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Laser flash photolysis of $IrCl_6^{2-}$ in aqueous solutions

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Abstract

The method of laser flash photolysis (308 nm) is used to study the photochemistry of $IrCl_6^{2-}$ complex in aqueous solutions with and without free Cl^- ions. Photolysis in aqueous solutions lead to photoaquation of initial complex within less than 20 ns with a quantum yield of 0.01. In aqueous solutions containing free Cl^- ions, the photoreduction of $IrCl_6^{2-}$ and the appearance of an absorption band of $Cl_2^{\bullet-}$ radical ion with a maximum at 350 nm are observed. An increase in the Cl^- ion concentration causes an increase in both the quantum yield of photoreduction and $Cl_2^{\bullet-}$ yield. These results allow one to conclude that a chlorine atom, precursor of $Cl_2^{\bullet-}$ radical ion, arises due to the electron transfer from an outerspheric Cl^- ion to the excited complex. The obtained experimental data have made it possible to estimate the rate constants of direct and back electron transfer in the $(IrCl_6^{2-})^*$–Cl^- pair. © 2000 Published by Elsevier Science B.V. All rights reserved.

Keywords: Photochemistry; $IrCl_6^{2-}$; Laser flash photolysis; Free Cl^- ion; Electron transfer

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1. Introduction

Study of $IrCl_6^{2-}$ phototransformations is highly important for determining primary processes in the photochemistry of the halide complexes of transition metals. The $IrCl_6^{2-}$ complex has an extremely consistent coordination sphere and is stable in aqueous and organic solutions in the absence of free Cl^- ions. Stability and spectral peculiarities make it convenient to study photoprocesses in various solvents with and without free halide ions [1–7]. Determination of the primary processes for halide complexes of transition metals in aqueous solutions is hampered by the small quantum yields of phototransformations. Therefore, for many complexes, these processes remain unknown. Note, however, that a study of the photochemistry of complexes in aqueous solutions is highly significant for investigating the transformations and balance of organic impurities in large volumes of natural water, in which the complexes of many metals are dissolved.

The photochemistry of $IrCl_6^{2-}$ in aqueous solutions and aqueous solutions containing free chloride ions has been studied in Refs. [5–7]. These papers give rather contradictory data. Thus, in Ref. [5], it is claimed that the only photochemical process for $IrCl_6^{2-}$ is photoaquation which results in the $IrCl_5(H_2O)^-$ complex. This viewpoint was

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criticised in Ref. [6]. The authors indicate the competition between photoaquation and photoreduction of Ir(IV) to Ir(III). They also demonstrate that the origin of products and quantum yield depend on the wavelength of exciting light and the concentration of free chloride ions in aqueous solution. Excitation in the region of a short-wave charge transfer band (254 nm) leads to the formation of complexes $IrCl_5(H_2O)^-$ (photoaquation product) and $IrCl_5(H_2O)^{2-}$ (photoreduction product) with a total quantum yield of 0.029 independent of the concentration of free Cl^- ions in solution. However, the contribution of photoreduction to quantum yield linearly increases with the concentration of chloride ions. The mechanism of photolysis proposed in Ref. [6] explains the dependence of the photoreduction quantum yield on Cl^- concentration. It includes a successive formation of two intermediates, $[IrCl_5^{2-}\cdots Cl^\bullet]$ (primary radical pair) and $[IrCl_5(H_2O)^{2-}\cdots Cl^\bullet]$ (secondary radical pair). The latter transforms into the final reaction products

$$IrCl_6^{2-}\underset{k_{-1}}{\overset{h\nu}{\rightleftarrows}}[IrCl_5^{2-}\cdots Cl^\bullet] \quad (1)$$

$$[IrCl_5^{2-}\cdots Cl^\bullet]\xrightarrow{H_2O}[IrCl_5(H_2O)^{2-}\cdots Cl^\bullet] \quad (2)$$

$$[IrCl_5(H_2O)^{2-}\cdots Cl^\bullet] \rightarrow IrCl_5(H_2O)^- + Cl^- \quad (3)$$

$$[IrCl_5(H_2O)^{2-}\cdots Cl^\bullet] \rightarrow IrCl_5(H_2O)^{2-} + Cl^\bullet \quad (4)$$

$$[IrCl_5(H_2O)^{2-}\cdots Cl^\bullet]\xrightarrow{Cl^-}IrCl_5(H_2O)^{2-} + Cl_2^{\bullet -} \quad (5)$$

On photolysis of $IrCl_6^{2-}$ in aqueous solutions in the region of d–d bands (313 nm), only the photoaquation with a quantum yield of 0.01 was observed [6]. The irradiation at this wavelength in the solution containing chloride ions (1.2 M) leads to photoreduction of $IrCl_6^{2-}$ resulting in $IrCl_6^{3-}$ (quantum yield is about 2×10^{-2}). The transformation of the mechanism (appearance of $IrCl_6^{3-}$) is not discussed in Ref. [6]. The electron transfer from a free outerspheric Cl^- ion to the excited complex is assumed [7] to be the primary process

$$IrCl_6^{2-} \xrightarrow{h\nu} (IrCl_6^{2-})^* \xrightarrow{Cl^-} IrCl_6^{3-} + Cl^\bullet \quad (6)$$

The $IrCl_6^{2-}$ charge transfer bands in the visible part of the spectrum ($\lambda > 420$ nm) are actually nonphotoactive (quantum yield being smaller than 10^{-4} [6]).

Earlier, using the methods of laser flash photolysis, low-temperature spectrophotometry, and ESR, we have established the primary photoprocesses for $IrCl_6^{2-}$ in alcohols and acetonitrile [1–3]. Under irradiation in alcohols in the region of the overlapping of d–d band with that of charge transfer (308 nm), the only primary process is the electron transfer from a solvent molecule to the light-excited complex [1,2]

$$IrCl_6^{2-} \xrightarrow{h\nu} (IrCl_6^{2-})^* \xrightarrow{RH} IrCl_6^{3-} + R^\bullet + H^+ \quad (7)$$

Irradiation at 248 nm (short-wave charge transfer band) also causes the photoreduction of the central ion. However, the electron transfer Eq. (7) in this case is accompanied by the action of an additional channel with the elimination of a chlorine atom from the coordination sphere of the excited complex (reaction similar to reaction (4)) giving rise to the $IrCl_5(CH_3OH)^{2-}$ complex. A share of this channel in the total process of Ir(IV) photoreduction is about 30% [1]. Finally, in acetonitrile solutions of $IrCl_6^{2-}$, a step-by-step photosolvation of the initial complex is observed [3].

