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# Mechanism of electron ejection induced by mono- and biphotonic excitation of $Cu(CN)_2^-$–halide ion systems

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## Contents

## Abstract

This contribution reviews recent studies devoted to understanding the mechanism of electron ejection in aqueous solutions of dicyanocuprate(I) in the presence of halide ions of high concentration using steady state and time resolved luminescence and absorption techniques. It has been demonstrated that electrons originate from two excited states: the

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lower energy level achieved by one-photon absorption, and the high energy state populated by biphotonic excitation.

*Keywords:* Cu(I) photochemistry; Electron ejection; Monophotonic or one-photon processes; Biphotonic or two-photon excitation

## 1. Introduction

An important goal in inorganic photochemistry is the development of artificial systems capable of conversion and storage of solar energy. In this regard the excited state of various copper(I) complexes have received considerable attention. Depending on the nature of ligands, charge transfer excitation can lead to the promotion of one electron from the reducing metal center to the ligand (MLCT) or to the solvent (CTTS). Upon UV excitation of halocuprate(I) or cyanocuprate(I) complexes the hydrated electron was detected as the primary product of the photoredox reaction in aqueous solutions [1–9].

A greenish–blue luminescence, which proved to be characteristic for excited halocuprate(I), has also been observed in aqueous solutions of $Cu(CN)_2^-$ in the presence of halide ions of high concentration (0.1–5.0 M) [10,11]. The dependence of the luminescence spectrum and its intensity, as well as the luminescence quantum yield on the nature of halide ions have been studied rigorously. It has been confirmed that the luminescence originates from an exciplex formed by the association of the excited dicyanocuprate(I) and halide ions in the ground-state. It was also pointed out that although association forms between the ground-state dicyanocuprate(I) and halide ion, the formation constant of this association is smaller than that of the excplex [12–15].

Recently, our attention returned to the investigation of the mechanism of electron ejection because typical double exponential transient absorption traces, consisting of a fast increase under the laser pulse followed by growing-in and decay terms, were observed in the red of the visible range and in a nanosecond time regime upon UV excitation of halocuprate(I) complexes in aqueous solutions [11,16]. It has been demonstrated that such a signal is detected when hydrated electrons are formed by two different mechanisms termed ‘prompt’ and ‘delayed’ electron ejection [16,17]. In order to reveal the intrinsic nature of the photoinduced electron ejection we decided to reinvestigate thoroughly the photophysics and photochemistry of halocuprate(I) and dicyanocuprate(I) in the presence of halide ions. Studies of the $Cu(CN)_2^- – Y^-$ systems, described in this contribution, have the following advantages: (a) the rate of photophysical and photochemical processes can be tuned by changing halide ion because their different ligand field strengths provide a shift in the energy levels of the mixed-ligand complexes, and the variation in spin-orbit coupling results in a considerable change in the rate of ISC, phosphorescence and spin relaxation within the radical pairs formed by CT excitation; (b) the concentration of halide ions can be varied over a wide range up to several molar; (c) the influence of cations and ionic strength can also be studied using various salts of halide ions and 'innocent' spectator salts to adjust the suitable ionic strength. We demonstrate by the results of systematically designed experiments that electron ejection is induced by mono- and biphotonic excitation.

## 2. Luminescence properties

The excitation of the dicyanocuprate(I) ion in aqueous solutions containing halide ions results in luminescence. The broad, bluish-green emission band is slightly shifted to longer wavelengths with the increase in the atomic number of the halide ion; the luminescence intensity has a maximum at 476 nm in the presence of chloride [18], while it is shifted to 482 and 486 nm in the presence of bromide and iodide ion, respectively [12–15]. The luminescence decay curves detected by nanosecond time resolution obey first-order kinetics at any wavelength of the emission spectra and at any concentration of the halide ion investigated. It has been pointed out that the luminescence quantum yield (Table 1) and the apparent lifetime of the luminescent species strongly depend on the nature and the concentration of the halide ion [12–14]. Because the ratio of luminescence quantum yield and apparent lifetime of luminescent species was found to range between 6500 and 3200 $s^{-1}$ [12], it was reasonable to suppose that the emitting species decay by a spin-forbidden process, hence they have a triplet nature.

