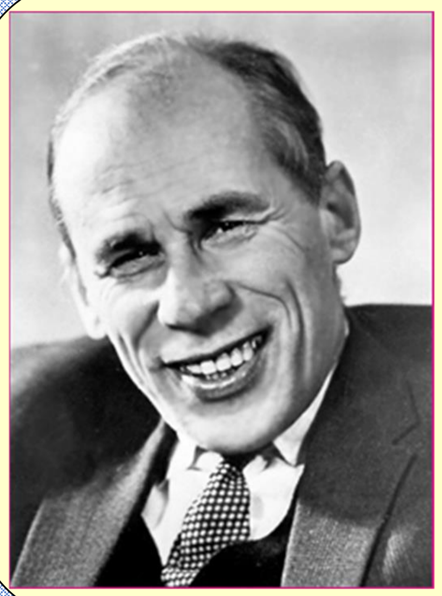


Photochemistry of $[IrCl_6]^{3-}$ complex in aqueous solutions

Zhdankin Grigory I.,[1,2]* Grivin Vjacheslav P.,[1] Plyusnin Victor F.[1,2], Glebov Evgeni M.[1]

[1] Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Institutskaya 3, 630090, Novosibirsk, Russia

[2] Chemistry department, Novosibirsk State University, Pirogova 1, 630090, Novosibirsk, Russia

g.zhdankin@g.nsu.ru

Introduction 1

- Applications of light-activated platinum metal complexes are solar energy, conversion, photocatalysis, molecular machine development, antitumor therapy (photochemotherapy, PCT)
- Therefore, a comprehensive and detailed knowledge of the photophysical and photochemical mechanisms of processes is necessary