The aim of this paper is to establish the primary processes of $IrCl_6^{2-}$ photochemistry in aqueous solutions by the method of laser flash photolysis. Nanosecond time resolution allows one to record reaction intermediates, and determine the mechanism of phototransformations at a qualitatively higher level as compared to stationary techniques.

2. Experimental

Solutions of the $IrCl_6^{2-}$ complex were prepared using $Na_2IrCl_6\cdot 6H_2O$ (Aldrich). LiCl (Aldrich) was employed as a source of chloride ions. Water was purified by double distillation. The optical absorption spectra were recorded on UNICAM 8735/50 or Specord UV–VIS (Carl Zeiss) spectrophotometers. The steady-state photolysis was performed using radiation of a high-pressure mercury lamp with glass filters for separating the necessary wavelengths. Sometimes, a pulsed XeCl laser (308 nm) was used as a light source. In this case, the identity of changes in the absorption spectra powdered by lamp and laser irradiation was controlled.

A set-up for laser flash photolysis [8] consisted of an excimer laser (308 nm, 20 ns) for excitation, pulse xenon arc lamp with a monochromator as a source of probing light and a monochromator with photomultiplier in a measuring channel. The signal, produced by photomultiplier, was recorded using a digital Tektronix 7912AD oscillograph connected to an IBM computer.

3. Results and discussion

3.1. Photolysis of $IrCl_6^{2-}$ in aqueous solutions

The electronic absorption spectrum of $IrCl_6^{2-}$ complex contains strong absorption bands both in visible and UV regions. Absorption bands in the region of 400–500 nm with an extinction coefficient of about 4000 $M^{-1}\,cm^{-1}$ (curve 1 in Fig. 1) are the bands of ligand-to-metal charge transfer (LMCT) [9]. A stronger band of charge transfer has a maximum at 232 nm, weak bands at 306 and 360 nm belong to d–d ligand-field (LF) transitions.

Fig. 1 shows a change in the absorption spectrum of $IrCl_6^{2-}$ in aqueous solution without addition of a free Cl^- ion under stationary irradiation at 308 nm in the region of d–d transition. In the course of photolysis, seven isosbestic points are preserved (at 289, 316, 397, 440, 526, and 569 nm). The resulting absorption band with a maximum at 443 nm belongs to a photosolvation product-$IrCl_5(H_2O)^-$ complex (curve 5 in Fig. 1). The quantum yield of photolysis is 10^{-2} [6].

Experiments on the $IrCl_6^{2-}$ flash photolysis (308 nm) revealed no time-dependent intermediate absorption in the wavelength range of 340–700 nm. Only the instant change in optical density is observed after a laser pulse (Fig. 2a). The spectrum of this instant change depends on both a decrease in optical density in the bands of initial complex and an appearance of absorption of the aquated $IrCl_5(H_2O)^-$ complex. Solid line in Fig. 2b shows the difference in spectra 1 and 5 (Fig. 1) under stationary irradiation (difference in the spectra of $IrCl_5(H_2O)^-$ and $IrCl_6^{2-}$). Dots mark a change in the optical density in pulsed experiments (steady state and pulsed measurements are normalised at 490 nm). Coincidence of the curves in Fig. 2b shows that a laser pulse (20 ns) is followed by the appearance of the aquated $IrCl_5(H_2O)^-$ complex without intermediate kinetic processes in the range of 20 ns to seconds.

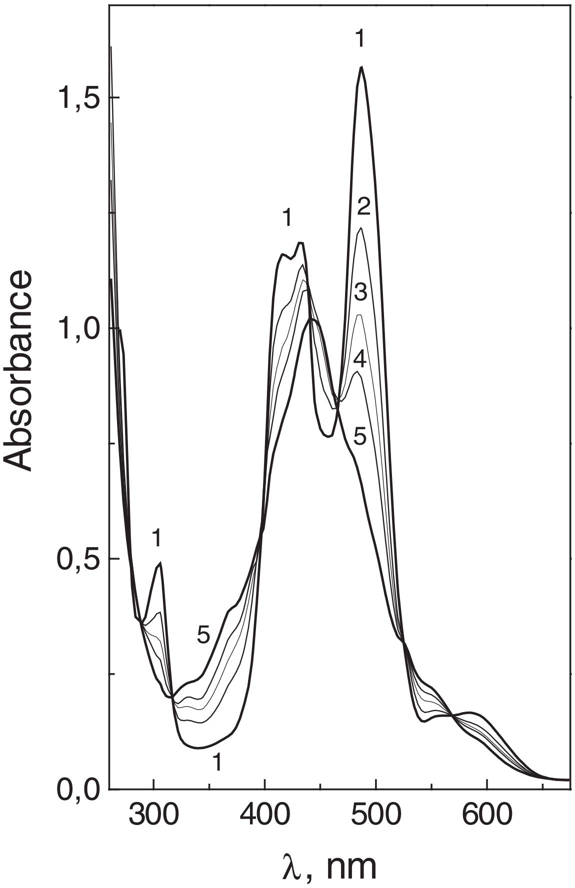

Fig. 1. Change in the optical spectrum of $IrCl_6^{2-}$ complex (4×10^{-3} M) in aqueous solution under stationary irradiation by an XeCl laser (308 nm, 10 mJ, 10 Hz). Temperature: 295 K; cuvette thickness: 0.1 cm; curves 1–5 denote 0, 60, 180, 360, 960 s of irradiation, respectively.

