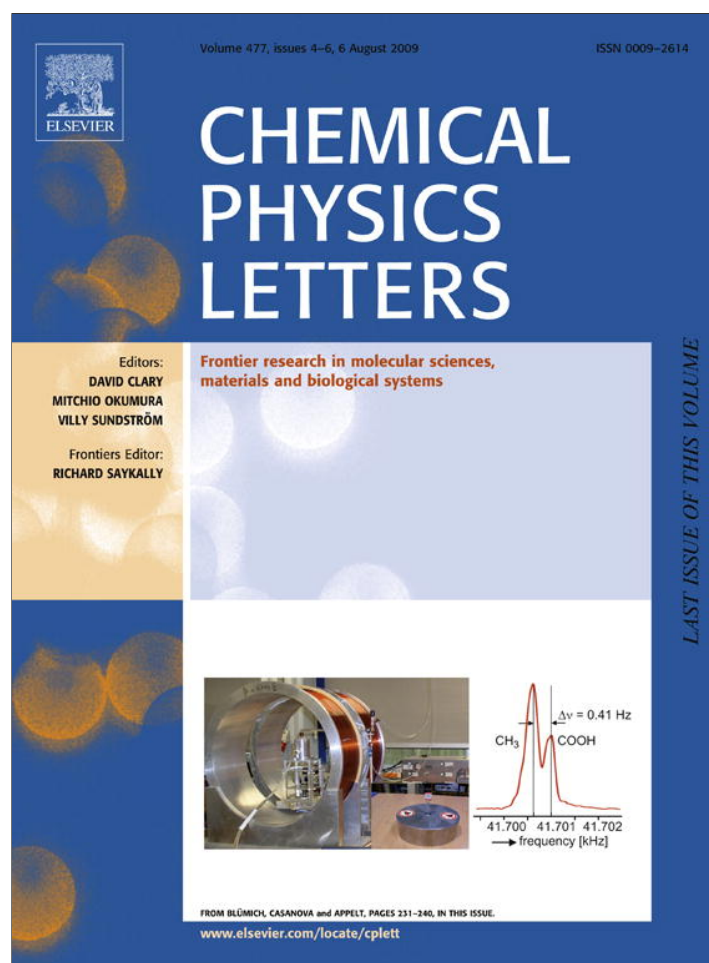


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ABSTRACT

Ultrafast pump–probe spectroscopy ($\lambda_{\text{pump}} = 420 \text{ nm}$) was applied to study the primary photochemical processes for IrCl_6^{2-} complex in aqueous solutions. The excitation to LMCT ${}^2T_{2u}$ state was followed by formation of an intermediate absorption completely decaying with two characteristic times of 0.5 and 18 ps. Complete recovery of the ground state is consistent with the absence of photochemical activity of visible LMCT bands of IrCl_6^{2-} . Possible interpretations of the observed two times are presented.

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1. Introduction

Ultrafast dynamics in transition metal complexes represent an active area of research in chemical physics [1–4]. These studies provide a direct insight into various aspects of electronic structure. In addition, photoinduced properties represent the basis upon which light-dependent molecular devices can be developed [5].

Transition metal complexes possess various types of excited states, which differ in their physical properties and reactivity. The excited state density is typically much higher than in organic molecules, and several different excited states can occur in a narrow energy range [1]. As a result, ‘ladder’ hierarchy of characteristic times typical for organic substances ((1) vibrational relaxation; (2) internal conversion; (3) intersystem crossing) is usually not applicable for coordination compounds [3].

Primary photophysical processes are known in details only for a few types of transition metal complexes. First of all, one can mention chromine(III) complexes [4], polypyridyl complexes of Ru(II) [1,2] and metal carbonyls [1]. Describing the situation in the field in general, one must conclude that photochemistry of coordination compounds is studied much better than their photophysics. For many compounds, mechanisms of photochemical reactions put forward in last century are based on stationary and (or) microsecond flash photolysis experiments [6–8]. In each case, it is an attractive problem to follow all the chain of transformations from an absorption of a light quantum to the final reaction products. In particular, hexahaloid complexes of noble metals, including IrCl_6^{2-} ,

represent an example of simple systems, for which empirical photochemistry is developed well enough, but nothing is known about primary photophysical processes.

IrCl_6^{2-} complex is stable in aqueous and organic solutions in the absence of free Cl^- ions. Stability and spectral peculiarities make it convenient to study primary photochemical processes in various solvents with and without free halide ions [9–17].