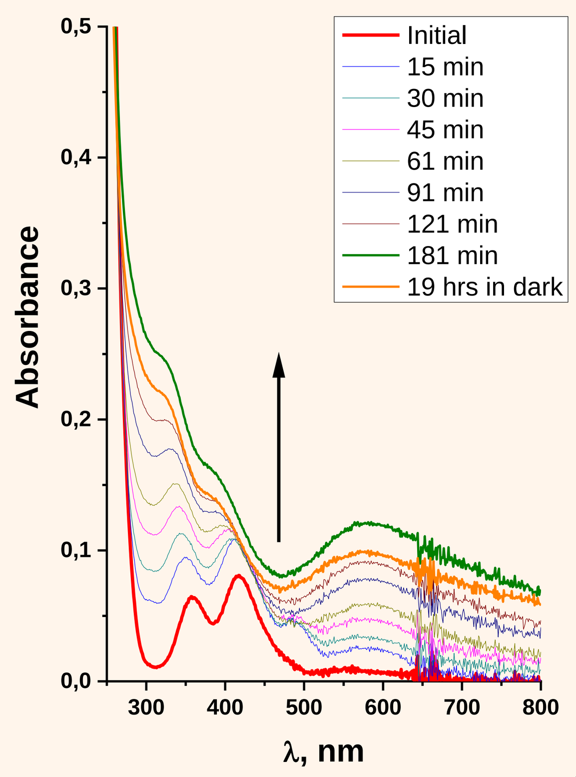
Goal

- The study of $[IrCl_6]^{3-}$ photochemistry in aqueous solutions

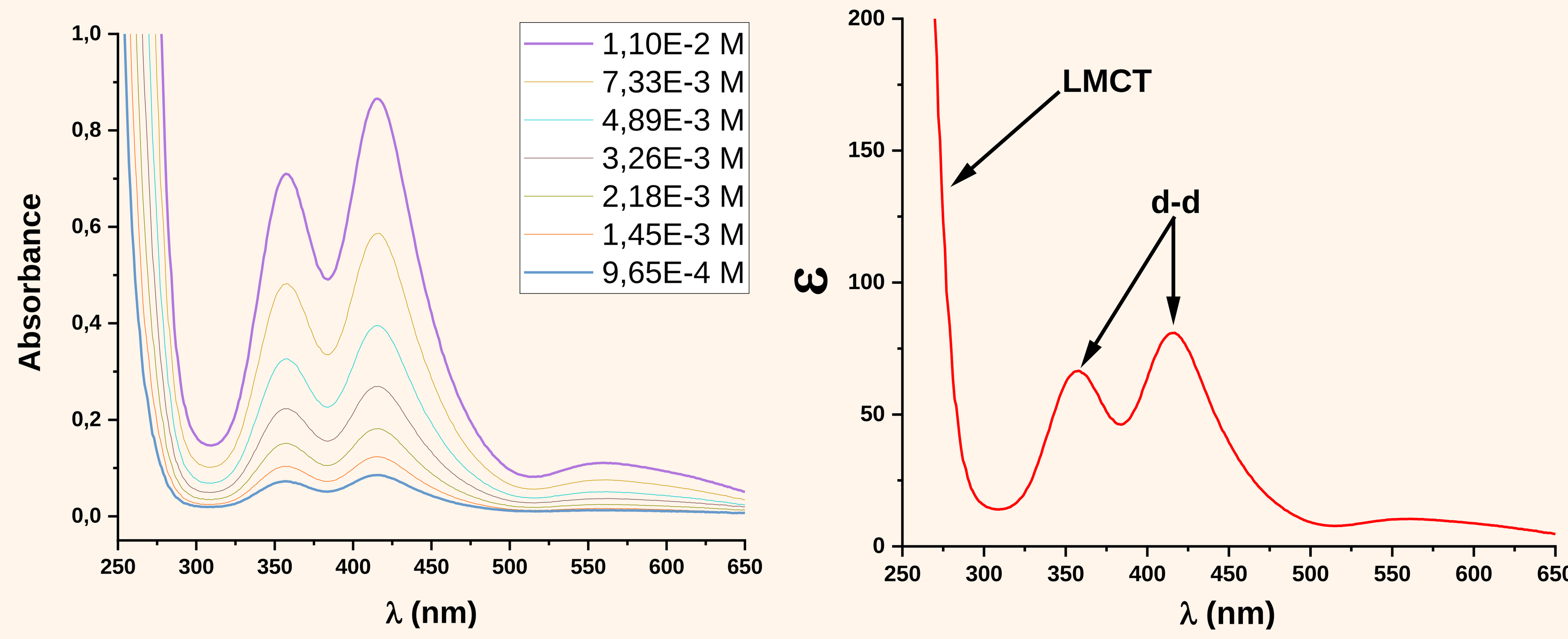
Methods

- Stationary photolysis
- Laser flash photolysis

Stationary photolysis (254 nm) of $Na_3[IrCl_6]$ in H_2O, Ar-saturated solution:



Beer-Lambert law in 2,5 M $HClO_4$ 2



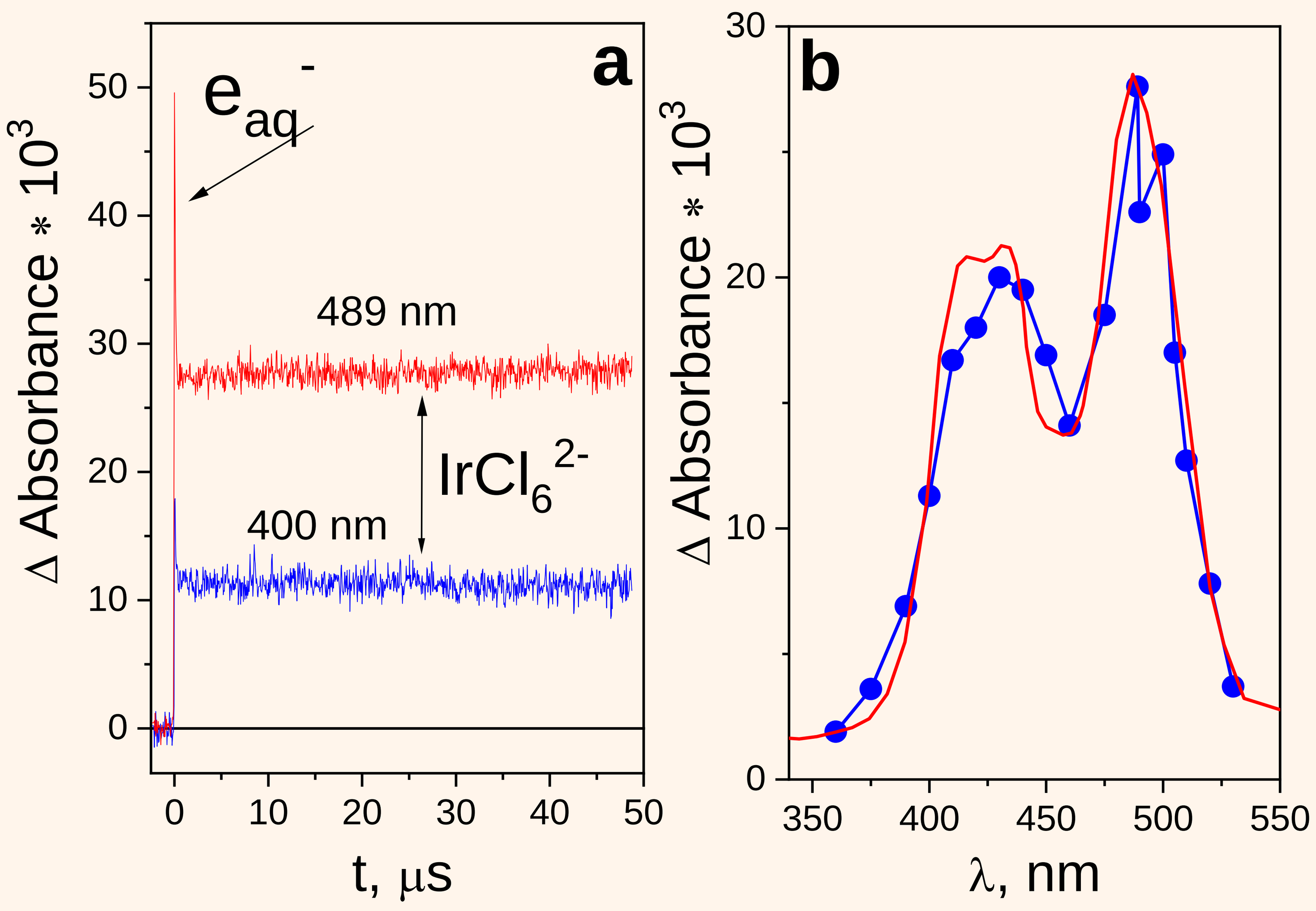
Electronic absorption spectrum of $[IrCl_6]^{3-}$ complex in aqueous solution:

Transition type	λ_{max},nm	ε_{max}, $M^{-1}cm^{-1}$
LMCT	206	28000
d-d	360	70
d-d	430	90

C.K. Jorgensen, *Mol. Phys.* **2**, 1959, 309

I.A. Poulsen, C.S. Garner, *J. Am. Chem. Soc.* **84**, 1962, 2032

Laser flash photolysis (266 nm) of $[IrCl_6]^{3-}$ 3

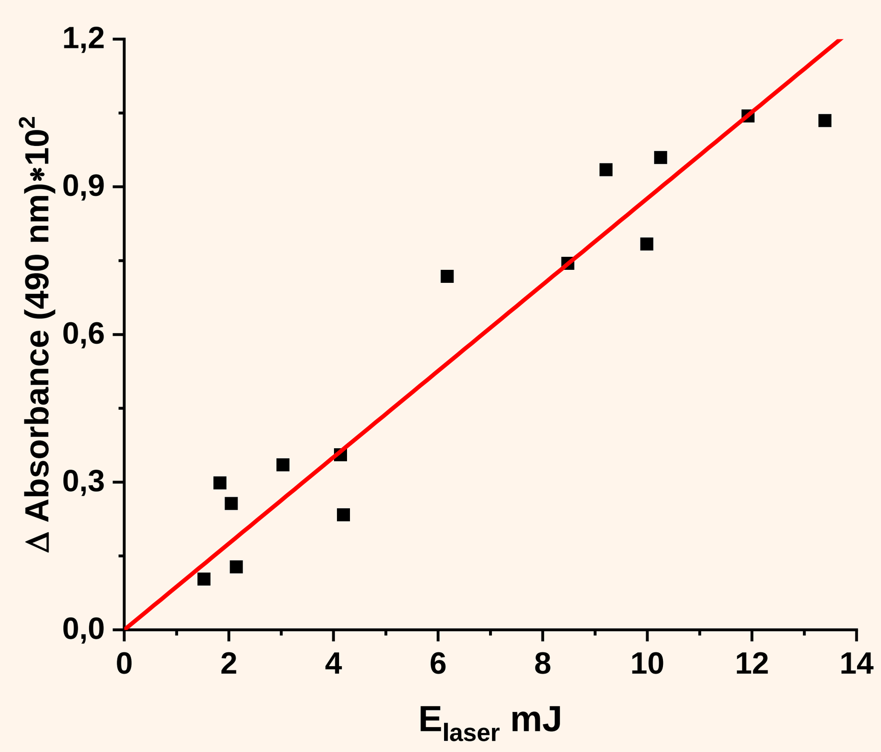


a – examples of kinetic curves

b – intermediate absorption spectrum (blue dots and line) and normalized $[IrCl_6]^{2-}$ spectrum (red line)