Thus, the main process of $IrCl_6^{2-}$ photochemistry in aqueous solutions under irradiation at

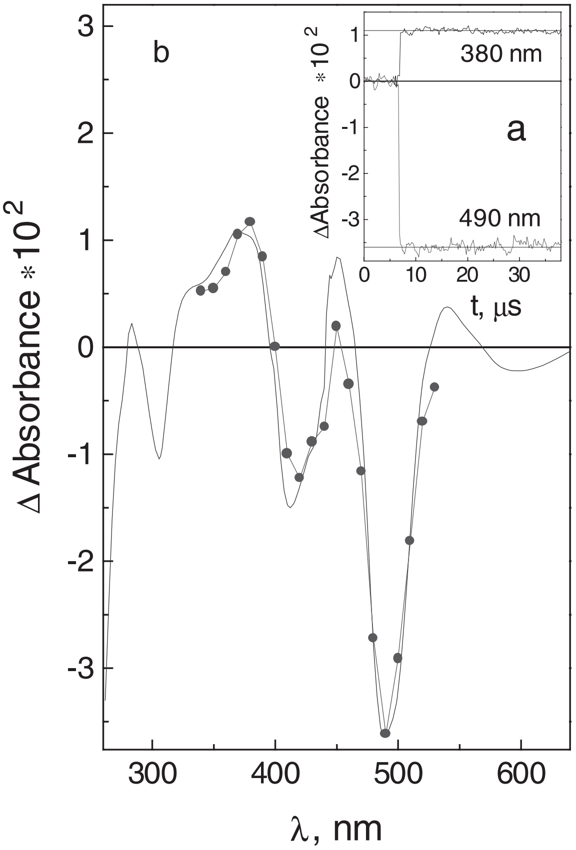

Fig. 2. Kinetic curves (a) and spectrum of the change in optical density (b) during laser flash photolysis (XeCl laser, 308 nm) of aqueous solution of $IrCl_6^{2-}$ (4.7×10^{-3} M). (temperature: 295 K; cuvette thickness: 1 cm). For (b), solid line represents change in optical density during stationary photolysis (difference in curves 5 and 1, presented in Fig. 1, represent difference in spectra of $IrCl_5(H_2O)^-$ and $IrCl_6^{2-}$), dots represent change in optical density after a laser pulse. Both the curves are normalised by the value at 490 nm.

308 nm is photoaquation. Some distortion of isosbestic points at large phototransformation depths can be assigned to further photoaquation of the resulting complex $IrCl_5(H_2O)^-$. The mechanism of the photolysis is discussed in Section 3.3.

3.2. Primary processes and formation of $Cl_2^{\bullet -}$ radical ion from $IrCl_6^{2-}$ photolysis in the presence of free chloride ions

Steady-state photolysis of the aqueous solutions of the $IrCl_6^{2-}$ complex in the presence of free Cl^- ions leads to a decrease in the relative yield of the aquated complex $IrCl_5(H_2O)^-$. Thus, some complexes are subjected to photoreduction which is confirmed by the results of laser flash photolysis. In the presence of even small amount (>0.01 M) of free Cl^- ions, the laser pulse is followed by intermediate absorption with a maximum at 350 nm (Fig. 3) belonging to the $Cl_2^{\bullet -}$ ion radical ($\varepsilon = 9600$ $M^{-1}\,cm^{-1}$ [10]). The chlorine atom is a precursor of this species

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet -} \qquad (8)$$

The rate constant of this reaction is close to the diffusion one and depends on the medium pH (2.1×10^{10} $M^{-1}\,s^{-1}$ (pH 2) [11], 8×10^9 $M^{-1}\,s^{-1}$

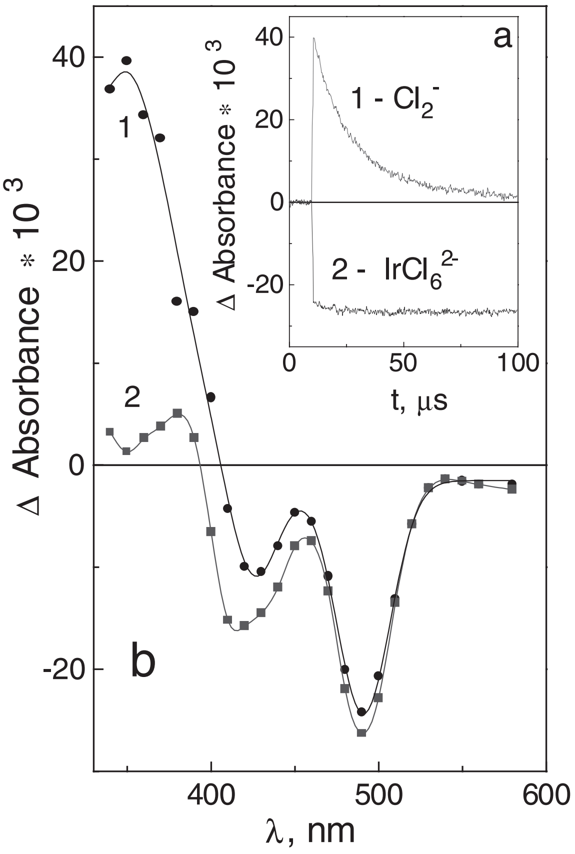

Fig. 3. Flash photolysis of $IrCl_6^{2-}$ in aqueous solution with 1 M LiCl. Cuvette thickness: 1 cm; initial $IrCl_6^{2-}$ concentration, 4.7×10^{-4} M. (a) Kinetic curves of a change in intermediate absorption at 350 nm (1) and 490 nm (2). (b) Spectra of intermediate absorption just after laser pulse (1) and after 90 μs (2).

(pH 3.5) [12], 6.5×10^9 $M^{-1} s^{-1}$ (pH is omitted) [13]. Reaction (8) is actually the only channel of chlorine atom disappearance in aqueous solutions. Indeed, the reactions involving water and hydroxide ion ($k_9 = 1.6 \times 10^5$ s^{-1}, $k_{10} = 1.8 \times 10^{10}$ $M^{-1} s^{-1}$ [13]) or the recombination of chlorine atoms ($k_{11} = 8.8 \times 10^7$ $M^{-1} s^{-1}$ [14]) at chloride ion concentration of about 10^{-2} M cannot compete with the reaction of $Cl_2^{\bullet -}$ formation:

$$Cl^{\bullet} + H_2O \rightarrow ClOH^- + H^+ \tag{9}$$

$$Cl^{\bullet} + OH^- \rightarrow ClOH^- \tag{10}$$

$$Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2 \tag{11}$$

The $IrCl_6^{2-}$ complex is a convenient object of pulsed experiments and the study of the processes of $Cl_2^{\bullet -}$ radical ion formation. In the absorption band of radical ion at 350 nm, the absorption of the initial and aquated complexes is much weaker ($\varepsilon^{350}(Cl_2^-) = 9600$ $M^{-1}cm^{-1}$ [10], $\varepsilon^{350}(IrCl_6^{2-}) = 235$ $M^{-1}cm^{-1}$, $\varepsilon^{350}(IrCl_5(H_2O)^-) = 720$ $M^{-1}cm^{-1}$). In the region of the long-wave absorption band of $IrCl_6^{2-}$ at 490 nm, the radical ion does not absorb. Therefore, the amounts of initial $IrCl_6^{2-}$ and resulting $Cl_2^{\bullet -}$ radical ion (quantum yield of $IrCl_6^{2-}$ disappearance and relative $Cl_2^{\bullet -}$ yield) can be determined just after the laser pulse.

