



Photochemical Processes of Nickel(II) Xanthate Complex in CCl₄

Mikheyliis A.V.^{1,@}, Grivin V.P.¹, Plyusnin V.F.^{1,2}

¹ Voevodsky Institute of Chemical Kinetics and Combustion SB RAS;

² Department of Natural Sciences, Novosibirsk State University

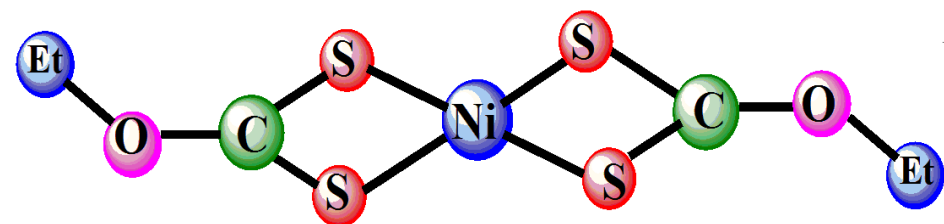
@ mikheyliis@kinetics.nsc.ru



Applications of dithiolate metals complexes of transient metals

- Nonlinear optical materials
- Photochromic system
- Photocatalysis
- Medicine

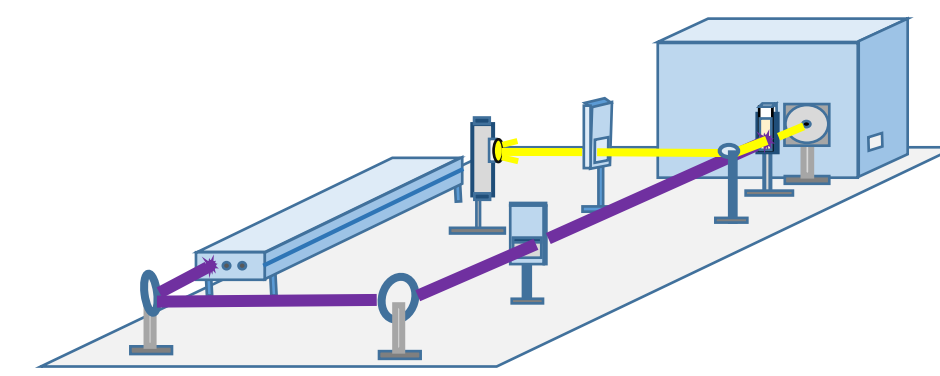
Complex of Ni(S₂COEt)₂ in CCl₄



Goal: Photochemistry of complex Ni(S₂COEt)₂ in CCl₄

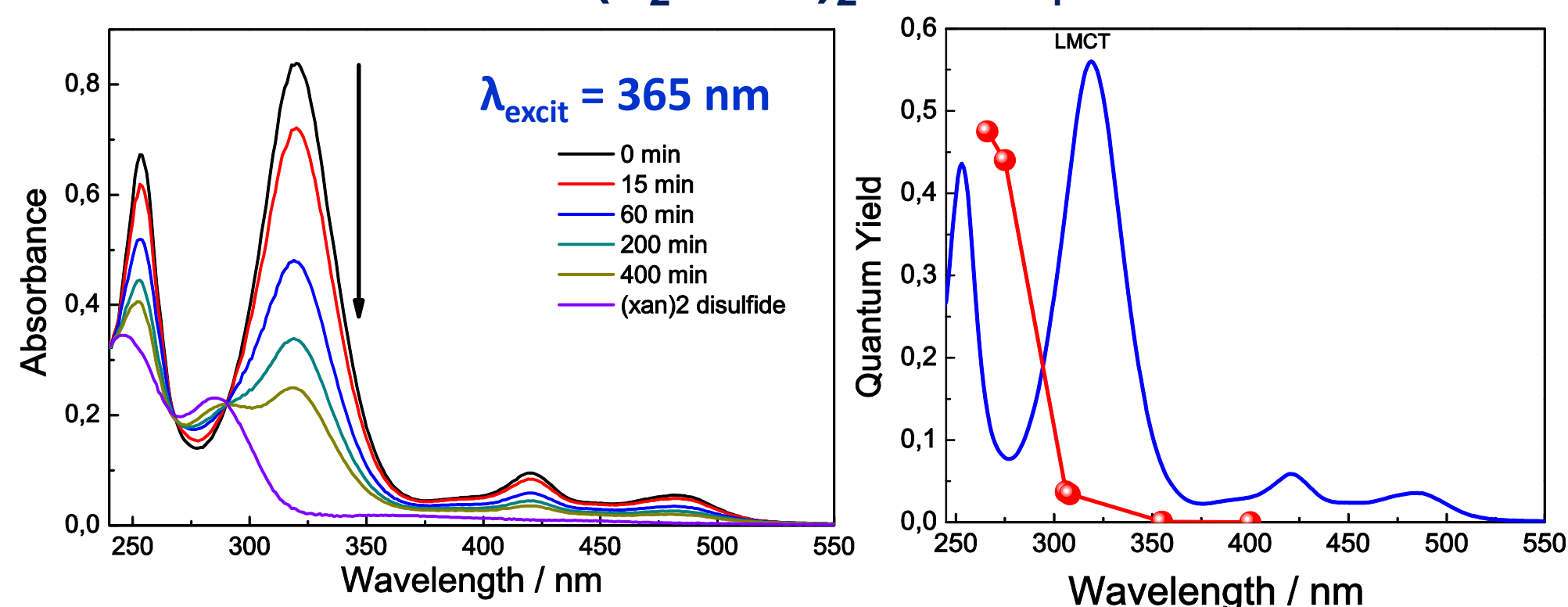
Methods:

- Steady-state photolysis
- Laser flash photolysis
- Thin-layer chromatography

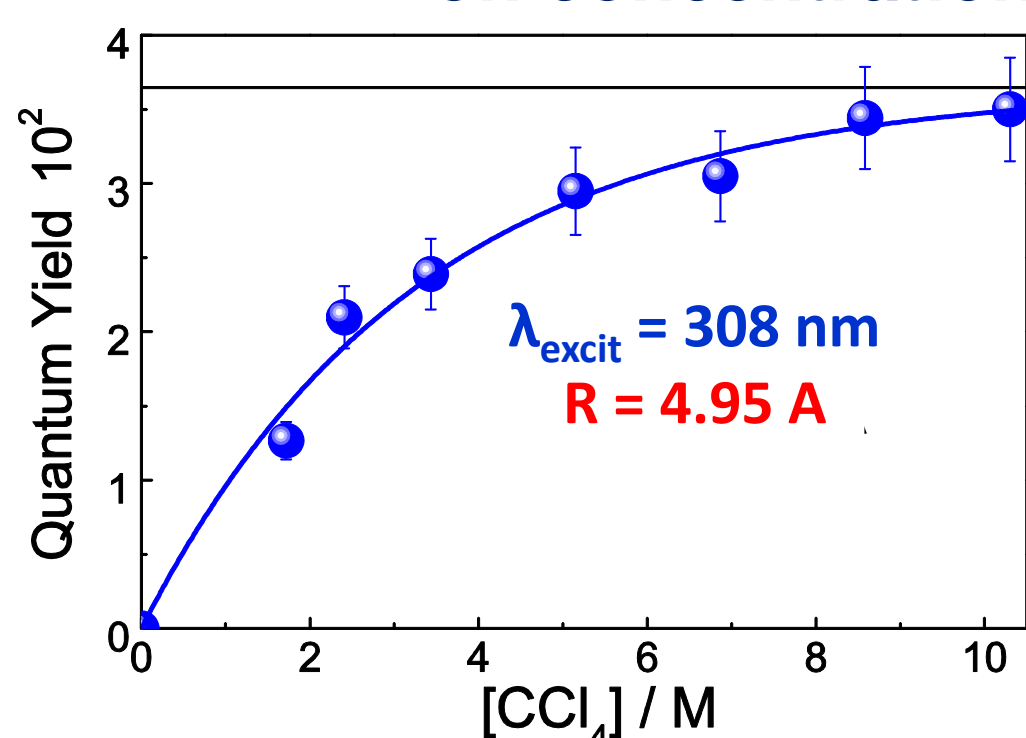


The Scheme of laser flash photolysis Installation

Steady-state photolysis and quantum yield of Ni(S₂COEt)₂ in CCl₄