## 3. Nature of transient absorption signals

In contrast to the simple monoexponential decay of the luminescence, the transient absorption signal detected in the red, e.g. at 675 nm, shows more complex features: a very sharp increase in absorption within the duration of the laser pulse followed by a biexponential curve consisting of a growing-in and a slow decay (Fig. 1). This type of signal has proved to be characteristic in the range of solvated electron absorption, between 500 and 900 nm. In principle, the process resulting in such a transient absorption can be interpreted by a mechanism involving the formation of the absorbing species, such us solvated electron, from a short- and a

Table 1
Luminescence properties of tris coordinated excited species in aqueous solutions of $Cu(CN)_2^-$–$X^-$ systems at 5 M ionic strength and at $[Cu(I)] = 7.83 \times 10^{-4}$ M

| System | $[X^-]$ (M) | $\lambda_{exc}$ (nm) | $\lambda_{em}$ (nm) | $\phi_{lum}$ |
|---|---|---|---|---|
| $Cu(CN)_2^-$–$Cl^-$ | 2.45 | 275[a] | 475 | $6.30 \times 10^{-4}$ |
| $Cu(CN)_2^-$–$Br^-$ | 1.65 | 278[a] | 482 | $1.25 \times 10^{-3}$ |
| $Cu(CN)_2^-$–$I^-$ | 0.16 | 285[a] | 486 | $3.30 \times 10^{-3}$ |

[a] Increases with concentration of halide ion from 272 nm.

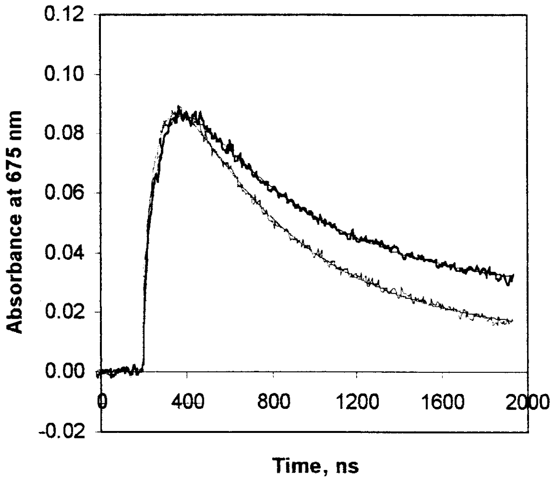


Fig. 1. Transient absorption signals detected in aqueous solution of $5.84 \times 10^{-4}$ and $6.67 \times 10^{-4}$ M dicyanocuprate(I) at 5 M NaCl (upper curves) and 5 M CsCl (lower curves) measured and fitted data, respectively.

longer-lived excited molecular entity and its scavenging by other solutes (e.g. the copper(I) complex itself or $H^+$).

$$e_{aq}^- + S \xrightarrow{k_s[S]} S^- \quad (1)$$

The electron ejection occurs from a longer-lived excited state, which has been reasonably assigned as a triplet state:

$${}^3Cu(I)^2 \xrightarrow{k_o} Cu(II) + e_{aq}^- \quad (2)$$

that competes with radiative and non-radiative decays,

$${}^3Cu(I) \xrightarrow{k_L} {}^1Cu(I) + h\nu \quad (3)$$

$${}^3Cu(I) \xrightarrow{k_{NR}} {}^1Cu(I) + kT \quad (4)$$

The rate law for the decay of the triplet state and for the change of hydrated electron concentration should thus be:

$$d[{}^3Cu(I)]/dt = -(k_L + k_{NR} + k_0)[{}^3Cu(I)] = -k_1[{}^3Cu(I)] \quad (5)$$

and that for the change of hydrated electron concentration should be:

$$d[e_{aq}^-]/dt = k_0[{}^3Cu(I)] - k_2[e_{aq}^-] \quad (6)$$

The integrated forms of Eqs. (5) and (6) can be combined to give:

$$[e_{aq}^-] = [e_{aq}^-]_0 \exp(-k_2 t) + \{k_0[{}^3Cu(I)]_0/(k_2 - k_1)\}\exp(-k_1 t) \quad (7)$$

where $[e_{aq}^-]_0$ and $[{}^3Cu(I)]_0$ are the concentrations of hydrated electrons and triplet excited states generated within the laser pulse duration, and hence are considered as initial concentrations. It should be noted that $[{}^3Cu(I)]_0 k_0/k_1$ is the total concentration of electrons that are ejected from triplet excited state, so that it is possible to substitute absorbances $A_p$ and $A_d$, respectively, for these electron concentrations, and Eq. (7) reduces to a simple biexponential expression in terms of measured electron absorbances:

$$A = (A_p + B)\exp(-t/\tau_2) - B\exp(-t/\tau_1) \quad (8)$$

where $\tau_1 = 1/k_1$, $\tau_2 = 1/k_2$, and $B = -A_d\tau_2/(\tau_1 - \tau_2)$. Hence, the fitting procedure results in $A_p$ and $A_d$ besides the characteristic lifetime values. (It should be noted, however, that using laser pulses of high energy produces copper(II) complexes in relatively large concentrations resulting in a bimolecular backward electron transfer in bulk that can compete efficiently with the pseudo first-order decay paths of the electron. In this case, the fitting to a simple exponential decay, and hence the $\tau_2$ value, can be regarded as a reasonable approximation only.)