Fig. 4 shows the dependencies of relative quantum yield and $Cl_2^{\bullet -}$ yield on the concentration of Cl^- ion. Let us consider the feasible processes of chlorine atom formation (and then of $Cl_2^{\bullet -}$ radical ion) and determine their agreement with experimental data. The first possible process of chlorine atom appearance is related to its formation in the first coordination sphere upon excitation of $IrCl_6^{2-}$ with the appearance of primary $[IrCl_5^{2-} \cdots Cl^{\bullet}]$ and then secondary $[IrCl_5(H_2O)^{2-} \cdots Cl^{\bullet}]$ radical pairs. A free Cl^- ion can accept the chlorine atom of the secondary pair giving rise to the $Cl_2^{\bullet -}$ radical ion (reaction (5)). The reaction of photoreduction resulting from the excitation of d–d transition can be assigned to the relaxation into the underlying charge transfer states [15], corresponding to the absorption bands of $IrCl_6^{2-}$ in the region of 410–500 nm. As these excited states show no photochemical activity, there is relaxation into the charge transfer states of another multiplicity.

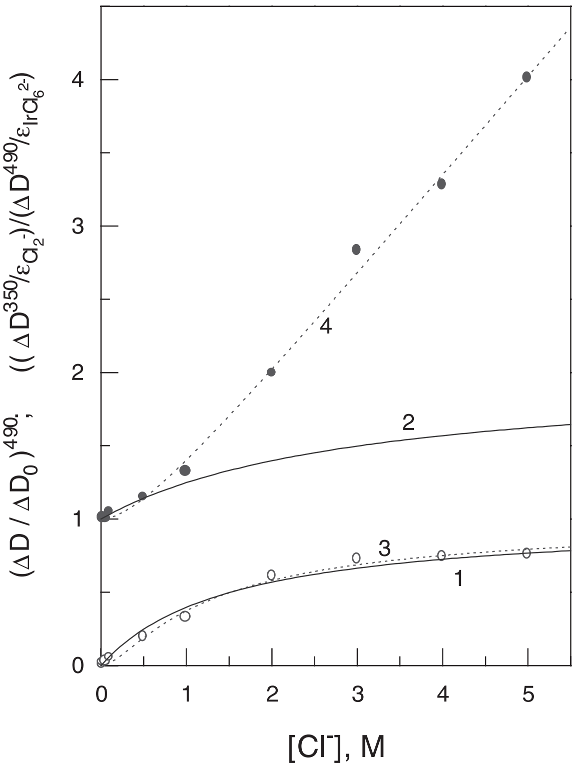

Fig. 4. A relative change in optical density at 490 nm ($\Delta D^{490}/\Delta D_0^{490}$) (bleaching in the $IrCl_6^{2-}$ absorption band) (●) and at 350 nm ($(\Delta D^{350}/\varepsilon^{350}_{Cl_2^-})/(\Delta D^{490}/\varepsilon^{490}_{IrCl_6^{2-}})$) (appearance of $Cl_2^{\bullet -}$ absorption) (○) just after a laser pulse vs LiCl concentration. ΔD_0^{490} represents a decrease in optical density for solutions without LiCl. Solid lines 1, 2 represent approximation with respect to Eqs. (13) and (15) with parameter $\alpha = 0.33$ M^{-1}. Dotted line 3 represents approximation with respect to Eq. (23) with parameters $\alpha = 0.36$ M^{-1}, $\beta = 1.4$ M^{-1}. Dotted line 4 represents approximation with respect to Eq. (24) with parameters $\alpha = 0.41$ M^{-1}, $\beta = 2.6$ M^{-1}.

The quantum yield of the disappearance of the initial $IrCl_6^{2-}$ complex in this case should be independent of the concentration of free chloride ions (equal to the quantum yield of secondary radical pair formation) and obeys the equation

$$\varphi_0 = \frac{k_2}{k_{-1} + k_2}. \tag{12}$$

As the concentration of Cl^- increases, a larger part of $[IrCl_5(H_2O)^{2-} \cdots Cl^{\bullet}]$ pairs avoids the back electron transfer and gives rise to $\mathrm{Cl}_2^{\bullet -}$ radical ions. Even at constant quantum yield, the bleaching at 490 nm after a laser pulse will increase with Cl^- concentration due to a decrease in the yield of the aquated $\mathrm{IrCl_5(H_2O)^-}$ complex which also has absorption at 490 nm

$$\frac{\Delta D^{490}}{\Delta D_0^{490}} = \frac{\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}}}{\left(\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}} - \varepsilon^{490}_{\mathrm{aq}}\right)}\left(1 - \frac{\varepsilon^{490}_{\mathrm{aq}}}{\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}}}\frac{k_3}{k_3 + k_5[\mathrm{Cl}^-]}\right) = \frac{1}{1-\tilde{\varepsilon}}\left(1 - \tilde{\varepsilon}\frac{1}{1+\alpha[\mathrm{Cl}^-]}\right), \tag{13}$$

where ΔD^{490} and ΔD_0^{490} are the changes in optical density at 490 nm with and without free Cl^- ions, $\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}}$ and $\varepsilon^{490}_{\mathrm{aq}}$ are the extinction coefficients of IrCl_6^{2-} and $\mathrm{IrCl_5(H_2O)^-}$ ($\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}} = 4000\ \mathrm{M^{-1}\,cm^{-1}}$, $\varepsilon^{490}_{\mathrm{aq}} = 2000\ \mathrm{M^{-1}\,cm^{-1}}$ (Fig. 1)), $\tilde{\varepsilon} = \varepsilon^{490}_{\mathrm{aq}}/\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}} = 1/2$ and $\alpha = k_5/k_3$. Note that Eq. (13) contains no rate constant of reaction (4), because the irradiation at 308 nm in solution without free Cl^- ions leads only to photoaquation. When a chlorine atom escapes into the solvent bulk, reactions (9)–(11) should follow the photoreduction of IrCl_6^{2-} complex. A relative yield of $\mathrm{Cl}_2^{\bullet -}$ radical ions in this mechanism obeys the equation

$$\frac{\Delta[\mathrm{Cl}_2^{\bullet -}]}{\Delta[\mathrm{IrCl}_6^{2-}]} = \frac{k_5[\mathrm{Cl}^-]}{k_3 + k_5[\mathrm{Cl}^-]} = \frac{\alpha[\mathrm{Cl}^-]}{1+\alpha[\mathrm{Cl}^-]}. \tag{14}$$