The UV absorption spectrum of IrCl_6^{2-} is shown in Fig. 1. It coincides with known from literature [18]. The spectrum contains strong absorption bands both in visible and UV regions. Absorption bands in the region of 400–500 nm with an extinction coefficient of ca. $4000 \text{ M}^{-1} \text{ cm}^{-1}$ are the bands of ligand-to-metal charge transfer (LMCT) [18]. A stronger charge transfer band has a maximum at 232 nm. Relatively weak ($\epsilon \sim 1000 \text{ M}^{-1} \text{ cm}^{-1}$) bands at 306 and 360 nm belong to d–d ligand-field (LF) transitions.

Photochemistry of IrCl_6^{2-} in water and polar organic solvents is quite different. The nature of the photolysis is wavelength-dependent.

In aqueous solutions, the competition between photoaquation and photoreduction of Ir(IV) to Ir(III) was reported [10]. The origin of products and quantum yield depend on the wavelength of exciting light and the concentration of free chloride ions in solution. Excitation in the region of a short-wave charge transfer band (254 nm, Fig. 1) leads to the formation of complexes $\text{IrCl}_5(\text{H}_2\text{O})^-$ (photoaquation product) and $\text{IrCl}_5(\text{H}_2\text{O})^{2-}$ (photoreduction product) with a total quantum yield of 0.029 independent of the concentration of free Cl^- ions in solution [2]. However, the contribution of photoreduction to quantum yield linearly increases with the concentration of chloride ions. The mechanism of photolysis in the region of 254 nm proposed in [10] (based on Adamson mechanism of radical pairs [19]) explains the dependence of

* Corresponding author. Address: Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russia. Fax: +7 (383)3307350

E-mail address: glebov@kinetics.nsc.ru (E.M. Glebov).

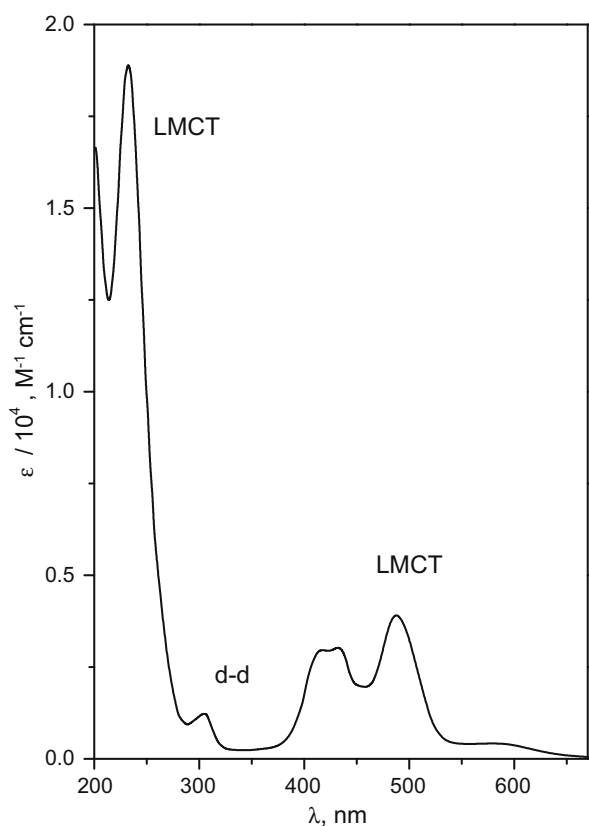
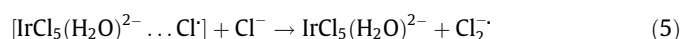
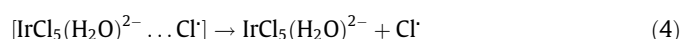
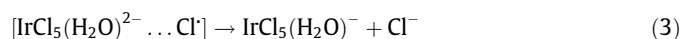
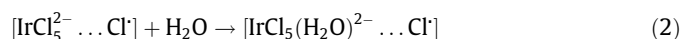
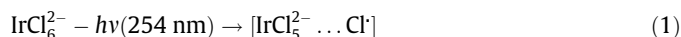
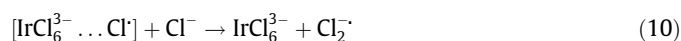
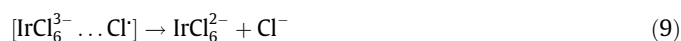
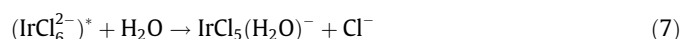
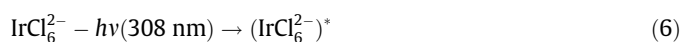


Fig. 1. UV absorption spectrum of IrCl_6^{2-} in aqueous solution.

the photoreduction quantum yield on Cl^- concentration. It includes a successive formation of two intermediates, $[\text{IrCl}_5^2 \dots \text{Cl}^-]$ (primary radical pair) and $[\text{IrCl}_5(\text{H}_2\text{O})^{2-} \dots \text{Cl}^-]$ (secondary radical pair).