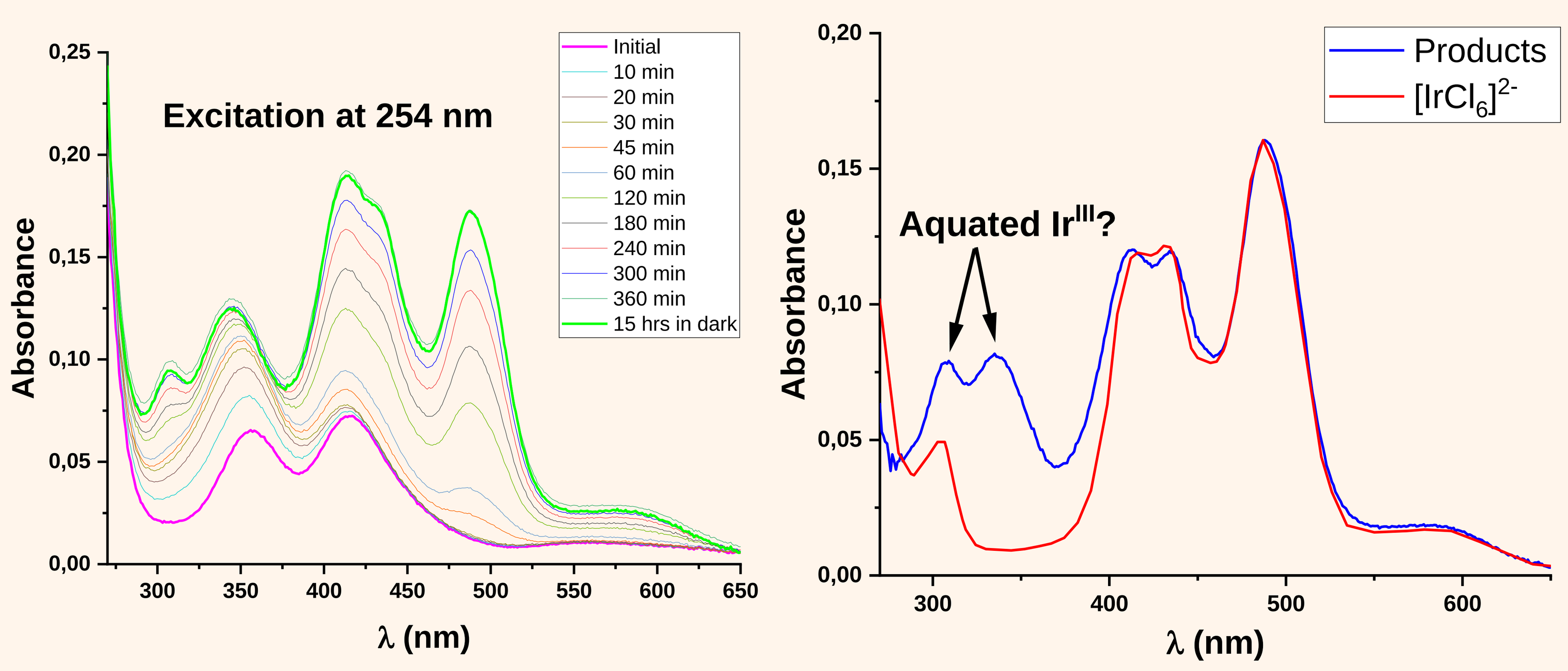
D_{int} *vs.* laser pulse energy 4

- Evident contradiction between the results of stationary photolysis and laser flash photolysis
  - In laser flash photolysis – photoionization
  - In stationary experiment – no $[IrCl_6]^{2-}$ formation
- Hypothesis: two-quantum process under the laser irradiation



However, the linear dependence of the optical density on the laser pulse energy indicates a **one-quantum process**