Transition to a change in optical densities in pulsed experiments transforms this equation as follows:

$$\frac{\Delta D^{350}}{\varepsilon^{350}_{\mathrm{Cl}_2^-}} \Bigg/ \frac{\Delta D^{490}}{\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}}} = \Delta D_{\mathrm{rel}} = \frac{\alpha[\mathrm{Cl}^-]}{(1-\tilde{\varepsilon}) + \alpha[\mathrm{Cl}^-]}. \tag{15}$$

Fig. 4 shows that the experimental dependence of ΔD_{rel} on $[\mathrm{Cl}^-]$ (solid circles) can be approximated by Eq. (15) with parameter $\alpha = 0.33 \pm 0.02\ \mathrm{M}^{-1}$ (solid line 1). Thus, the relative yield of $\mathrm{Cl}_2^{\bullet -}$ is described in this model. Owing to the relation between extinction coefficients ($\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}} = 2\varepsilon^{490}_{\mathrm{aq}}$), the value of $\Delta D^{490}/\Delta D_0^{490}$ must nonlinearly vary from 1 to 2 with increasing a Cl^- ion concentration. However, Fig. 4 shows (open circles) that this parameter increases from 1 to 4 with a change in the concentration of Cl^- ions from 0 to 5 M. Solid line 2 demonstrates the calculation of $\Delta D^{490}/\Delta D_0^{490}$ with $\alpha = 0.33\ \mathrm{M}^{-1}$. So, a relative quantum yield does not correspond to Eq. (13).

Another possible reaction of chlorine atom formation is the electron transfer from a free outerspheric chloride ion to the excited complex. To calculate the relative quantum and radical ions yields, we reduce the scheme of reactions

$$\mathrm{IrCl}_6^{2-} \underset{k_{-16}}{\overset{h\nu}{\rightleftarrows}} (\mathrm{IrCl}_6^{2-})^* \tag{16}$$

$$(\mathrm{IrCl}_6^{2-})^* \xrightarrow{\mathrm{H_2O}} \mathrm{IrCl_5(H_2O)^-} + \mathrm{Cl}^- \tag{17}$$

$$(\mathrm{IrCl}_6^{2-})^* \xrightarrow{\mathrm{Cl}^-} [\mathrm{IrCl}_6^{3-} \cdots \mathrm{Cl}^\bullet] \tag{18}$$

$$[\mathrm{IrCl}_6^{3-} \cdots \mathrm{Cl}^\bullet] \rightarrow \mathrm{IrCl}_6^{2-} + \mathrm{Cl}^- \tag{19}$$

$$[\mathrm{IrCl}_6^{3-} \cdots \mathrm{Cl}^\bullet] \xrightarrow{\mathrm{Cl}^-} \mathrm{IrCl}_6^{3-} + \mathrm{Cl}_2^{\bullet -} \tag{20}$$

Reaction (19) of the back electron transfer is similar to reaction (3). The quantum yield of IrCl_6^{2-} disappearance is determined, in this case, by the competition between the different relaxation channels of electron excitation and with regard to reaction (19) is equal to

$$\varphi = \frac{k_{17} + k_{18}[\mathrm{Cl}^-]}{k_{-16} + k_{17} + k_{18}[\mathrm{Cl}^-]} \times \left[1 - \frac{k_{18}[\mathrm{Cl}^-]}{(k_{17} + k_{18}[\mathrm{Cl}^-])}\frac{k_{19}}{(k_{19} + k_{20}[\mathrm{Cl}^-])}\right] = \varphi_0\frac{1}{1+\varphi_0\alpha[\mathrm{Cl}^-]}\left[1 + \frac{\alpha\beta[\mathrm{Cl}^-]^2}{1+\beta[\mathrm{Cl}^-]}\right], \tag{21}$$

where k_{-16}, k_{17} and k_{18} are the rate constants of radiationless transition to the ground state, aquation, and electron transfer, respectively, from Cl^- ion, $\varphi_0 = k_{17}/(k_{-16} + k_{17}) = 0.01$ is the quantum yield in the absence of a free Cl^- ion, $\alpha = k_{18}/k_{17}$, $\beta = k_{20}/k_{19}$. A relative yield of $\mathrm{Cl}_2^{\bullet -}$ radical ions in the model of outerspheric electron transfer is determined by the equation

$$\frac{\Delta[\mathrm{Cl}_2^{\bullet -}]}{\Delta[\mathrm{IrCl}_6^{2-}]} = \frac{\alpha\beta[\mathrm{Cl}^-]^2}{1+\beta[\mathrm{Cl}^-]+\alpha\beta[\mathrm{Cl}^-]^2}. \tag{22}$$

For experiments on laser flash photolysis, Eqs. (21) and (22) can be rewritten by substituting the quantum yield and relative yield of $\mathrm{Cl}_2^{\bullet-}$ by a change in optical density after a laser pulse

$$\frac{\Delta D^{490}}{(\Delta D)_0^{490}} = \frac{1}{1+\varphi_0\alpha[\mathrm{Cl}^-]}\left[1+\frac{\alpha\beta[\mathrm{Cl}^-]^2}{(1-\tilde{\varepsilon})(1+\beta[\mathrm{Cl}^-])}\right], \qquad (23)$$

$$\frac{\Delta D^{350}}{\varepsilon^{350}_{\mathrm{Cl}_2^-}} \bigg/ \frac{\Delta D^{490}}{\varepsilon^{490}_{\mathrm{IrCl}_6^{2-}}} = \Delta D_{\mathrm{rel}} = \frac{1}{1+(1-\tilde{\varepsilon})\frac{(1+\beta[\mathrm{Cl}^-])}{\alpha\beta[\mathrm{Cl}^-]^2}}. \qquad (24)$$