Dependence quantum yield photolysis of Ni(S₂COEt)₂ on concentration CCl₄ in CH₃CN



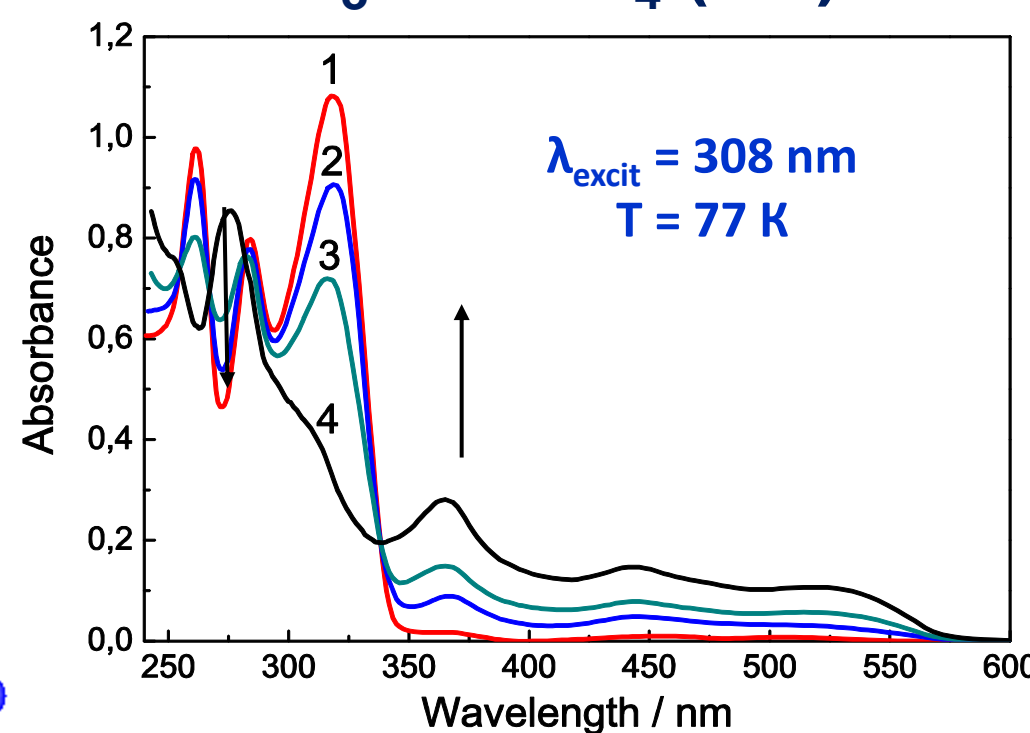
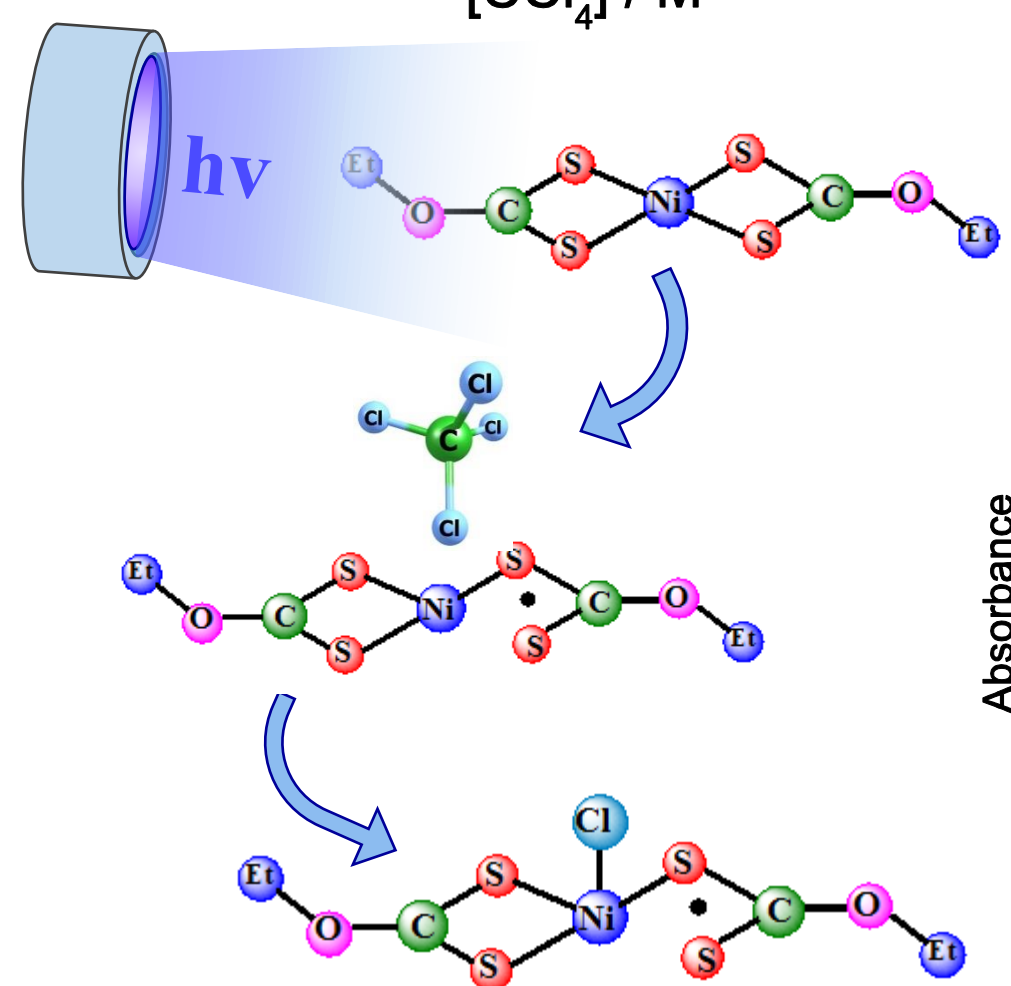
Electron transfer from excited molecule of complex to CCl₄

