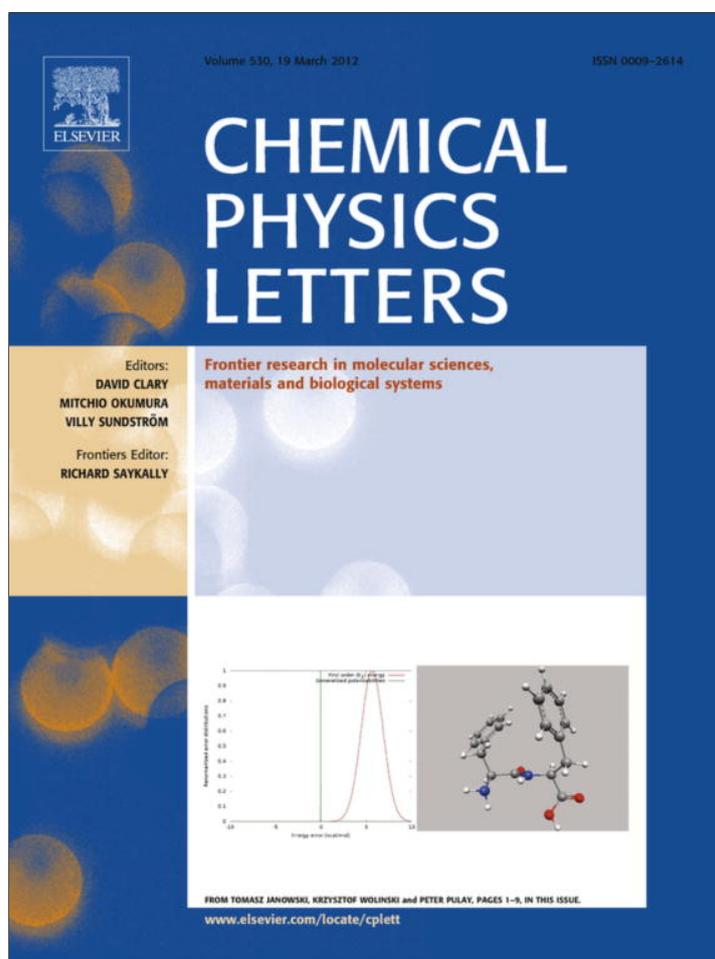


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## Photophysics of Fe(III)–tartrate and Fe(III)–citrate complexes in aqueous solutions

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## ABSTRACT

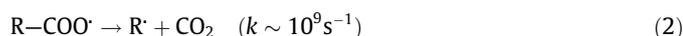
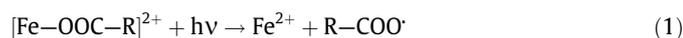
Femtosecond pump–probe spectroscopy was used to determine the photophysical processes of Fe(III) complexes with citric and tartaric acids ([Fe(Cit)] and [Fe(tart)]<sup>+</sup>) in aqueous solutions. The excitation of the complexes in the charge transfer bands is followed by formation of an intermediate absorbance decaying with two characteristic times. The shorter time constant (0.2, 0.4 ps) is ascribed to vibrational cooling and solvent relaxation of Frank–Condon excited state of corresponding complex and the second time constant (1.4, 40 ps) is assigned to superposition of internal conversion to the ground state and formation of the long-lived Fe(II) radical complex. The competition of these processes determines the quantum yield of photolysis of Fe(III)–carboxylates.

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## 1. Introduction

During the last two decades growing interest to the investigation of fast light-induced processes in natural waters was observed. This is connected with increased anthropogenic activity, importance of understanding of photoprocesses in environment and search for new high-efficient photocatalysts for water treatment. Natural water systems as well as model systems are investigated widely [1–10]. Accumulated data supports an importance of transient metal photochemistry (especially Fe(III)) in transformation of organic compounds dissolved in natural waters.

Among iron(III) complexes the photochemistry of Fe(III) complexes with carboxylic acids contribute substantially to the degradation of pollutants in aqueous systems. It is typically believed that the primary process in the photochemistry of Fe(III)–carboxylate complexes is an inner-sphere electron transfer with the formation of Fe(II) and an escape of an organic radical to the solution bulk (reaction 1) [2,4,5] followed by its fast decarboxylation (reaction 2) [11,12]:

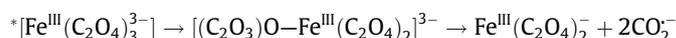


The secondary radical formed as the result of decarboxylation could react with the different components of the reaction system (e.g., Fe(III) complexes or molecular oxygen). Active oxygen species are formed consequently which provide the mineralization of organic compounds in natural waters [2,4,5].