When the IrCl_6^{2-} complex is excited in the region of d-d bands (313 nm, Fig. 1), only photoaquation with a quantum yield of 0.01 was observed by means of stationary photolysis [10]. The mechanism of photolysis in this region was studied in [17] using nanosecond laser flash photolysis (308 nm). Photolysis in the absence of free chloride ions was shown to result in photoaquation of initial complex within less than 20 ns [17]. In solutions containing free Cl^- ions, the photoreduction of IrCl_6^{2-} and the formation of Cl_2^\cdot radical ion were observed. The analysis of the dependencies of relative quantum yield and relative Cl_2^\cdot yield on Cl^- concentration indicated that a chlorine atom (radical ion precursor) results from the electron transfer from the outerspheric Cl^- ion to the excited complex. The resulted reaction pathway [17] is shown below



The excitation of IrCl_6^{2-} in aqueous solutions in the region of low-energy charge transfer bands (400–520 nm, Fig. 1) was reported not to cause any photochemical reaction [10].

Photochemical properties of IrCl_6^{2-} in polar organic solvents and in water are different. In alcohols, photoreduction of Ir(IV) to Ir(III) is followed by excitation both at 254 and 308 nm [13]. Excitation to the region of d-d bands (308 nm) was found to result in the formation of IrCl_6^{3-} complex due to the electron transfer from the solvent molecule to the excited complex [13,16]. Irradiation of IrCl_6^{2-} in methanol solutions in the region of UV charge transfer bands (248 nm) results in the formation of two Ir(III) complexes, IrCl_6^{3-} and $\text{IrCl}_5(\text{CH}_3\text{OH})^{2-}$ [13]. When photolysis is performed at 248 nm, the electron transfer from the solvent molecule is accompanied by photodissociation of excited complex with the elimination of a chlorine atom from the first coordination sphere of iridium.

Primary photophysical processes for IrCl_6^{2-} have never been studied by the direct experimental methods. The objective of the current work was to study the photophysics of IrCl_6^{2-} in femto- and picosecond time domains. The simplest case of excitation to the ligand-to-metal charge – transfer bands in the visible spectral region was examined.

Recently we have applied the femtosecond pump-probe spectroscopy to examine the primary processes in photochemistry of PtBr_6^{2-} complex in aqueous solutions [20]. The literature mechanism of photolysis [21,7] based on stationary experiments was directly supported.

2. Experimental

A pump-probe spectroscopy was used to study transient absorption in femto- and picosecond time domains. The experimental setup was described in details elsewhere [22]. The samples were excited by ~60 fs pulses at ~420 nm (second harmonic of a Ti:sapphire

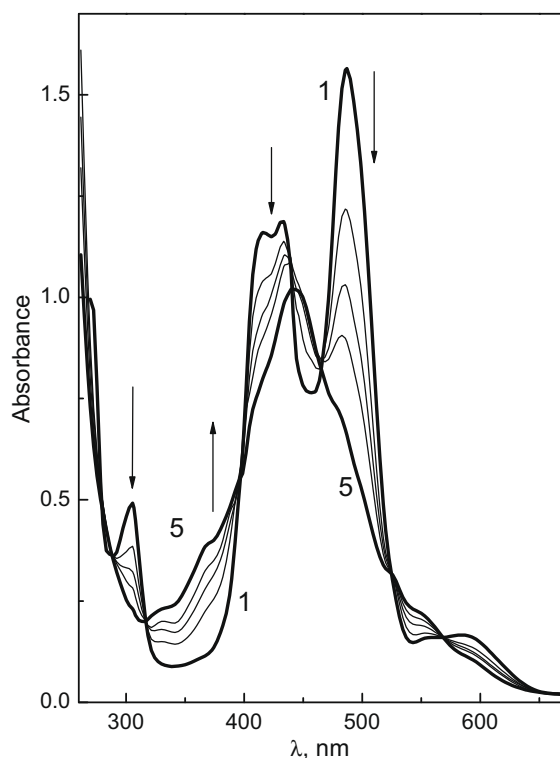


Fig. 2. Change in the UV spectrum of IrCl_6^{2-} complex in aqueous solution under irradiation at 308 nm (XeCl laser, 10 Hz, 10 mJ/pulse). Temperature, 295 K; initial concentration, 4×10^{-3} M; cuvette thickness, 0.086 cm; curves 1–5 denote 0, 60, 180, 360, 960 s of irradiation, respectively.

