steeper, and the lifetime approaches nearly the same value as that obtained at a constant ionic strength of 5 M. It is interesting to note that the shapes of the τ vs. $[X^-]$ curves obtained in water–glycerol solvent mixtures are different for bromide and iodide. This results from two effects: on the one hand, the stepwise formation constant (i.e. k_E/k_E^-) of $^*Cu(CN)_2X^{2-}$ is larger for the iodide than the bromide ligand, as observed in water at 5 M ionic strength [2,3], and, on the other hand, an increase in the viscosity of the solvent reduces the decay rate of $^*Cu(CN)_2Br^{2-}$ to a greater extent than that of $^*Cu(CN)_2I^{2-}$.

The luminescence quantum yield increases effectively with the mole fraction of glycerol ($X_{glycerol}$) in the presence of bromide ions, as depicted in Fig. 3. The position of the peak value shifts to higher concentrations of bromide ion in solutions at a constant ionic strength of 5 M with an increase in the mole fraction of glycerol.

The time-resolved absorption measurements performed on the $Cu(CN)_2^-$–Br^- system in different water–glycerol solvent mixtures reveal that the 266 nm laser pulse initiates the formation of at least three different species absorbing in the 300–900 nm range.

(1) The transient absorption band with a peak at 700 nm was identified as that due to the solvated electron [4]. This species is ejected by the excited state of higher energy possessing charge transfer to solvent (CTTS) character achieved by photon absorption [18] and disappears rapidly (inset in Fig. 4).
(2) The short-lived absorption between 300 and 400 nm possessing the same lifetime as the luminescence was assigned as the absorption of the exciplex [4] (inset in Fig. 5).
(3) The longer lived intermediate exhibiting absorption bands with peaks at 360 nm (strong) and 700 nm (weak) is assigned as the $^{\cdot}Br_2^-$ radical anion [4,21,22].

The intensity of the transient absorption band of the solvated electron, detected 50 ns after the laser pulse, decreases (Fig. 4), while the emission intensity at 480 nm and the absorption of the luminescent species at 360 nm increase (Fig. 5) with an increase in the mole fraction of glycerol at the same concentration of bromide ion. This clearly indicates that solvated electron formation from the excited state, achieved by photon absorption, competes with a photophysical process leading to either the precursor of the luminescent species (when the photon is absorbed by $Cu(CN)_2^-$) or the

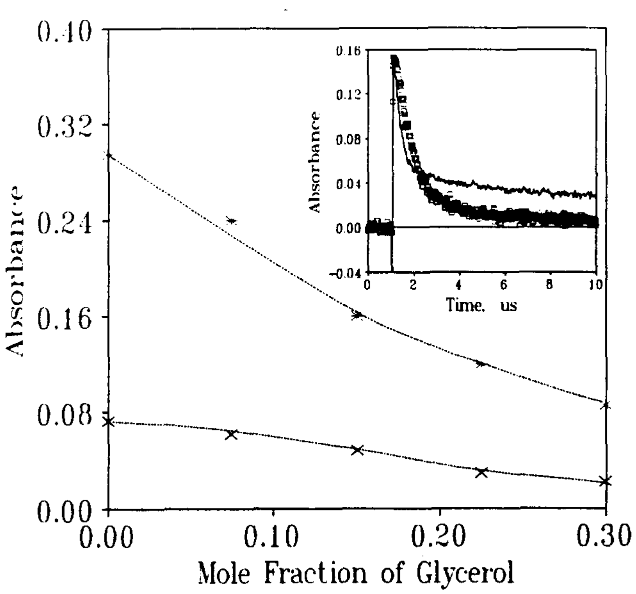


Fig. 4. Influence of the solvent composition on the yield of the transient species initiated by a 266 nm laser pulse in solutions of $[Br^-]_0 = 1$ M and $[Cu(CN)_2^-] = 8 \times 10^{-4}$ M: absorption of the solvated electron detected 50 ns after the laser pulse at 700 nm (✱); absorption of $^{\cdot}Br_2^-$ radical 50 ns after the laser pulse estimated from the second stage of the transient absorption detected at 360 nm (×). Inset: transient absorption detected at 360 nm (full line) and 700 nm (□) in water–glycerol solvent mixture with $X_{glycerol} = 0.15$.