The reaction mechanism (reactions 1, 2) was put forward based on the results of the stationary experiments. In our previous works nanosecond laser flash photolysis technique was used to clarify mechanism of photolysis of Fe(III)–carboxylate complexes [13–15]. The main intermediate in photochemistry of Fe(III) complexes with several natural organic acids (tartaric, ([Fe(Tart)]<sup>+</sup>; pyruvic, [Fe(Pyr)]<sup>2+</sup>; oxalic [Fe(Ox)<sub>3</sub>]<sup>3-</sup> and glyoxalic [Fe(AG)]<sup>2+</sup>) was found to be corresponding long-lived radical complex rather than short-lived organic radical:



It is worth to note that the investigation of femtochemistry of Fe(III)–carboxylate complexes is a challenge for experimentalists due to rather low absorption coefficients of initial compounds and transient species. Few publications concerning ultrafast spectroscopy of [Fe(Ox)<sub>3</sub>]<sup>3-</sup> complex could be found in literature [16]. As a primary photoprocess the sequential cleavage of Fe(III)–O bond (between one oxalate ligand and Fe(III) ion) and the C–C bond of the ligand was proposed leading to tetrahedral-like four-coordinated Fe<sup>III</sup>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub><sup>-</sup> complex and CO<sub>2</sub><sup>-</sup> radical:



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The interpretation [16] was contradictory to our mechanism based on formation of the radical complex  $[(C_2O_4)_2Fe^{II}(C_2O_4)]^{3-}$  as a primary photoproduct [13]. Therefore, the primary stage of the mechanism of photolysis of Fe(III)–carboxylates is still open for discussion.

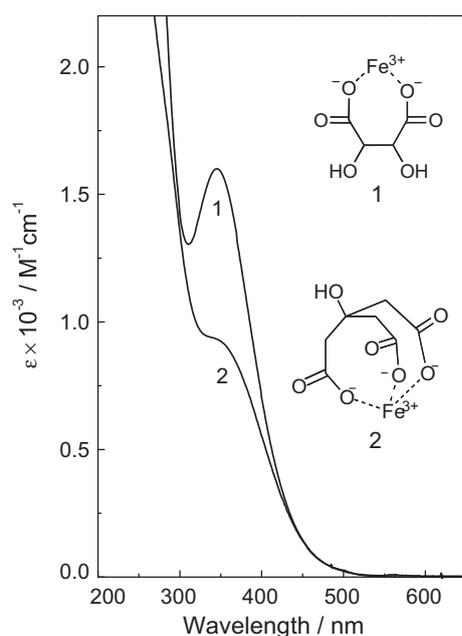
In the present work, we investigate the photophysical properties of aqueous solutions of Fe(III) complexes with tartaric and citric acid in the coordination sphere using femtosecond pump–probe spectroscopy. The main attention was focused on determination of the origin, the spectral and kinetic parameters of the precursors of the radical complexes – the excited states of the complexes.

## 2. Experimental

A pump–probe spectroscopy was used to study transient absorption of the samples in femto–picosecond time domain. The samples were excited by  $\sim 60$  fs pulses at  $\sim 405$  nm (second harmonic of a Ti:sapphire generator–amplifier system, CDP Ltd., Moscow, Russia) or by  $\sim 100$  fs pulses at  $\sim 320$  nm (fourth harmonic of a signal wave of TOPAS parametric amplifier). The instruments used were described in details elsewhere [17,18]. Both excitation wavelengths (405 and 320 nm) fall to the same broad LMCT band of the complexes [19] from right and left side of the maximum of the absorption band, accordingly (Figure 1).

For excitation at 405 nm (ca. 20–25  $\mu$ J/pulse) the excitation pulse repetition rate was 10 Hz, excitation beam size was 0.4–0.5 mm in diameter and 200 pulses were used to record single time-resolved spectrum. The samples were placed in 1 mm rotating cuvette (total volume of 1 ml) to provide the uniform irradiation of the sample and to avoid unwanted thermal effects from the heating of the sample by the pump pulse. The degradation of the sample after photochemical studies did not exceed 5%.