$$\varphi = \varphi_{\infty} (1 - e^{-C \cdot \Omega})$$

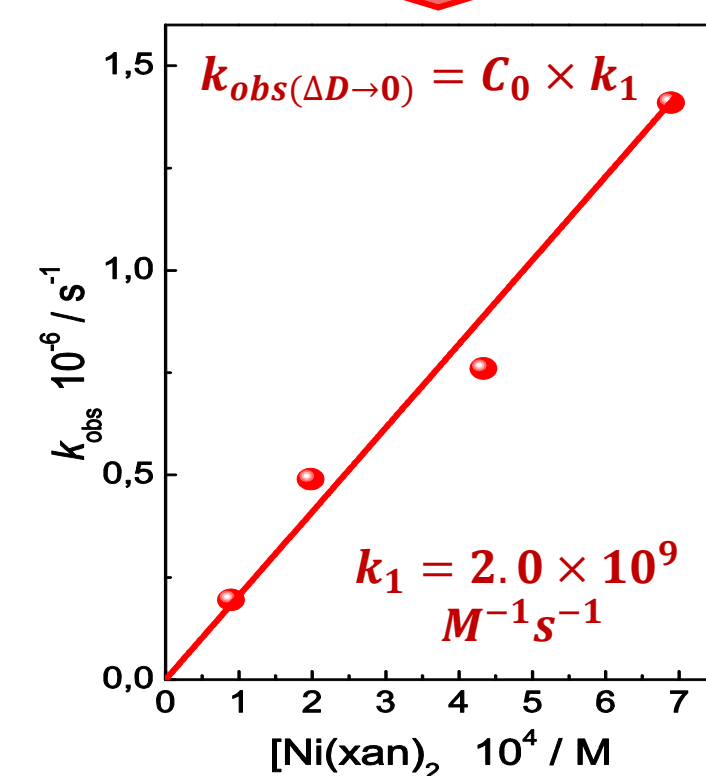