generator – amplifier system, CDP Ltd., Moscow, Russia). The excitation pulse repetition rate was 10 Hz, and 200 pulses were used to record a single time-resolved spectrum. The samples were placed in 1 mm rotating cuvette to provide a uniform irradiation of the sample and to avoid unwanted thermal effects from heating of the sample by the pump pulse. Typically time-resolved spectra were collected with delay displacement of 100 fs in first 3 ps after excitation and with exponentially increasing delay times at longer delays. Usually 60–70 spectra were collected for each sample with longest delay of ~ 100 ps. The experimental data were globally fitted by a two-exponential model. The fitting program performed corrections of the group velocity dispersion and calculated the response time of the instrument. The overall time resolution was 150–200 fs. All pump–probe measurements were carried out at room temperature.

Steady-state photolysis was performed using the irradiation of an excimer XeCl laser (308 nm). The absorption spectra were recorded using an Agilent 8453 spectrophotometer (Agilent Technologies).

Solutions of IrCl_6^{2-} complex were prepared from $\text{Na}_2\text{IrCl}_6 \times 6\text{H}_2\text{O}$ synthesized as described in [23]. The solutions were prepared using deionized water. When necessary, the samples were deaerated by saturation with argon.

3. Results and discussion

3.1. UV spectrum and photochemistry of IrCl_6^{2-}

The mechanism of IrCl_6^{2-} photolysis in aqueous solutions, as it was mentioned in Introduction, is wavelength-dependent. For

example, excitation to the region of d–d bands (308 nm) results in the photoaquation of the initial complex [17]. Fig. 2 shows the characteristic changes in the UV spectrum due to photoaquation. Conservation of seven isosbestic points (at 289, 316, 397, 440, 526, and 569 nm) relies to $\text{IrCl}_6^{2-} \rightarrow \text{IrCl}_5(\text{H}_2\text{O})^-$ transition. The final absorption band with the maximum at 443 nm belongs to the $\text{IrCl}_5(\text{H}_2\text{O})^-$ complex [17]. The quantum yield of the photolysis is 10^{-2} [10], and the final product of photoreaction is formed within less than 20 ns [17].

The excitation to the region of the visible LMCT bands, as mentioned in Introduction, does not result in any changes of the UV spectra of the initial complex.

3.2. Femtosecond laser flash photolysis of IrCl_6^{2-}

Ultrafast pump–probe experiments were performed with the excitation of IrCl_6^{2-} to the region of low-energy LMCT charge transfer band (420 nm). The absorption of light quantum by the complex leads to the formation of transient absorption which was completely decayed in 100 ps. Kinetic curves at several selected wavelengths are presented in Fig. 3. The global analysis of the time profiles in the wavelength range 440–780 nm by iterative reconvolution shows that the use of a two-exponential function (11) with the instrument response function gives a good fitting with the time constants $\tau_1 = 0.5$ ps and $\tau_2 = 18$ ps.

$$\Delta D(\lambda, t) = A_1(\lambda)e^{-\frac{t}{\tau_1}} + A_2(\lambda)e^{-\frac{t}{\tau_2}} \quad (11)$$