Fig. 4 shows that in this model of chlorine atom appearance both of the dependencies ($\Delta D^{490}/(\Delta D)_0^{490}$) and ΔD_{rel} on Cl^- concentration are well approximated by Eqs. (23) and (24) (dotted lines 3 and 4). In this case, the optimal values of parameters for Eq. (23) are $\alpha = 0.36 \pm 0.02\ \mathrm{M}^{-1}$, $\beta = 1.4 \pm 0.5\ \mathrm{M}^{-1}$, and for Eq. (24), they are $\alpha = 0.41 \pm 0.05\ \mathrm{M}^{-1}$, $\beta = 2.6 \pm 1.5\ \mathrm{M}^{-1}$. These values are clearly enough within the experimental accuracy. Thus, the dependencies of both the quantum yield and relative yield of $\mathrm{Cl}_2^{\bullet-}$ radical ions on the concentration of free Cl^- ions in aqueous solution with the close parameters α and β indicate that the photoreduction of IrCl_6^{2-} in the presence of free chloride ions occurs due to the electron transfer from the outerspheric Cl^- ion to the excited complex.

The Onsager radius ($R_o = 2e^2/\varepsilon kT$) for the IrCl_6^{2-}–Cl^- pair in water at room temperature (20°C) is 13.5 Å which is comparable with the total radius of partners (6.5 Å). Therefore, the Coulomb repulsion of the similarly charged ions cannot much hamper particle approach and electron transfer. Besides, the electron transfer can occur through the orbitals of a water molecule serving as an interlayer between the partners.

3.3. Mechanism of photolysis in ligand-to-metal charge transfer and d–d bands

In this section, we discuss the dependence of the mechanism of IrCl_6^{2-} photolysis on the nature of the excited states. The approximate structure of electronic levels of the IrCl_6^{2-} complex made according to Ref. [16] is shown in Fig. 5. The irradiation of IrCl_6^{2-} in the region of 254 nm causes the ligand-to-metal electronic transition $\mathrm{t_{1u}}$–$\mathrm{e_g^*}$. The corresponding excited term is $^2\mathrm{A_{1g}}$ [9]. The experimental facts concerning photochemistry in this state were explained in Ref. [6]. Conservation of the total quantum yield of IrCl_6^{2-} disappearance with decreasing photoaquation quantum yield (formation of $\mathrm{IrCl_5(H_2O)^-}$) and increasing photoreduction quantum yield (appearance of $\mathrm{IrCl_5(H_2O)^{2-}}$) with a rise in the concentration of a free Cl^- ion allowed the authors of Ref. [6] to assume that both the processes follow from the same LMCT state via the formation of radical pairs (reactions (1)–(5)). With LMCT excitation, the electron density moves from halide ions to the central ion which gives rise to a halogen atom in the coordination sphere. The bond between the halogen atom and metal ion substantially weakens, which makes the halogen atom move. This results in the formation of primary (reaction (1)) and secondary (reaction (2)) radical pairs.

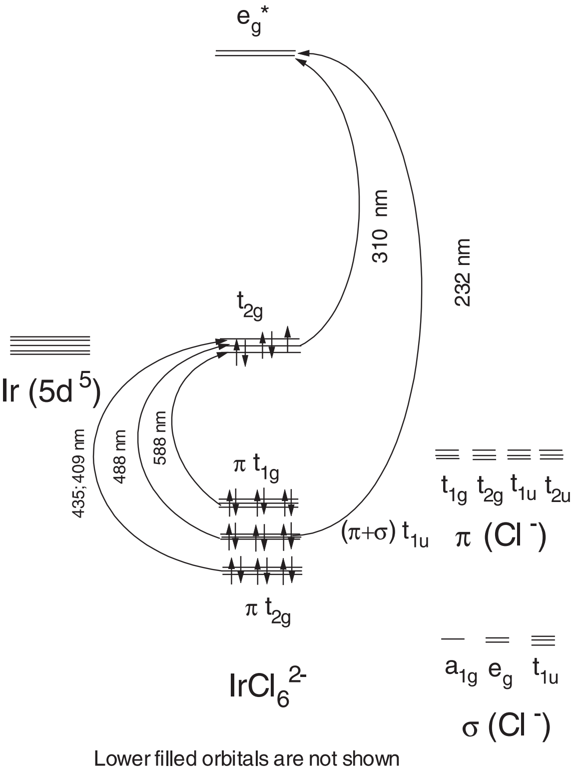

Fig. 5. The approximate structure of molecular orbitals of the IrCl_6^{2-} complex according to Ref. [16].

The total lifetime of the secondary radical pair is $\tau \approx R^2/D$ [17], where $R = 6.5$ Å is the total radius of the partners ($IrCl_5H_2O^{2-}$ complex and $Cl^\bullet$ atom), $D \approx 10^{-5}$ $cm^2\,s^{-1}$ is the overall diffusion coefficient. So, τ falls in the range 0.4–1 ns. As a first approximation, it is possible to consider the chlorine atom escape into the solvent bulk (reaction (4)) as the monomolecular decay of radical pair with the rate constant $k_4 = 1/\tau$ falling in the range 1×10^9–2.5×10^9 s^{-1}. Another way of radical pair disappearance is the back electron transfer from the $IrCl_5H_2O^{2-}$ complex to chlorine atom (reaction (3)).