For excitation at 320 nm (ca. 1  $\mu$ J/pulse) the excitation pulse repetition rate was 1 kHz and 200 pulses were used to record single time-resolved spectrum. The investigated solutions (total volume of 10 ml) were pumped through a 1 mm cuvette at room temperature to provide uniform irradiation and avoid possible degradation due to photochemical reactions.



**Figure 1.** Absorption spectra and chemical structures of Fe(III) complexes with tartaric (1) and citric acids (2).

The absorption spectra were recorded using a Shimadzu UV 2501 PC and Agilent HP8453 spectrophotometers. Citric acid monohydrate (Merck, 99%), tartaric acid (Aldrich, 98%) and Fe(III) perchlorate hydrate (Aldrich) were employed without further purification. The solutions were prepared using bidistilled or deionized water.

$[Fe(Cit)]$  ( $\lambda_{max} = 345$  nm,  $\epsilon_{max} = 930$  M $^{-1}$  cm $^{-1}$ ) and  $[Fe(tart)]^+$  ( $\lambda_{max} = 347$  nm,  $\epsilon_{max} = 1600$  M $^{-1}$  cm $^{-1}$ ) complexes were prepared by mixing the solutions of Fe(III) perchlorate with the solutions of the corresponding organic acids. In pump–probe experiments with excitation at 320 nm the concentrations of the reagents were: Fe(III) perchlorate –  $5 \times 10^{-3}$  M, tartaric acid and citric acid – 0.01 M, pH = 2. In pump–probe experiments with excitation at 405 nm the concentrations of the reagents were: Fe(III) perchlorate –  $1.5 \times 10^{-2}$  M, tartaric acid –  $2.3 \times 10^{-2}$  M and citric acid – 0.167 M, pH = 2. At all conditions used, about 96% and 85% of Fe(III) exists as  $[Fe(tart)]^+$  and  $[Fe(Cit)]$  complex, accordingly (Figure 1). The composition of Fe(III)–citric acid and Fe(III)–tartaric acid systems was calculated using Visual MINTEQ program (ver. 2.53) [20].

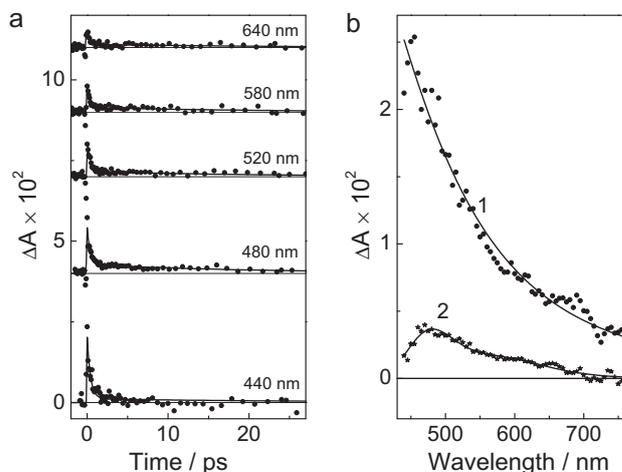
## 3. Results and discussion

### 3.1. Ultrafast processes for $[Fe(Cit)]$ and $[Fe(tart)]^+$ complexes

The excitation of  $[Fe(tart)]^+$  complex with a femtosecond pulse ( $\lambda_{pump} = 405$  nm) leads to the formation of transient absorption which is almost completely decayed in 30 ps. Kinetic curves at several selected wavelengths are presented in Figure 2a. The global analysis of the time profile in the wavelength range 440–760 nm by iterative reconvolution shows that the use of a two-exponential function (4) with the instrument response function gives a good fitting with the time constants  $\tau_1 = 0.4$  ps and  $\tau_2 \approx 40$  ps.

$$\Delta A(\lambda, t) = A_1(\lambda)e^{-t/\tau_1} + A_2(\lambda)e^{-t/\tau_2} \quad (4)$$

Spectra of  $A_1(\lambda)$  and  $A_2(\lambda)$  amplitudes allow one to construct the spectra at different times (Figure 2b). Immediately after excitation (zero time, sum of amplitudes) the transient absorption is the very wide band with observed maximum shorter than 440 nm. After the finishing of first fast process ( $\tau_1$ ) the absorption band is narrowed and centered at  $\lambda \approx 470$  nm. Similar results were obtained in