Stationary photolysis in 2,5 M $HClO_4$ 5

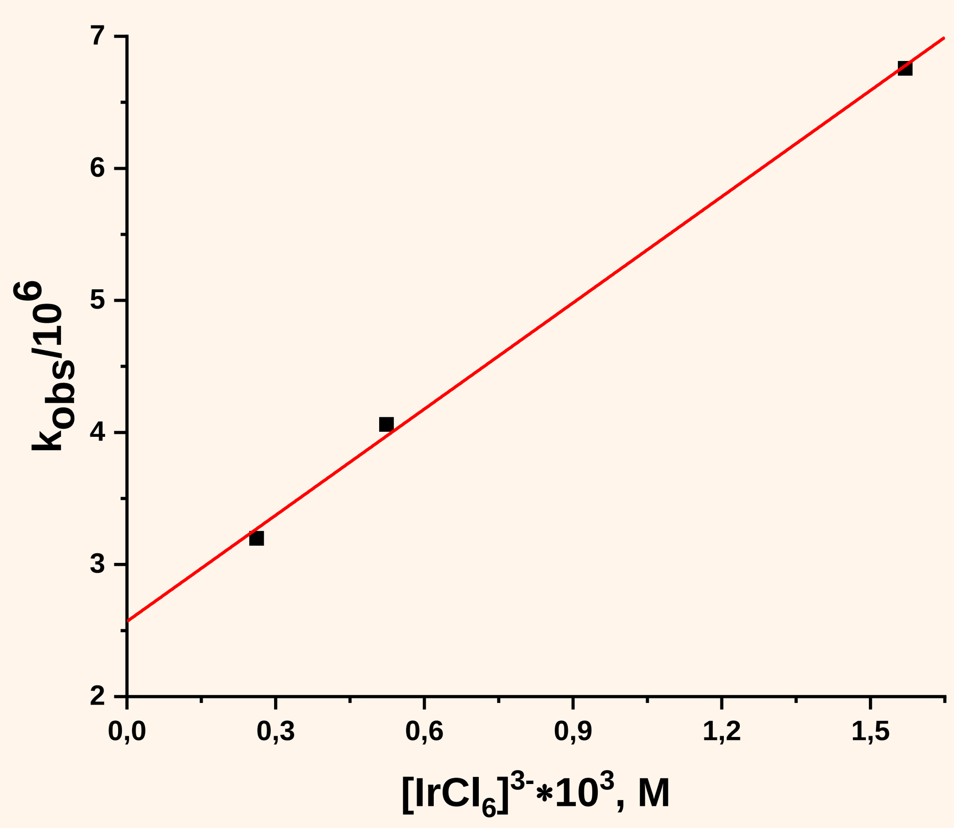


The expected reactions:

1. $[IrCl_6]^{3-} \xrightarrow{hv} [IrCl_6]^{2-} + e_{aq}^-$
2. $[IrCl_6]^{3-} + e_{aq}^- \xrightarrow{k} [IrCl_6]^{4-}$
3. $[IrCl_6]^{2-} + H_2O \xrightarrow{hv} [IrCl_5(H_2O)]^- + Cl^-$

- Reaction 2 does not occur in aqueous solutions (effect of acid or ionic strength?)

Rate constant of $[IrCl_6]^{3-} + e_{aq}^- \xrightarrow{k} [IrCl_6]^{4-}$ 6



$$\frac{k}{k_0} = \exp\left(\frac{8,38 \cdot 10^6 \cdot Z_A \cdot Z_B \cdot f(I)}{(\varepsilon T)^{3/2}}\right)$$

$$f(I) = \frac{\sqrt{I}}{1+\sqrt{I}}$$

$I = 9,42 \cdot 10^{-3}$ – ionic strength

$T = 298$ K – temperature

$\varepsilon = 78$ – absolute permittivity

$Z_A = -1, Z_B = -3$ – charges

$k = 2,68 \cdot 10^9$ – rate constant at the experimental conditions

$k_0 = 1,43 \cdot 10^9$ – rate constant at zero ionic strength

Conclusions

- Parallel processes of one-quantum photoionization and photoaquation
- Rate constant of reaction 2 ($[IrCl_6]^{3-} + e_{aq}^-$) is measured
- Reaction 2 does not occur in aqueous solutions (the reason is still not clear)