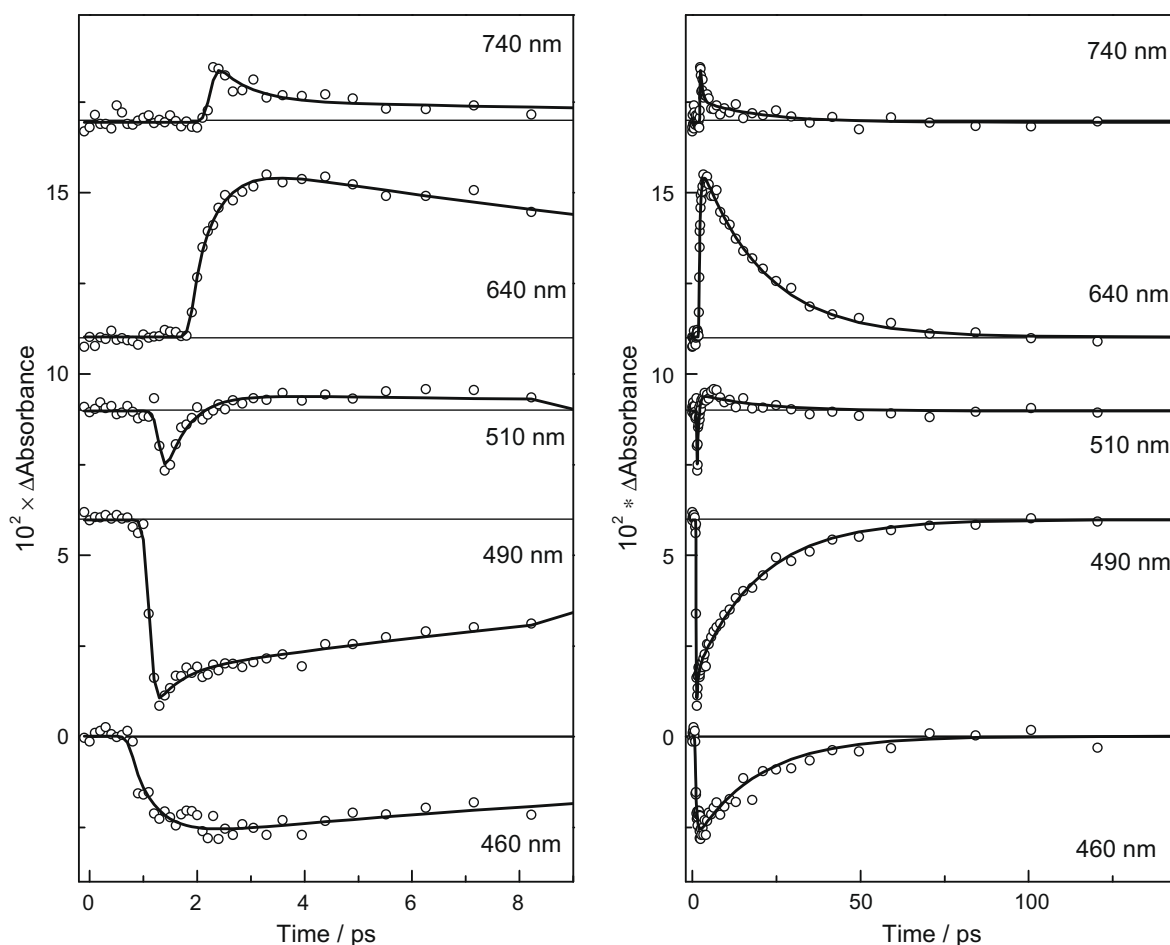
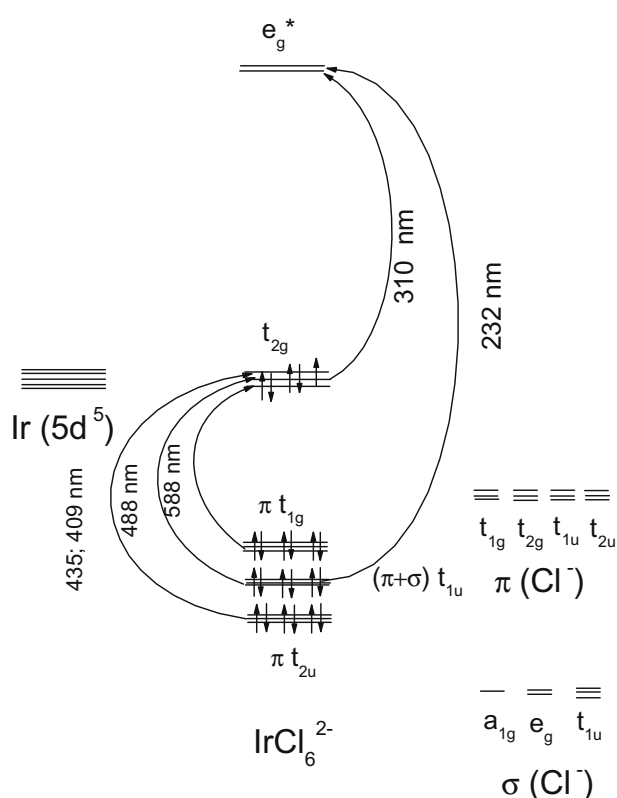


Fig. 3. ($\lambda_{\text{pump}} = 420$ nm) photolysis of IrCl_6^{2-} (3×10^{-3} M) in aqueous solutions. Kinetics of transient absorption at different wavelengths and time domains. Solid lines are the best two-exponential fits (Eq. (11)) after reconvolution with the instrument response function.

Intermediate absorption spectra corresponding to different times are shown in Fig. 4. Curve 1 is the total sum of amplitudes in Eq. (11) corresponding to the spectrum at zero time. Curve 2 is the $A_2(\lambda)$ corresponding to the spectra at the end of first process ($\tau_1 = 0.5$ ps). Immediately after excitation the transient absorption spectrum has a very wide band in the region of 530–760 nm. After finishing of the first process ($\tau_1 = 0.5$ ps) the band is narrowed and a pronounced maximum at 640 nm is formed, which is accompanied by a small (ca. 10 nm) blue-side shift of the spectrum. No residual absorption is observed in the time domain > 100 ps. The disappearance of the initial IrCl_6^{2-} absorption in the region 440–500 nm (Fig. 4) is completely recovered (Fig. 3). The absence of residual absorption at $t > 100$ ps correlates with the low quantum yield of IrCl_6^{2-} photolysis in aqueous solutions and with the absence of intermediate absorption in the microsecond time domain [17].