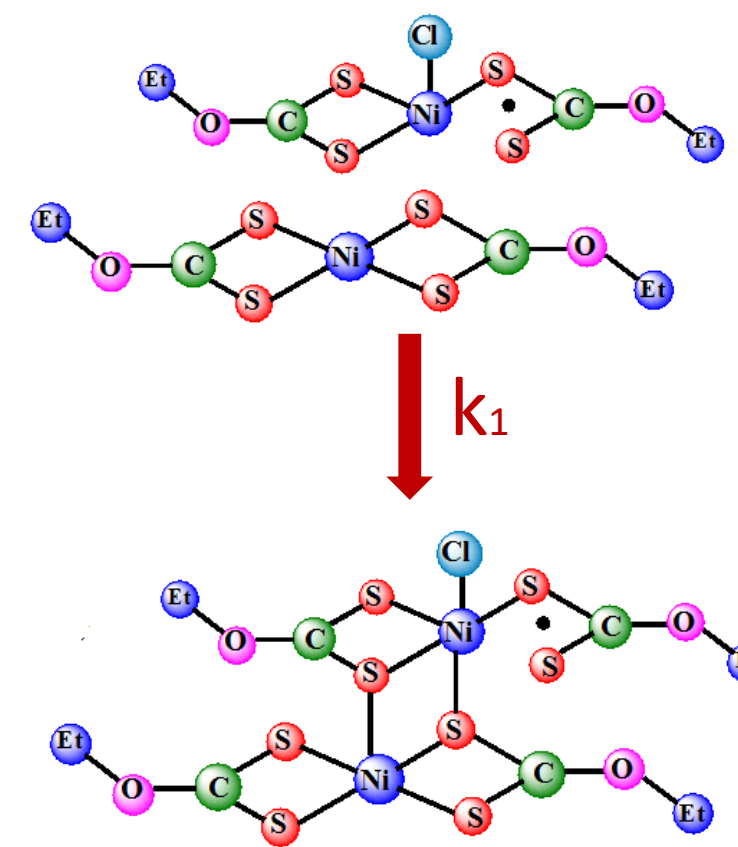
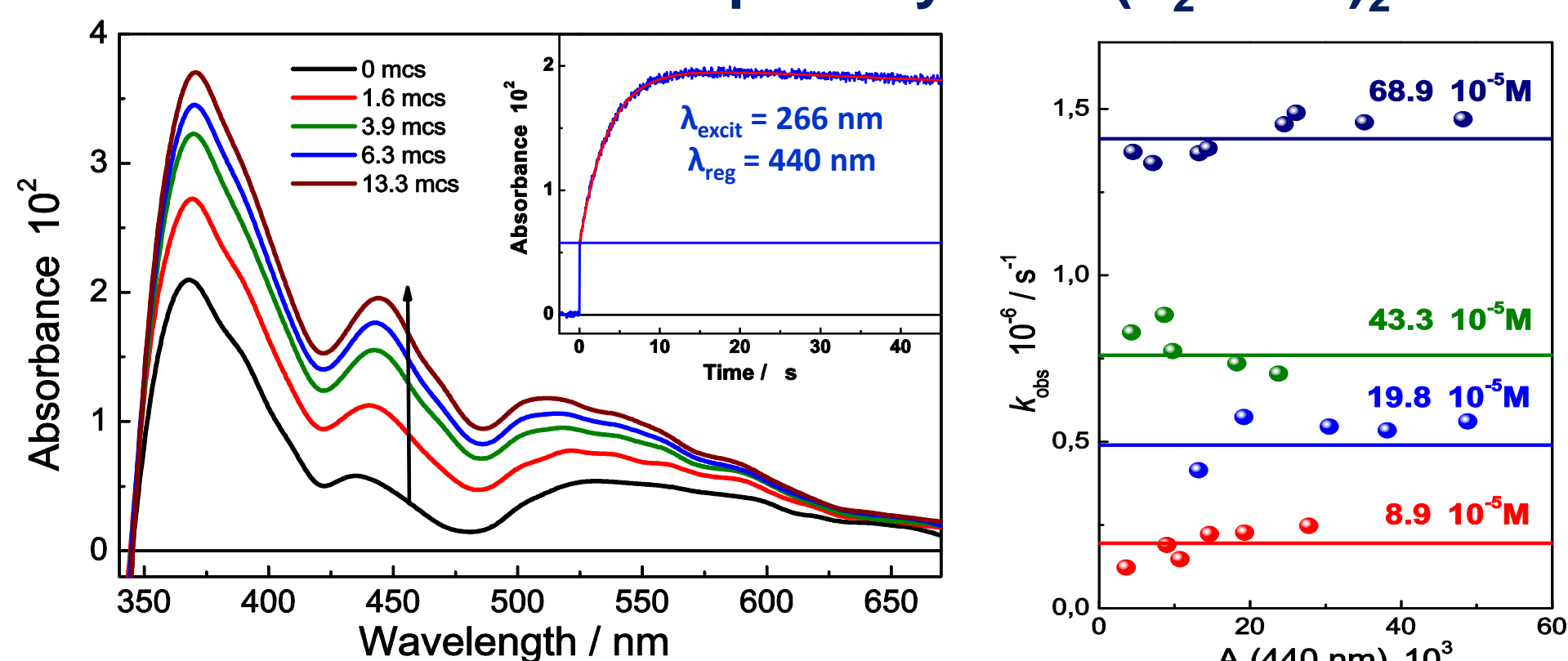
$$R = \sqrt[3]{\frac{3\Omega}{4\pi R}}$$