## 4. Characteristics of longer-lived excited states

It has also been shown that the excited molecular entities generated by 266 nm excitation of $Cu(CN)_2^-$ in the presence of halide ion have a very strong absorption that peaks at 320 nm with a shoulder at 400 nm [14]. The maximum of this absorption was found to be comparable to that of the solvated electron at 700 nm. Moreover the decay rate of the luminescence and 400-nm absorption are almost identical suggesting that it is the luminescent species that has a strong absorption in this range. However no appropriate attention was focussed on assigning the transient absorption in the UV. Our recent measurements indicate that absorption of the excited species is relatively strong between 250 and 300 nm too (Fig. 2). For the case of aqueous solutions of chlorocuprate(I) and bromocuprate(I) complexes it has been demonstrated that the lifetime of the luminescent species ($\tau_{lum}$) and the growing-in stage of the electron absorption signal ($\tau_{e,1}$) were virtually identical at a variety of halide ligands and concentrations of quencher and electron scavenger [4,11]. Thus, it was concluded that the source of the ‘delayed’ electron is either the emitting triplet excited complexes [19] or another excited state which is in equilibrium with the luminescence state. It is interesting to contrast the nature of halo- and mixed-ligand dicyanohalocuprate(I) complexes in this respect. The growing-in lifetime of transient absorption detected at 675 nm for $Cu(CN)_2^- - Y^-$ equilibrium systems at various ligand concentrations and at different temperatures is always shorter than the lifetime of the luminescent species (Table 2). This strongly suggests that the excited state that is the source of the ‘delayed’ electron is different from that of the emitting molecular entity. Although the lifetime of electron ejecting species is shorter than the lifetime of the luminescent excited state, it is still sufficiently long to suppose that it has a triplet character.

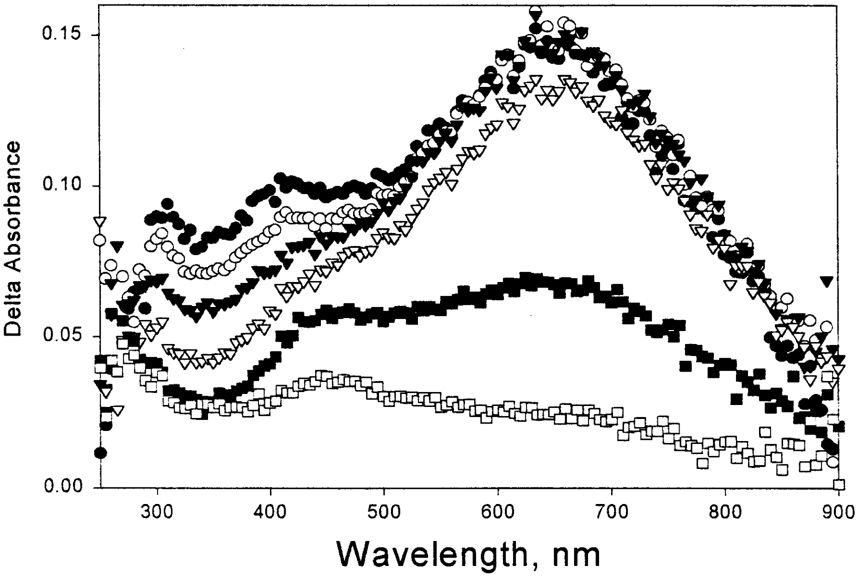


Fig. 2. Time resolved transient absorption spectra measured in aqueous solution of $4.78 \times 10^{-4}$ M dicyanocuprete(I) at 5 M ionic strength and 2 M NaCl, $\lambda_{exc} = 266$ nm, time delay after laser pulse: (●) 20 ns, (○) 50 ns, (▼) 100 ns, (▽) 200 ns, (■) 600 ns, (□) 1600 ns.