3.3. Possible processes followed by the excitation (420 nm) of IrCl_6^{2-}

The approximate structure of electronic levels of the IrCl_6^{2-} complex according to [18,24,25] is shown in Fig. 5. IrCl_6^{2-} is a $5d^5$ octahedral complex. Five degenerate d-orbitals of Ir(IV) in octahedral complexes form two equivalent e_g orbitals and three equivalent t_{2g} orbitals. The set of σ -orbitals of six ligands in the crystal field form a_{1g} , e_g and t_{1u} group orbitals, and the set of π -orbitals of ligands form t_{1u} , t_{2u} , t_{1g} and t_{2g} group orbitals. The interaction of group orbitals of ligands with 5d-, 6s- and 6p-orbitals of Ir(IV) results in the structure shown in Fig. 5. The t_g -sub-shell of the complex has one hole, therefore $d(t_{2g})^5$ configuration of the ground



Lower filled orbitals are not shown

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

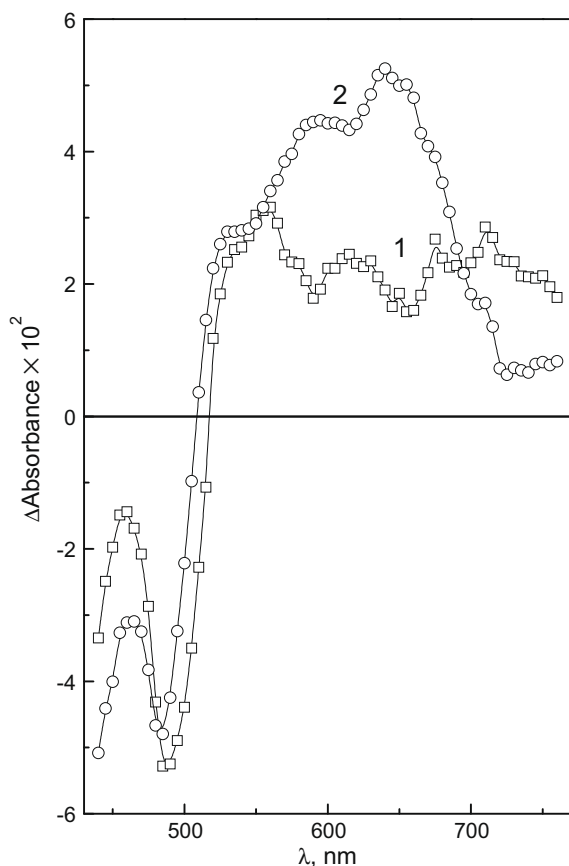


Fig. 4. ($\lambda_{\text{pump}} = 420$ nm) photolysis of IrCl_6^{2-} (3×10^{-3} M). Intermediate absorption spectra at different times. Treatment of the data of Fig. 3. Curve 1 – zero time (sum of amplitudes $A_1(\lambda) + A_2(\lambda)$); curve 2 – after the end of the first process (amplitude $A_2(\lambda)$).

state forms an only doublet term ${}^2T_{2g}$, which corresponds to the ground state of IrCl_6^{2-} .

The excitation of IrCl_6^{2-} in the region of 420 nm (Fig. 1, Fig. 5) corresponds to the first Laporte-allowed LMCT band $\pi(t_{2u}) \rightarrow d(t_{2g})$ [25]. As a result of an electron transfer, the hole moves from the lower 5d-sub-shell to the filled $\pi(t_{2u})$ molecular orbital of ligands, forming an only excited term ${}^2T_{2u}$. According to this, one can explain the results on the femtosecond pump-probe experiments.