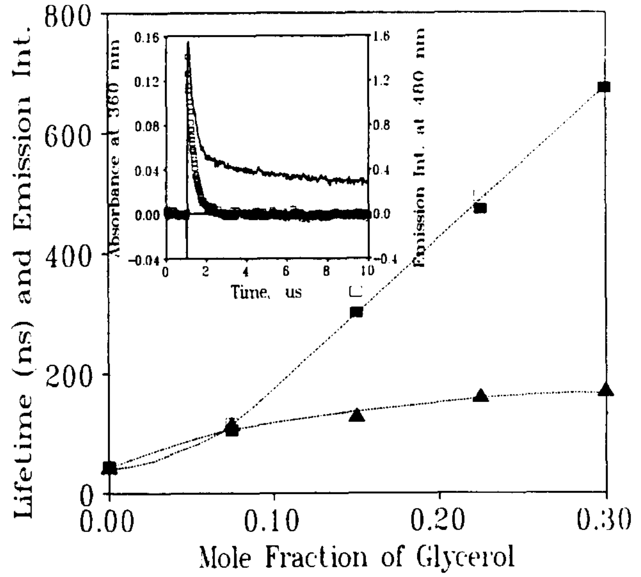


Fig. 5. Influence of the solvent composition on the yield of the transient species initiated by a 266 nm laser pulse in solutions of $[Br^-]_0 = 1$ M and $[Cu(CN)_2^-] = 8 \times 10^{-4}$ M: emission intensity at 480 nm (▲); lifetime of the luminescent exciplex obtained by emission signals at 480 nm (■) and by the first stage of transient absorption at 360 nm (□). Inset: transient absorption detected at 360 nm (full line) and relative emission intensity detected at 480 nm (□) in water–glycerol solvent mixture with $X_{glycerol} = 0.15$.

luminescent complex itself (when the photon is absorbed by $Cu(CN)_2Br^{2-}$). Thus the solvent effect demonstrates the importance of competition between electron ejection and a photophysical process leading to the luminescent species.

Considering the formation of the longer lived intermediate assigned as the $^{\cdot}Br_2^-$ radical, two different mechanisms are possible.

(1) The intramolecular electron transfer of the exciplex releasing $^{\cdot}Br$ radical competes with luminescence and the relaxation process is followed by the reaction of the bromide ion and the radical

$$^*Cu(CN)_2Br^{2-} \longrightarrow Cu(CN)_2^{2-} + {}^{\cdot}Br \qquad (3)$$

$$^{\cdot}Br + Br^- \longrightarrow {}^{\cdot}Br_2^- \qquad (4)$$

(2) The intermolecular electron transfer leads directly to the $^{\cdot}Br_2^-$ radical

$$^*Cu(CN)_2Br^{2-} + Br^- \longrightarrow Cu(CN)_2^{2-} + {}^{\cdot}Br_2^- \qquad (5)$$

Since the yield of the radical decreases with increasing viscosity of the solvent, which is contrary to the direction of the changes in both the luminescence intensity and lifetime (Fig. 5), we suggest that the second reaction pathway is dominant.