## 5. Mono- and biphotonic processes

A series of transient absorption are presented in Fig. 3. The signals were detected in aqueous solution of dicyanocuprate(I) in the presence of chloride ions (5 M). An increase in laser pulse energy results in the enhancement of the transient absorption, which is accompanied by a considerable change in the shapes of the curves. At very low laser energy the slow growing-in can be observed after the excitation. The signal peaks at about 350 ns, and then there is a very slow decay. The increase of the laser energy leads to a 'prompt' increase of the absorption within the duration of the laser pulse which is followed by the slow development of the absorption. It

Table 2
The lifetime of different excited species and the quantum yield for hydrated electron formation by monophotonic excitation in different systems at 5 M ionic strength and at ambient temperature

| System | $\tau_{lum}$ (ns) | $\tau_1$ (ns) | $\phi_{e,1}$ | [Cu(I)] (M) |
|---|---|---|---|---|
| $Cu(CN)_2^-$ | – | $16 \pm 4$ | $0.24 \pm 0.03$ | $5.05 \times 10^{-4}$ |
| $Cu(CN)_2^-$–2 M NaCl | $157 \pm 7$ | $118 \pm 8$ | $0.27 \pm 0.03$ | $4.78 \times 10^{-4}$ |
| $Cu(CN)_2^-$–5 M NaCl | $120 \pm 8$ | $76 \pm 7$ | $0.28 \pm 0.03$ | $5.84 \times 10^{-4}$ |
| $Cu(CN)_2^-$–5 M CsCl | $113 \pm 5$ | $72 \pm 7$ | $0.28 \pm 0.03$ | $6.67 \times 10^{-4}$ |
| $Cu(CN)_2^-$–1.5 M NaBr | $248 \pm 8$ | $178 \pm 15$ | $0.11 \pm 0.02$ | $5.06 \times 10^{-4}$ |
| $Cu(CN)_2^-$–0.1 M NaI | $120 \pm 8$ | $76 \pm 7$ | $0.06 \pm 0.01$ | $5.02 \times 10^{-4}$ |

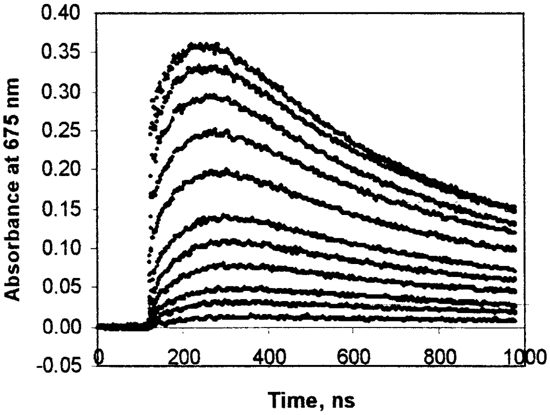


Fig. 3. Dependence of transient absorption signals on pulse energy measured in aqueous solution of $5.84 \times 10^{-4}$ M dicyanocuprate(I) at 5 M NaCl, $\lambda_{exc} = 266$ nm. Pulse energies: 0.64, 1.18, 2.54, 3.66, 4.41, 5.75, 7.93, 9.46, 11.0, 12.1, and 13.6 mJ.

should be noted that the maximum of the transient absorption is shifted to a shorter time and a faster decay can be observed after the maximum upon increasing the pulse intensity. At very high energy the increase of the absorption under the laser pulse is more pronounced than within the slow 'growing-in' period. Hence, we can conclude that the electron is ejected by two excited species and the dependence of the efficiency of these processes on laser energy is rather different.

It can be seen in Fig. 4 that the yield of electrons originating from both sources and the luminescence intensity increase with the laser pulse energy. However, the shapes of the curves are different. The yield of electrons formed after the excitation increases with pulse energy, and then it levels off at higher energies. On the other hand the yield of electrons ejected under the excitation seems to increase as a quadratic function of laser energy. It should be noted that the luminescence intensity measured at the end of the laser shows nearly linear dependence on the pulse intensity. These observations suggest not only that the electrons are ejected by different excited states but that the emission also originates from a third excited molecular entity, consistent with a 'three excited state model' assumed by considering the lifetime data obtained by transient absorption and luminescence measurements. It is reasonable to suggest that a monophotonic process results in the luminescence from the lowest energy triplet excited state, and the 'delayed' electron escapes from the higher level intermediate excited state (IES). The absorption of the second photon by this IES leads to a very short-lived energy-rich excited state that can 'promptly' eject an electron.