The observed two-exponential dynamics of the excited IrCl_6^{2-} complex (Fig. 3, Fig. 4) could be described in two different ways, depending on the reactions followed by the formation of the hot Frank-Condon ${}^2T_{2u}^*$ state just after the excitation at 420 nm. The distribution of ${}^2T_{2u}$ state vibrational levels leads to a wide absorption band (curve 1 in Fig. 4). The first possibility is that the fast process ($\tau_1 = 500$ fs) is vibrational cooling of hot ${}^2T_{2u}^*$ state. This suggestion is supported by the fact that the initial band (curve 1 in Fig. 4) is narrowed (Curve 4 in Fig. 4), which is characteristic for vibrational cooling of Frank-Condon excited state [3]. According to this interpretation, curve 2 in Fig. 4 represents the absorption of the thermalized excited ${}^2T_{2u}$ state of IrCl_6^{2-} . In this scheme, the second process with the characteristic time $\tau_2 = 18$ ps is the relaxation of the excited ${}^2T_{2u}$ state to the ground ${}^2T_{2g}$ state. Thermalization is probably accompanied by solvent relaxation. The time scale for nondiffusive solvent dynamics falls in the range of 50–500 fs; diffusive processes are generally on the order of picoseconds [2].

It should be noted that the characteristic times of vibrational relaxation could differ dramatically. Typically these times lie in a picosecond time domain (1–10 ps) [3,26]. Moreover, as long times of thermalization as 10–40 ps were reported for metal carbonyls [27,28]. In our case, the first time is 0.5 ps. The characteristic time

of vibrational cooling is less than 1 ps, when it occurs as a single step process with the electronic relaxation [29,30]. Therefore, it is essential to consider another possibility of interpretation.

Assume that the first time corresponds to the internal conversion of Frank–Condon ${}^2T_{2u}^*$ state to the lowest excited state ${}^2T_{1g}$. This state is formed by the electronic configuration with a hole in ligands $\pi(t_{1g})$ orbital (Fig. 5). The electronic transition could be accompanied by vibrational cooling, like described in [29,30]. In this interpretation, curve 2 in Fig. 4 represents the spectrum of lowest excited ${}^2T_{1g}$ state of IrCl_6^{2-} , and the time τ_2 corresponds to the transition from ${}^2T_{1g}$ to the ground state ${}^2T_{2g}$.

It should be noted that both interpretations do not seem to be contradictive. It is possible that both pathways can realize, and the two-exponential fitting curve represents a set of several exponential functions with close characteristic times. Vibrational cooling and electronic relaxation can occur in coordination compounds as a single, convoluted process [1]. Solvent relaxation time could be included to this set.

The recovery of the initial state is complete, that corresponds to the absence of photochemical processes followed by the excitation to the visible LMCT bands of IrCl_6^{2-} .

4. Conclusion

In this Letter, the simplest case of LMCT excitation of IrCl_6^{2-} was examined. Only one excited term ${}^2T_{2u}$ is populated due to $\pi(t_{2u}) \rightarrow d(t_{2g})$ excitation. In fact, the fast recovery of the initial state (independent on its mechanism) is the only photophysical process. When other transitions of IrCl_6^{2-} are excited, one can assume more rich photophysics and photochemistry. For example, excitation to the region of d–d band $d(t_{2g}) \rightarrow d(e_g^*)$ at 310 nm results in the formation of $d(t_{2g})^4 e_g^*$ electronic configuration, which forms a number of excited doublet terms (four ${}^2A_{1g}$, three ${}^2A_{2g}$, seven 2E_g , eight ${}^2T_{1g}$ and ten ${}^2T_{2g}$ energy levels [31]). The lowest of these terms could be resonant with the energy levels of an aquated complex $\text{IrCl}_5(\text{H}_2\text{O})^-$. Therefore, in this case photoaquation is possible (Eqs. (6) and (7)).

In the case of the excitation to the UV LMCT band (232 nm) the electronic configuration $(\pi + \sigma)t_{1u}^{-1} d(t_{2g})^5 e_g^*$ occurs. In fact, this excited configuration with a hole in the t_{1u} π -orbital of ligands is represented in Eqs. (1) and (2) by the primary radical pair $[\text{IrCl}_6^{3-} \dots \text{Cl}^\cdot]$. In addition to the relaxation of the primary radical pair to the initial state, the formation of the secondary radical pair $[\text{IrCl}_5(\text{H}_2\text{O})^{2-} \dots \text{Cl}^\cdot]$ is possible. The reactions of the secondary radical pair (3–5) are responsible for the content of the photolysis products.

It is necessary to stress that the existence of irreversible photochemistry of IrCl_6^{2-} implies its ultrafast character. The formation of reactive intermediates like Adamson's radical pairs should be fast

enough to be kinetically competitive with conversion to the low-lying LMCT states studied in the present work.

Therefore, the femtosecond pump–probe experiments using the UV excitation of IrCl_6^{2-} are attractive in order to observe reactive intermediates and to examine the literature mechanism [10] directly.