The main process of $Cl^\bullet$ atom disappearance in the solvent bulk is its reaction with water molecules ($k_9 = 1.6 \times 10^5$ s^{-1} [13]). In conditions of steady state lamp photolysis (254 nm), the concentration of the $IrCl_5(H_2O)^{2-}$ complex is very low. Therefore, its reaction with a chlorine atom is unlikely, and the ratio between the quantum yields of photoaquation and photoreduction is equal to

$$\frac{\varphi_{aq}}{\varphi_{red}} = \frac{k_3}{k_4}. \tag{25}$$

The experimental ratio between the quantum yields on irradiation at 254 nm is equal to $\varphi_{aq}/\varphi_{red} \approx 5$ [6], and $k_3/k_4 \approx 5$. Thus, the effective rate constant of the electron transfer in the $[IrCl_5^{2-} \cdots Cl^\bullet]$ radical pair (k_3) can fall within the range between 0.5×10^{10} and 1.25×10^{10} s^{-1}. Before the escape of chlorine atom into the bulk, the partners undergo $N \approx R/\Delta$ repeated collisions in the cage. The time of a collision is about $\tau_{coll} \approx R\Delta/D$ [17], where Δ is the thickness of the reactionary layer in which the electron transfer takes place. If $\Delta \approx 0.1$ Å and $R = 6.5$ Å, $N \approx 65$, $\tau_{coll} \approx 6.5$ ps and the real time of electron transfer can be much shorter than the value $\tau = 1/k_3 \approx$ 100 ps.

In the presence of free Cl^- ions in solution, the photolysis products are the same ($IrCl_5(H_2O)^-$ and $IrCl_5(H_2O)^{2-}$ complexes). The total quantum yield of the $IrCl_6^{2-}$ disappearance remains invariable while the quantum yield of photoreduction increases and the quantum yield of photoaquation decreases. It can be explained by the fact that a Cl^- ion is a good acceptor of chlorine atoms. The reaction between these species has the rate constant close to the diffusion limit and leads to the formation of the $Cl_2^{\bullet-}$ radical ion. Thus, the Cl^- ion accepts the chlorine atom out of the radical pair and prevents its collisions with the $IrCl_5(H_2O)^{2-}$ complex in the bulk (reaction (5)). In the case of large Cl^- concentrations ($[Cl^-] \gg [IrCl_5^{2-} \cdots Cl^\bullet]$), this reaction is the process of pseudo-first order ($k_5 = k_{bim}[Cl^-]$). The ratio between the quantum yields of photoaquation and photoreduction in these conditions is

$$\frac{\varphi_{aq}}{\varphi_{red}} = \frac{k_3}{k_4 + k_5}. \tag{26}$$

At $[Cl^-] = 1.2$ M $\varphi_{aq}/\varphi_{red} \approx 0.37$ [6], which yields the values k_5 lies in the range 1.2×10^{10} – 3.1×10^{10} s^{-1} and k_{bim} lies in the range 1×10^{10}–2.6×10^{10} $M^{-1}\,s^{-1}$. The latter value is about two to four times higher than the normal diffusion rate constant for water solutions ($k_{diff} = 0.57 \times 10^{10}$ $M^{-1}\,s^{-1}$). It can be attributed to the considerable size of the secondary radical pair ($k_{diff} = 4\pi RD$), the certain simplification reducing the complex dynamics of radical pair to monomolecular reactions, and the existence of additional ways of the reaction between Cl^- and $Cl^\bullet$ (for example, tunnel electron transfer at a distance considerably exceeding the total radius of partners). Thus, both the nature of products and the behaviour of quantum yields on irradiation of $IrCl_6^{2-}$ at 254 nm satisfactorily agree with the existence of reactions (3)–(5).

The irradiation of $IrCl_6^{2-}$ at 308 nm demonstrates the essentially different results as compared with the 254 nm wavelength. The quantum yield of $IrCl_6^{2-}$ disappearance is less, and the only product is the aquated Ir(IV) complex $IrCl_5(H_2O)^-$ [6]. Irradiation in this region causes d–d transitions (t_{2g}–e_g^*) to the excited $^2T_{1g}$, $^2T_{2g}$ and ^2E_g terms [9]. It is well known that the photoaquation is the usual process for many coordination compounds on irradiation at d–d absorption bands [15,18].

The addition of free Cl^- ions into solution results in an increase of both the quantum yield and the appearance of the $IrCl_6^{3-}$ complex as a final product [6]. As shown above, the formation of $Cl_2^{\bullet-}$ radical ions confirms the photoreduction of iridium ion. Parameters α and β obtained in Section 3.2 allow one to estimate the rate constants of reactions (17)–(20). Assuming that $k_{-16} = 10^{10}$ s^{-1}, according to the value of quantum yield $\varphi_0 = 0.01$, we get the value $k_{17} \approx 10^8$ s^{-1}. Then, using the value $\alpha \approx 0.4$ M^{-1}, we obtain $k_{18} \approx 4 \times 10^7$ M^{-1} s^{-1}. The reaction of a chloride ion with the chlorine atom of the $[\mathrm{IrCl}_6^{3-} \cdots \mathrm{Cl}^\bullet]$ radical pair should have the diffusion rate constant $k_{20} \approx 10^{10}$ M^{-1} s^{-1}, as well as the reaction between these species in the free state [11–13]. In this case, the parameter $\beta \approx 2$ M^{-1} results in the value $k_{19} \approx 5 \times 10^9$ s^{-1}. Certainly, the k_{17} and k_{18} values depend on a selection of the rate constant k_{-16}. However, the k_{19} and k_{20} rate constants are determined only by the properties of the $[\mathrm{IrCl}_6^{3-} \cdots \mathrm{Cl}^\bullet]$ radical pair and do not depend on the rate of non-radiative relaxation of the excited state of IrCl_6^{2-} complex.

Estimation of the bimolecular rate constant k_{18} allows one to evaluate the rate constants of the electron transfer between the partners at the moment of collision (monomolecular constant). The electron transfer from an outersphere Cl$^-$ ion to the excited complex needs the overlapping of partners orbitals, therefore, the dependence of the transfer rate constant on the distance between species is determined by an exponential law [19]

$$k(r) = k_0 \mathrm{e}^{-(r-R)/L}, \tag{27}$$

where k_0 is the rate constant at contact, R is the total radius of species and L is the parameter determined by the orbitals overlapping. For many reactions of tunnel electron transfer, the L parameter lies in the range of 0.1–1 Å. The exponential dependence of rate constant on distance predetermines the possibility of transfer in the narrow reactionary layer, whose width is about L. The monomolecular rate constant of reaction at collision is determined by the bimolecular rate constant and the reaction volume

$$k_{\mathrm{mono}} = k_{\mathrm{bim}}/V, \tag{28}$$

where $V = 4\pi R^2 L$, and R is the total radius of the partners $((\mathrm{IrCl}_6^{2-})^*$ complex and Cl$^-$ ion). For $R = 6.5$ Å and $L \approx 0.1$–1 Å, the reactionary volume is $V \approx 0.04$–0.4 M^{-1}. If the bimolecular rate constant k_{18} lies in the range 4×10^7–4×10^8 M^{-1} s^{-1} (at $k_{-16} = 10^{10}$–10^{11} s^{-1}), the rate constant of electron transfer at the moment of collision $k_{18\ \mathrm{mono}}$ varies from 10^8 to 10^{10} s^{-1}. Thus, direct electron transfer rate constant ($k_{18\ \mathrm{mono}}$) is close or somewhat less than that of the inverse process in the $[\mathrm{IrCl}_6^{3-} \cdots \mathrm{Cl}^\bullet]$ radical pair ($k_{19} \approx 5 \times 10^9$ s^{-1}).