The yields of electrons originating from the intermediate state as a function of pulse intensity are shown in Fig. 5 for aqueous solutions of dicyanocuprate(I) at different concentrations of various halide ions. The figure clearly indicates that the yield of this type of electrons strongly depends on the nature on the halide ion and its concentration. While chloride ion increases its efficiency the bromide and

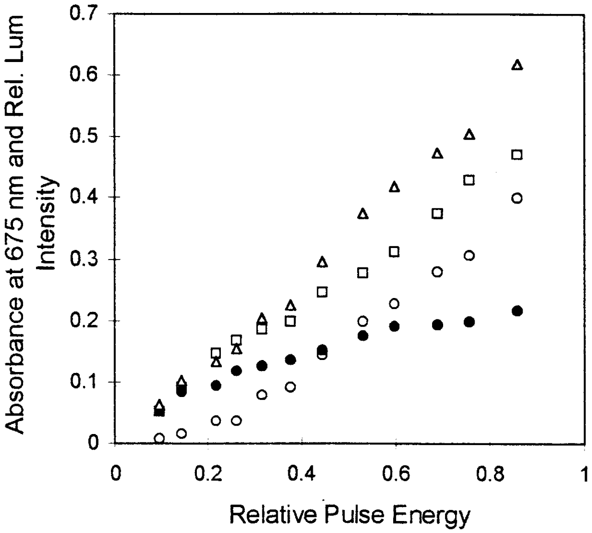


Fig. 4. Dependence of the yield of solvated electrons and the luminescence intensity measured after the laser pulse on excitation power in aqueous solution of $6.67 \times 10^{-4}$ M dicyanocuprate(I) at 5 M CsCl: (■) electrons formed after the laser pulse, (●) electrons formed under the laser pulse, (★) luminescence intensity, (○) total yield of electrons.

especially the iodide ions reduce the electron formation by this mechanism. It is important to note that at 5 M chloride concentration there is a considerable influence of the 'innocent' cations on the efficiency of electron formation. The effect that heavy atoms, either as innocent cations or within the anionic complex, have on the ejection efficiency suggests the importance of intersystem crossing between the singlet and triplet states and/or spin relaxation within the IES, which is a radical pair generated either in singlet or triplet form.

The dependence of quantum yield of electrons generated by two-photon absorption on pulse energy is depicted in Fig. 6. The inset confirms the quadratic nature of this relation. In contrast to a monophotonic process, these results suggest that the yield of electrons ejected by the biphotonic process is not sensitive to the nature and the concentration of halide ions. Thus, the products of the absorption cross sections, $\sigma$, and the quantum yield, $\phi$, for the formation of the IES and that of electrons by second-photon absorption, i.e. $\sigma_{GS}\phi_{IES}\sigma_{IES}\phi_{spe}$, are nearly the same for all systems investigated [20,21] (where $\sigma_{GS}$ is the absorption cross section of the ground-state species, $\phi_{IES}$ is the quantum yield of the formation of the IES, $\sigma_{IES}$ is the absorption cross section of IES and $\phi_{spe}$ is the quantum yield of the solvated electron formation generated by the second-photon absorption of IES). This is somewhat unexpected because the molar absorption coefficients and, hence, the values of $\sigma_{GS}$ of the ground-state complexes are slightly different. In order to obtain reliable values of $\sigma_{GS}$, $\phi_{IES}$, $\sigma_{IES}$ and $\phi_{spe}$ for a more sophisticated analysis further investigations need to be performed. On the other hand, it is reasonable to suppose