Acknowledgements

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References

- [1] A. Vlcek Jr., *Coord. Chem. Rev.* 200–202 (2000) 933.
- [2] J.K. McCusker, *Acc. Chem. Res.* 36 (2003) 876.
- [3] E.A. Juban, J.K. McCusker, *J. Am. Chem. Soc.* 127 (2005) 6857.
- [4] L.S. Forster, *Coord. Chem. Rev.* 250 (2006) 2023.
- [5] V. Balzani, G. Bergamini, S. Campagna, F. Punzioriero, *Top. Curr. Chem.* 280 (2007) 1, doi:10.1007/128_2007_132.
- [6] V. Balzani, V. Carassiti, *Photochemistry of Coordination Compounds*, Academic Press, London–New York, 1970.
- [7] P.G. Ford, J.D. Petersen, R.E. Hintze, *Coord. Chem. Rev.* 14 (1974) 67.
- [8] J. Sykora, J. Sima, *Coord. Chem. Rev.* 107 (1990) 1.
- [9] T.P. Sleight, C.R. Hare, *Inorg. Nucl. Chem. Lett.* 4 (1968) 165.
- [10] L. Moggi, G. Varani, M.F. Manfrin, V. Balzani, *Inorg. Chim. Acta* 4 (1970) 335.
- [11] P.K. Eidem, A.W. Mawerick, H.B. Gray, *Inorg. Chim. Acta* 50 (1981) 59.
- [12] S. Fukuzumi, J.K. Kochi, *Inorg. Chem.* 19 (1980) 3022.
- [13] E.M. Glebov, V.F. Plyusnin, N.I. Sorokin, V.P. Grivin, A.B. Venediktov, H. Lemmetyinen, *J. Photochem. Photobiol. A: Chem.* 90 (1995) 31.
- [14] E.M. Glebov, V.F. Plyusnin, V.L. Vyazovkin, A.B. Venediktov, *J. Photochem. Photobiol. A: Chem.* 107 (1997) 93.
- [15] E.M. Glebov, V.F. Plyusnin, V.P. Grivin, Yu.V. Ivanov, N.V. Tkachenko, H. Lemmetyinen, *J. Photochem. Photobiol. A: Chem.* 113 (1998) 103.
- [16] E.M. Glebov, V.F. Plyusnin, V.P. Grivin, Yu.V. Ivanov, N.V. Tkachenko, H. Lemmetyinen, *Int. J. Chem. Kinet.* 30 (1998) 711.
- [17] E.M. Glebov, V.F. Plyusnin, N.V. Tkachenko, H. Lemmetyinen, *Chem. Phys.* 257 (2000) 79.
- [18] C.K. Jorgensen, *Mol. Phys.* 2 (1959) 309.
- [19] A.W. Adamson, A.H. Sporer, *J. Am. Chem. Soc.* 80 (1958) 165.
- [20] I.P. Pozdnyakov, E.M. Glebov, V.F. Plyusnin, N.V. Tkachenko, H. Lemmetyinen, *Chem. Phys. Lett.* 442 (2007) 78.
- [21] V. Balzani, M.F. Manfrin, L. Moggi, *Inorg. Chem.* 6 (1967) 354.
- [22] N.V. Tkachenko, L. Rantala, A.Y. Tauber, J. Helaja, P.H. Hynninen, H. Lemmetyinen, *J. Am. Chem. Soc.* 121 (1999) 9378.
- [23] E.N. Sloth, C.S. Garner, *J. Amer. Chem. Soc.* 77 (1955) 1440.
- [24] C.K. Jorgensen, *Acta Chem. Scand.* 10 (1956) 518.
- [25] C.K. Jorgensen, W. Pretz, *Z. Naturforsch.* 22a (1967) 945.
- [26] P.J. Reid, C. Silva, P.F. Barbara, L. Karki, J.T. Hupp, *J. Phys. Chem.* 99 (1995) 2609.
- [27] J.R. Hill, C.J. Ziegler, K.S. Suslick, D.D. Dlott, C.W. Rella, M.D. Fayer, *J. Phys. Chem.* 100 (1996) 18023.
- [28] T. Lian, S.E. Bromberg, M.C. Asplund, H. Yang, C.B. Harris, *J. Phys. Chem.* 100 (1996) 11994.
- [29] A. Hauser, J. Jetic, H. Romstedt, R. Hinek, H. Spiering, *Coord. Chem. Rev.* 190–192 (1999) 471.
- [30] M.D. Edington, W.M. Diffey, W.J. Doria, R.E. Ritter, W.F. Beck, *Chem. Phys. Lett.* 275 (1997) 119.
- [31] J.N. Murrell, S.F.A. Kettle, J.M. Tedder, *Valence Theory*, John Wiley and Sons Ltd., London, New York, Sydney, 1965, p. 296.