Effective distance between donor and acceptor in electron transfer

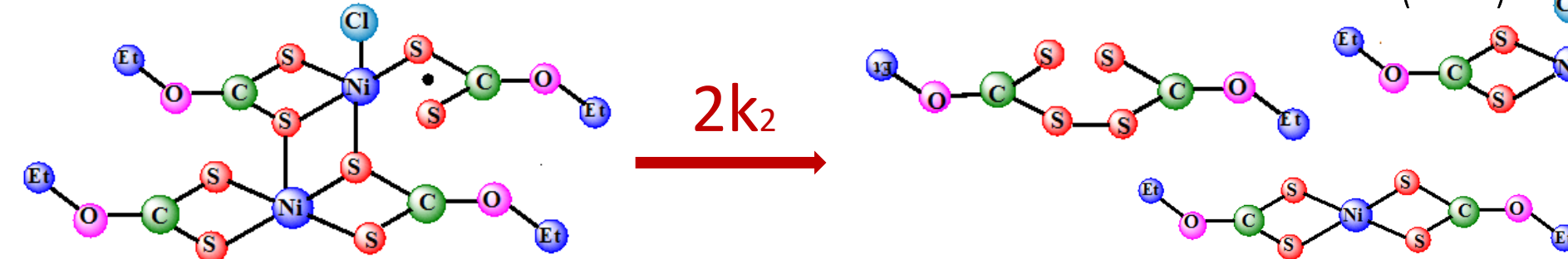
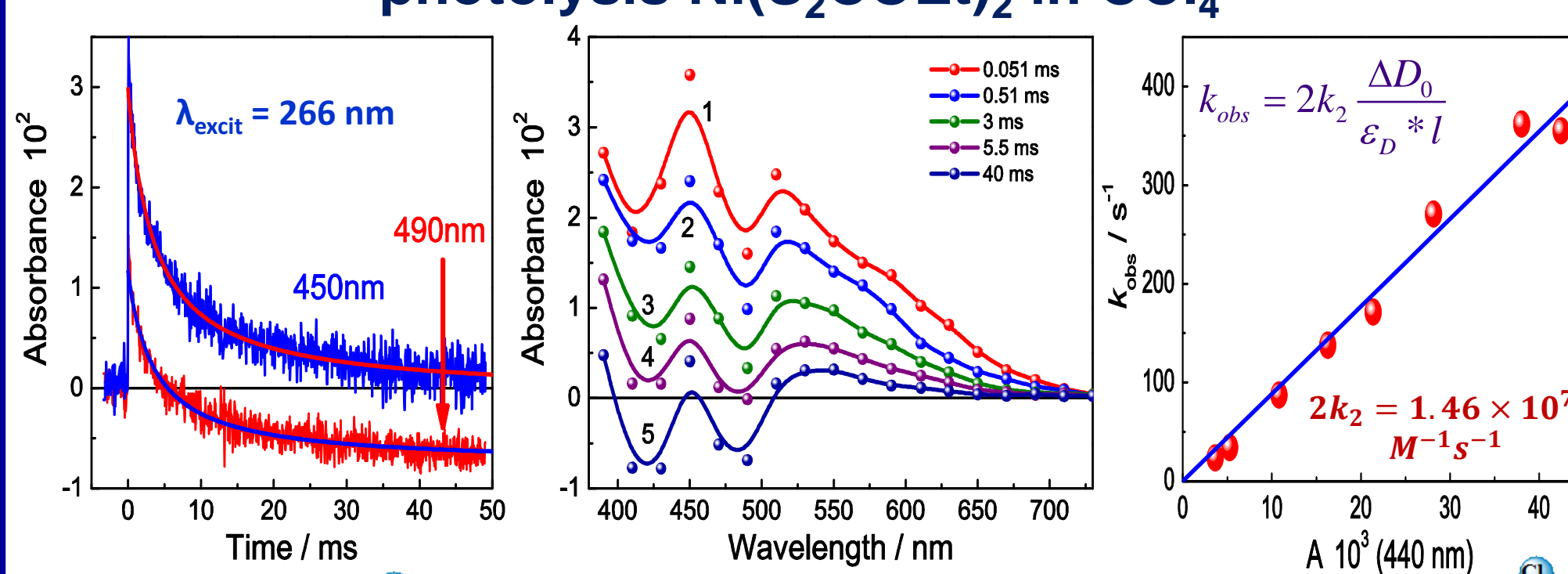
Photolysis Ni(S₂COEt)₂ in frozen matrices CH₃OH:CCl₄ (4:1)