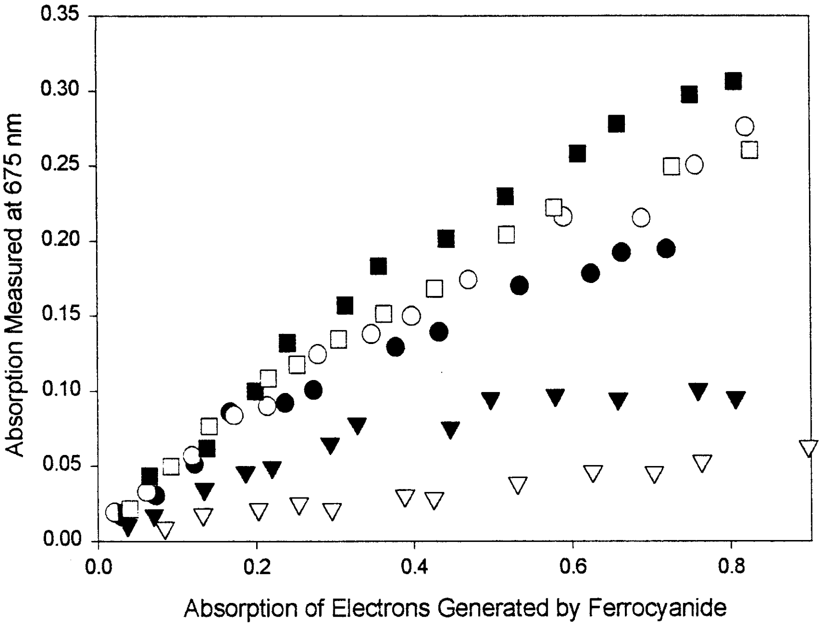


Fig. 5. Dependence of the yield of the hydrated electrons formed after the laser pulse on excitation power in aqueous solutions of $Cu(CN)_2^- - Y^-$ systems, [Cu(I)] $\cong 5 \times 10^{-4}$ M, $\mu = 5$ M: (●) [halide] = 0 M, (○) 2 M NaCl, (■) 5 M NaCl, (□) 5 M CsCl, (▼) 1.5 M NaBr, (▽) 0.1 M NaI.

that the values of $\sigma_{GS}\phi_{IES}$ as well as $\sigma_{IES}\phi_{spe}$ are rather similar for all dicyanocuprate(I)–halide systems; hence, the differences between the curves for $\phi_{e,mono}$ versus pulse energy can be attributed to the various efficiencies of the electron escape, $\varphi_{esc} = k_{esc}/(k_{esc} + k_{nr})$ from the IES. As demonstrated in Fig. 5, the yield of monophotonic electrons decreases in the order: chloride > bromide > iodide, such that an increase in the rate of non-radiative deactivation, $k_{nr}$, from the intermediate state is expected with an increase of the atomic number of the halide ions.

## 6. Temperature dependence

The decay rate of the luminescence transients is considerably increased by increasing the temperature providing evidence for efficient non-radiative deactivation of the emitting triplet state, while an enhancement is observed in the transient absorption signals when the temperature increases from ~10 to ~50°C. In addition to the enhancement of the absorption signals, the shape of the transients is also changed, especially for the dicyanocuprate(I)–bromide ion system (Fig. 7). There is a small increase in the absorption under the laser pulse, suggesting a very weak temperature effect on the biphotonic electron ejection. On the other hand, the

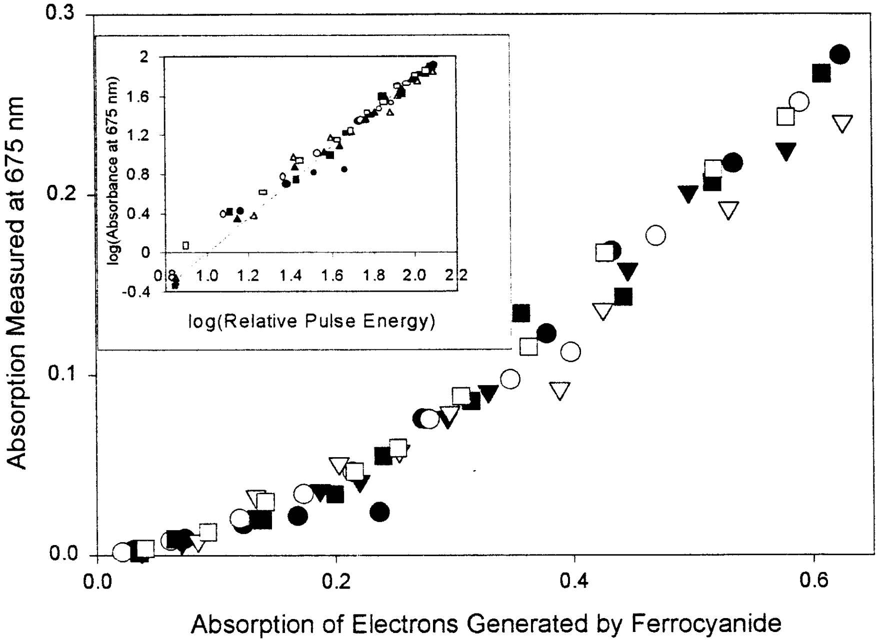


Fig. 6. Dependence of the yield of the hydrated electrons formed under the laser pulse on excitation power in aqueous solutions of Cu(CN)$_2^-$–Y$^-$ systems, [Cu(I)] $\cong 5 \times 10^{-4}$ M, $\mu = 5$ M: (●) [halide] = 0 M, (○) 2 M NaCl, (■) 5 M NaCl, (□) 5 M CsCl, (▼) 1.5 M NaBr, (▽) 0.1 M NaI. Inset shows the log–log representation of the data.