The assumed picture of potential surfaces corresponding to d–d excitation (308 nm) is shown in Fig. 6. In the absence of free Cl$^-$ ions, the d–d excited state may either undergo the non-radiative relaxation into the ground state or fall into a state

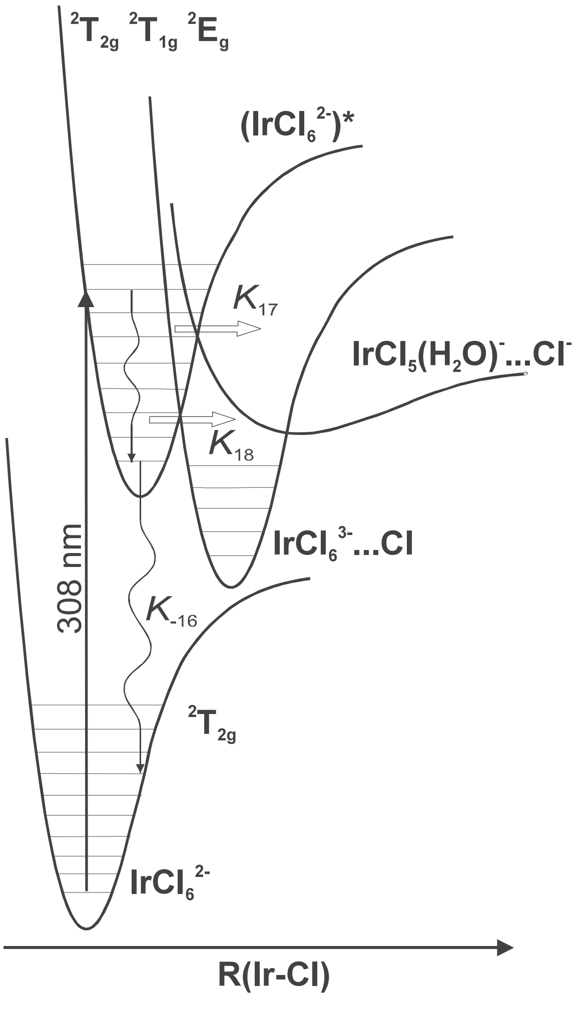

Fig. 6. The assumed picture of potential surfaces for the case of IrCl_6^{2-} photolysis at 308 nm.

corresponding to an aquated complex. In the presence of a free Cl^- ion, there is an additional potential surface corresponding to the outersphere electron transfer. Hypothesis for the outersphere electron transfer from a free Cl^- ion to the excited complex is in fair agreement with the processes of outersphere electron transfer in the photochemistry of $IrCl_6^{2-}$ in organic solvents on irradiation at 308 nm [1,2].

3.4. Process of $Cl_2^{\bullet -}$ radical ion disappearance

The $Cl_2^{\bullet -}$ radical ions are often the intermediates in radiation-chemical and photochemical processes. Therefore, the processes of their disappearance are well studied. The main process of $Cl_2^{\bullet -}$ radical ion disappearance in many systems is the reaction of disproportionation [20–23]

$$Cl_2^{\bullet -} + Cl_2^{\bullet -} \rightarrow Cl_3^- + Cl^- \qquad (29)$$

whose rate constant is close to the diffusion one (with respect to the charges of reacting particles). This species react with a fairly large rate constant with the ions of transition metals in the low degrees of oxidation (for Fe(II) and Cu(I) ions the rate constant is 1.5×10^7 and 1.5×10^8 $M^{-1}\,s^{-1}$ [24], respectively). This reaction is usually limited by the entrance of a chlorine atom of the radical ion into the first coordination sphere of a metal ion, i.e., is determined by the ligand exchange rate. Reaction between the $Cl_2^{\bullet -}$ radical ion and organic molecules is substantially slower (the rate constant of its reaction with methanol is 3.5×10^3 $M^{-1}\,s^{-1}$, ethanol -4.5×10^4 $M^{-1}\,s^{-1}$, acetone -1.4×10^3 $M^{-1}\,s^{-1}$ [25]).

Analysis of the kinetic curves of $Cl_2^{\bullet -}$ radical ions disappearance (Fig. 3a) arising from photoexcitation of the $IrCl_6^{2-}$ complex in aqueous solutions with different LiCl concentrations shows that in this case, the main reaction is also the reaction of disproportionation (reaction (29)). Taking into account the influence of the ionic strength of solution on the reaction between two charged particles, we have provided (at zero ionic strength) the value $2k_{29} = (2.1 \pm 0.3) \times 10^9$ $M^{-1}\,s^{-1}$, which is in fair agreement with the published data [20–23]. We have found no evidence for the reaction between $IrCl_6^{3-}$ and $Cl_2^{\bullet -}$, so, its rate constant is slow in comparison with reaction (29).

4. Conclusions

When using laser flash photolysis (308 nm), it has been demonstrated that in aqueous solutions, the photoaquation of $IrCl_6^{2-}$ complex occurs at timescale shorter than 20 ns. In aqueous solutions containing free Cl^- ions, the photoreduction of $IrCl_6^{2-}$ and the formation of $Cl_2^{\bullet -}$ radical ion have been observed. The analysis of the dependencies of relative quantum yield and relative $Cl_2^{\bullet -}$ yield on Cl^- concentration indicates that a chlorine atom (radical ion precursor) results from the electron transfer from the ourterspheric Cl^- ion to the excited complex. The same mechanism of photoreduction (electron transfer from particles located in the second coordination sphere to the excited complex) is realised for $IrCl_6^{2-}$ in many polar organic solvents.

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