4. Conclusions

This investigation of medium effects, such as solvent–solute interactions and ionic strength, on the luminescence dynamics of the UV-excited $Cu(CN)_2^-$–X^- system confirms the mechanism involving the equilibrium reaction between the excited dicyanocuprate(I) and the halide ion in the ground state. It has been demonstrated that the ionic strength influences the formation and decay of the luminescent exciplex via an encounter and dissociation reaction of charged particles. On the other hand, the solvent molecules affect the radiative and non-radiative decay due to the change in viscosity, permittivity, relaxation properties and electronic interaction with the solutes, i.e. donor–acceptor interaction. Increasing the concentration of glycerol in glycerol–water solvent mixtures results in a significant increase in the viscosity and relaxation time of the solvent molecules surrounding a charged species. Hence the rates of bimolecular reactions and the energy dissipation via rotation interaction decrease as does the non- radiative decay by vibration. These effects result in a very efficient increase in the lifetime of the luminescent species. However, there is another very important solvent effect on molecules in the charge transfer excited state: on UV excitation of cyanocuprate(I) complexes, solvent molecules of strong electron acceptor nature can stimulate electron ejection from either the d^9s^1 or charge transfer to ligand (CTTL) (π^*) state. The interaction of water molecules with the d^9s^1 excited state can be very effective in the coordinatively unsaturated dicyanocuprate(I). Hence increasing the number of glycerol molecules in the environment of the excited copper(I) complex results in a decrease in the efficiency of primary redox pair formation and an increase in the cage recombination of the primary redox pair consisting of an electron and the copper(II) species. This is concomitant with an increase in the probability of a competing reaction, resulting in either the precursor of the luminescent species or the luminescent molecular entity itself.

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References

[1] A. Horváth and K.L. Stevenson, *Inorg. Chim. Acta, 186* (1991) 61.
[2] A. Horváth and K.L. Stevenson, *Inorg. Chem., 32* (1993) 2225.
[3] A. Horváth, C.E. Wood and K.L. Stevenson, *J. Phys. Chem., 98* (1994) 6490.
[4] A. Horváth, C.E. Wood and K.L. Stevenson, *Inorg. Chem., 33* (1994) 5351.
[5] K.L. Stevenson, J.L. Braun, D.D. Davis, K.S. Kurtz and R.I. Sparks, *Inorg. Chem., 27* (1988) 3472.
[6] K.L. Stevenson, R.M. Berger, M.M. Grush, J.C. Stayanoff, A. Horváth and O. Horváth, *J. Photochem. Photobiol. A: Chem., 60* (1991) 215.
[7] O. Horváth, J.H. Fendler and K.L. Stevenson, *Inorg. Chem., 32* (1993) 227.
[8] D.M. Knotter, G. Blasse, J.P.M. van Vliet and G. van Koten, *Inorg. Chem., 31* (1992) 2196.
[9] G. Blasse and D.R. McMillin, *Chem. Phys. Lett., 70* (1980) 1.
[10] M.W. Blaskie and D.R. McMillin, *Inorg. Chem., 19* (1980) 3519.
[11] J.R. Kirchoff, R.E. Gamache, Jr., M.W. Blaskie, A.A. Del Paggio, R.K. Lengel and D.R. McMillin, *Inorg. Chem., 22* (1983) 238.
[12] R.E. Gamache, Jr., R.A. Rader and D.R. McMillin, *J. Am. Chem. Soc., 107* (1985) 1141.
[13] C.E.A. Palmer, D.R. McMillin, C. Kirmaier and D. Holten, *Inorg. Chem., 26* (1987) 3167.
[14] D.R. Crane, J. Di Benedetto, C.E.A. Palmer, D.R. McMillin and P.C. Ford, *Inorg. Chem., 27* (1988) 3698.
[15] D.R. Crane and P.C. Ford, *Inorg. Chem., 32* (1993) 2391.
[16] C. Pedrini, *Phys. Status Solidi B, 87* (1978) 273.
[17] H. Chermette and C. Pedrini, *J. Chem. Phys., 75* (1981) 1869.
[18] A. Vogler and H. Kunkely, *J. Am. Chem. Soc., 108* (1986) 7211.
[19] A. Horváth, O. Horváth and K.L. Stevenson, *J. Photochem. Photobiol. A: Chem., 68* (1992) 155.
[20] D.F. Eaton, *Pure Appl. Chem., 60* (1988) 1107.
[21] D. Zehavi and J. Rabani, *J. Phys. Chem., 76* (1972) 312.
[22] V. Nagarajan and W. Fessenden, *J. Phys. Chem., 89* (1985) 2330.