electron ejection from the excited state achieved by one-photon absorption is more efficient and the rate of decay of IES is faster at ~ 50°C than at ~ 10°C. The activation energy of the non-radiative deactivation of IES was estimated using the

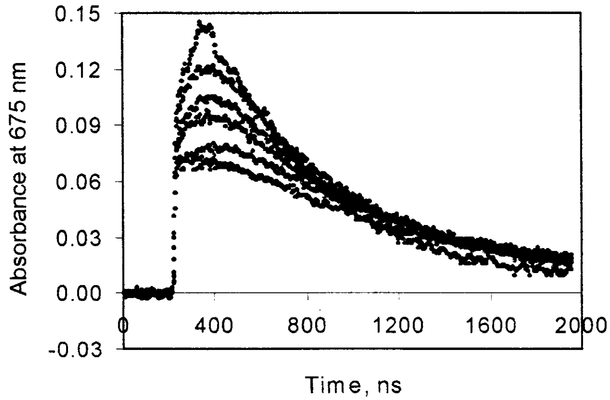


Fig. 7. Transient absorption signals detected at constant laser pulse energy in aqueous solution of Cu(CN)$_2^-$–Br$^-$ system at different temperatures: [Cu(I)] = $5.06 \times 10^{-4}$ M, [Br$^-$] = 1.5 M, $\mu = 5$ M.

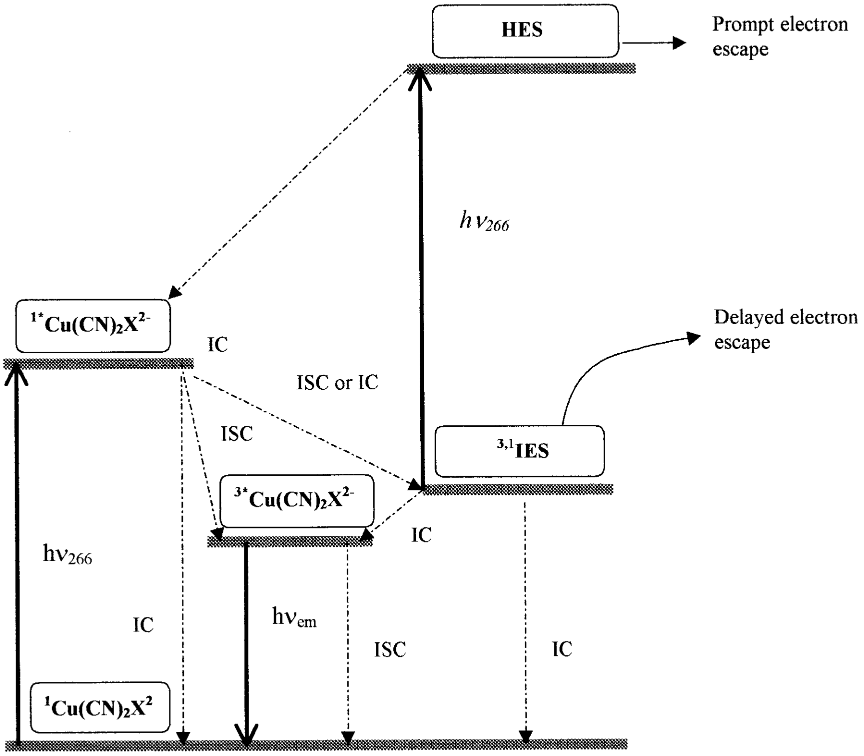
simple Arrhenius equation. The $E_a$ values obtained by this procedure are about 20–25 kJ mol$^{-1}$, suggesting a relatively small potential barrier for deactivation of IES. It should be noted that rather similar values were obtained for the deactivation of the luminescent species in spite of the fact that the lifetime of the luminescent species is considerable longer than that of IES.

## 7. Proposed model

All of these diverse experimental observations can be rationalized by the following model and depicted in Scheme 1 (where ISC = intersystem crossing, IC = internal conversion).

Upon UV excitation of dicyanocuprate(I) the efficient electron ejection occurs by two different mechanisms, namely the mono- and biphotonic processes.