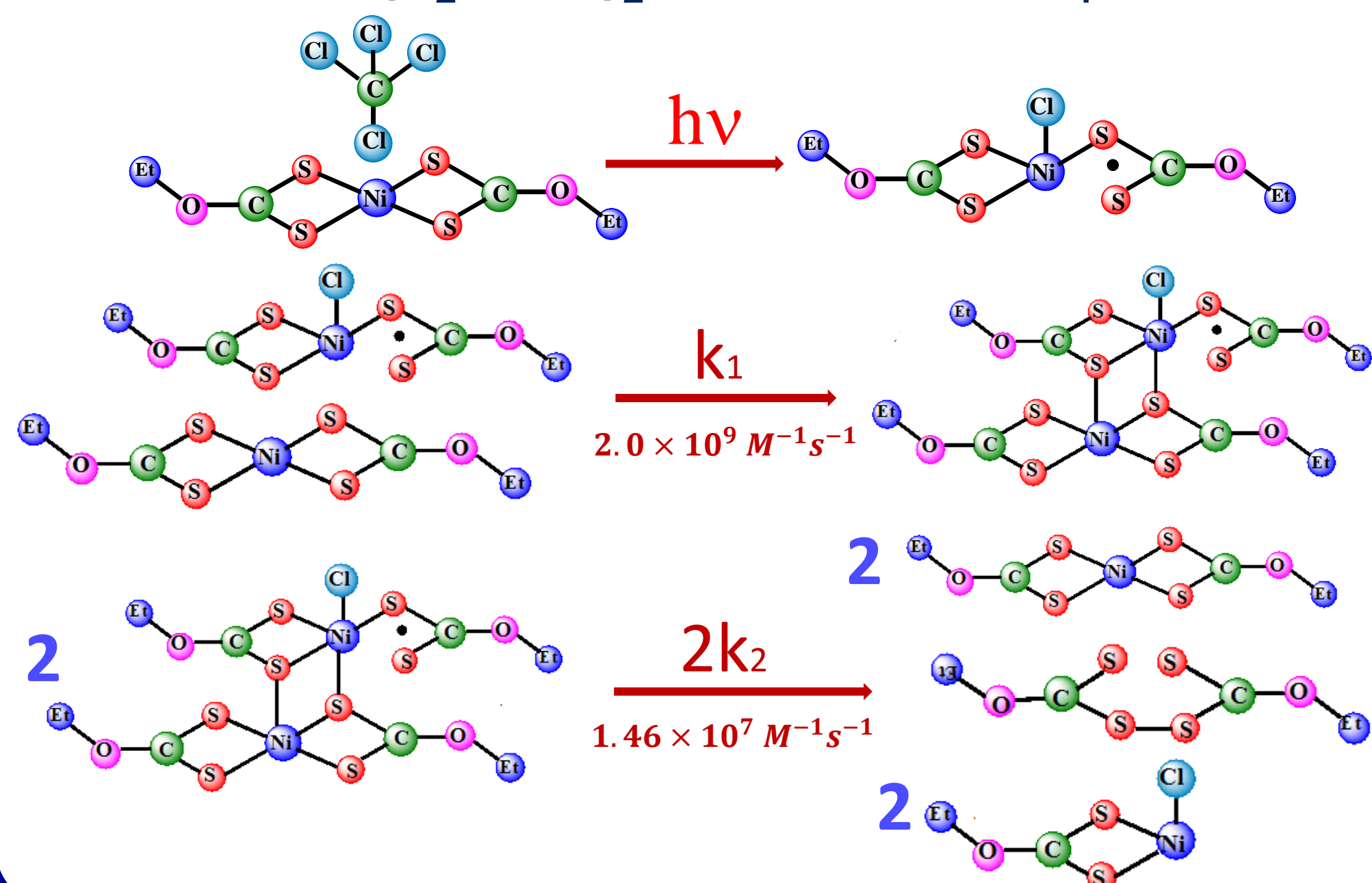
Nanosecond laser flash photolysis Ni(S₂COEt)₂ in CCl₄



Absorption spectrum of the intermediate and rate constant in the millisecond timeframe during flash photolysis Ni(S₂COEt)₂ in CCl₄



Mechanism of photochemical transformation Ni(S₂COEt)₂ solution in CCl₄



Conclusion:

- A mechanism for photochemical transformation of Ni(S₂COEt)₂ into CCl₄ was proposed based on kinetic and optical data.
- Photochemistry Ni(S₂COEt)₂ is determined by fast electron transfer from excited complex to solvent with formation of radical complex C₁Ni(S₂COEt)([•]S₂COEt).
- Radical complex disappears in reaction with initial complex to form dimer. Dimer particles decomposes in recombination reaction to final products – disulfide (S₂COEt)₂ and NiCl₂

Acknowledgment – the financial support of the Russian Foundation of Basic Investigation (Grants №20-03-00708 and 20-33-90193) is gratefully acknowledged.