The excited state achieved by one-photon absorption from which the electron can escape by a relatively slow process has higher energy and a shorter lifetime than the luminescent species. Formation of radicals $Y_2^{-\bullet}$ was confirmed in dicyanocuprate(I)–halide systems [14,15] as well as in halocuprate(I) systems [4,11].



Scheme 1.

This radical could be formed in a variety of ways, such as from $Y^{\bullet}$ radical released from a longer-lived intermediate excited state (e.g. $^{3}$IES) or by bimolecular reactions of this intermediate with a halide ion in the ground state [4].

$$^{1}Cu(CN)_{2}Y^{2-} + h\nu_{(266\ nm,1)} \rightarrow {}^{1*}Cu(CN)_{2}Y^{2-} \tag{9}$$

$$^{1*}Cu(CN)_{2}Y^{2-} \rightarrow {}^{1*}Cu(CN)_{2}Y^{2-} \tag{10}$$

$$^{1*}Cu(CN)_{2}Y^{2-} \xrightarrow{k_{IC}} {}^{1}\{IES\} \tag{11}$$

$$^{1}\{IES\} \overset{k_{ST}}{\leftrightarrow} {}^{3}\{IES\} \tag{12}$$

$$^{1}\{IES\} \rightarrow {}^{1}Cu(CN)_{2}Y^{2-} \tag{13}$$

$$^{3}\{IES\} \rightarrow {}^{2}Cu(CN)_{2}^{2-} + Y \tag{14}$$

$$^{3}\{IES\} + Y^{-} \rightarrow {}^{2}Cu(CN)_{2}^{2-} + Y_{2}^{-\bullet} \tag{15}$$

$$^{1,3}\{IES\} \rightarrow {}^{2}Cu(CN)_{2}Y^{-} + e_{aq}^{-} \tag{16}$$

The efficiency of the electron formation from this excited state strongly depends on the power of the laser pulse. At higher pulse intensity the yield of electrons levels off and decreases slightly. Hence, it can be regarded as a state that absorbs the second photon.

The presence of heavy atoms either in the coordination sphere or in the outer sphere results in a decrease of the electron escape from IES because of the efficient intersystem crossing or a spin relaxation followed by a spin allowed process.

The luminescent state is the lowest energy excited triplet state which can be formed from the lowest energy singlet excited state or from the intermediate state that may possess both singlet and triplet character.

$$^{1*}Cu(CN)_{2}Y^{2-} \xrightarrow{k_{ISC1}} {}^{3*}Cu(CN)_{2}Y^{2-} \tag{17}$$

$$^{3}\{IES\} \rightarrow {}^{3*}Cu(CN)_{2}Y^{2-} \tag{18}$$

$$^{3*}Cu(CN)_{2}Y^{2-} \xrightarrow{k_{ISC2}} {}^{1}Cu(CN)_{2}Y^{2-} \tag{19}$$

$$^{3*}Cu(CN)_{2}Y^{2-} \xrightarrow{k_{Phos}} {}^{1}Cu(CN)_{2}Y^{2-} \tag{20}$$

Electron ejection also occurs from a very high energy excited state (HES) achieved by the second-photon absorption. The overall yield of the biphotonic electron ejection does not seem to be dependent on the nature of the halide ligands.

$$^{1,3}\{IES\} + h\nu_{(266\ nm,2)} \rightarrow HES \tag{21}$$

$$HES \rightarrow {}^{2}Cu(CN)_{2} + Y^{-} + {}^{2}e_{aq}^{-} \tag{22}$$

$$HES \rightarrow {}^{1**}Cu(CN)_{2}Y^{2-} \tag{23}$$

Because $\sigma_{GS}\phi_{IES}\sigma_{IES}\phi_{spe}$ products should be nearly the same (Fig. 6) and the molar absorption coefficient, $\varepsilon$, of the ground state species (the absorption cross section $\sigma_{GS}$) depends slightly on the nature of halide ions, we should conclude that the intermediate states have also rather similar molar absorption. Hence, it is reasonable to suppose that the light-absorbing intermediates of the different systems are identical or at least rather similar. Because the intersystem crossing to the ground-state or the spin relaxation within the radical pair is relatively slow when the third ligand is the chloride the electron escape is very efficient from this state. In contrast, the ISC or radical pair recombination is fast in the presence of iodide because of strong spin-orbit coupling, therefore the delayed electron ejection is not so efficient.

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