**Figure 2.** Femtosecond ( $\lambda_{pump} = 405$  nm) photolysis of  $[Fe(Tart)]$  complex ( $1.5 \times 10^{-2}$  M). (a) Kinetic curves of transient absorption change at different wavelengths. Solid lines: best two-exponential fit after reconvolution with the instrument response function. (b) Spectra at different times. (1) Spectrum at zero time (sum of amplitudes  $A_1(\lambda) + A_2(\lambda)$ ); (2) spectrum after the end of ultrafast process (amplitude  $A_2(\lambda)$ ).

pump–probe experiments with excitation at 320 nm. At initial time after excitation the broad structureless absorption band with a maximum wavelength smaller than 440 nm is formed accompanying with a strong bleaching in UV part of spectrum due to depopulation of the ground state of complex (Figure 3a). During the first 3 ps after excitation this broad band decays and shifts to the shorter wavelengths with parallel decrease of bleaching in UV part. At longer timescale the slow decrease of transient absorption was observed leading to the constant bleaching in UV part of spectrum (Figure 3a, b). This is good coinciding with the data obtained by nanosecond laser flash photolysis technique [15].

Unfortunately, extremely low transient signal (due to low excitation energy used) and rather big coherent artifact [21] makes impossible the global fit analysis procedure. However, simple biexponential fit of kinetic curves at characteristic wavelengths (Figure 3b) gives time constants which have the same order of magnitude as those obtained in experiments with 405 nm excitation (Table 1).

The excitation of [Fe(Cit)] complex both at 320 and 405 nm leads to the formation of a transient absorption which is almost completely decayed in 5 ps (Figure 4a). Kinetic curves at several-selected wavelengths are presented in Figure 4b. The global analysis of the time profile in the wavelength range 440–760 nm by iterative reconvolution shows that the use of a two-exponential function (4) with the instrument response function gives a good fitting with the time constants  $\tau_1 = 0.2$  ps and  $\tau_2 = 1.4$  ps. In the case of excitation at 320 nm first fast component is masked by coherent artifact and only second time constant could be determined ( $\tau_2 \approx 2$  ps). Fitting results for [Fe(Cit)] complex are presented in Table 1.

It is worth to note that characteristic absorption bands of [Fe<sup>II</sup>... OOC-R]<sup>2+</sup> complexes ( $\lambda_{\max} = 620$ –650 nm, recorded by nanosecond laser flash photolysis [13–15]) were not observed in femtosecond experiments. This is due to the extremely low absorption coefficients of the radical complexes ( $\epsilon^{620} = 18 \text{ M}^{-1} \text{ cm}^{-1}$  for [Fe(tart)]<sup>+</sup> [15]).

### 3.2. Mechanism of relaxation of the excited states of Fe(III)-carboxylate complexes

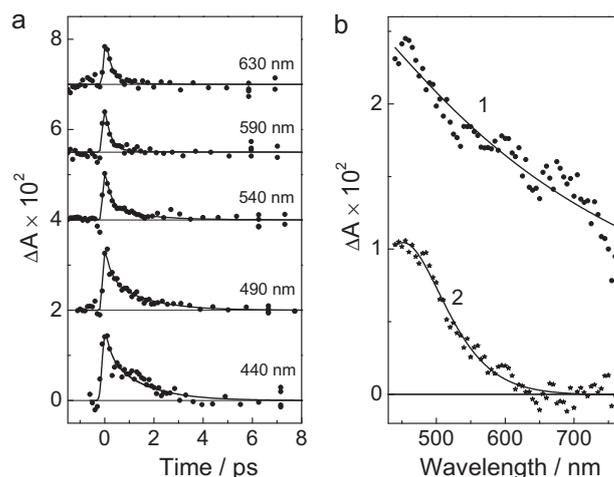
The identification of final photochemical reaction products (i.e. Fe(II) and oxidized ligand [19,22]) for both [Fe(Cit)] and [Fe(tart)]<sup>+</sup> complexes leads to conclusion that the primary photo-process is an electron transfer from the ligand to Fe(III) [2,4,22]. It is known that quantum yield of Fe(II) formed by photolysis of

**Table 1**

Lifetimes and observed absorption maxima of the excited states of Fe(III)-carboxylate complexes.

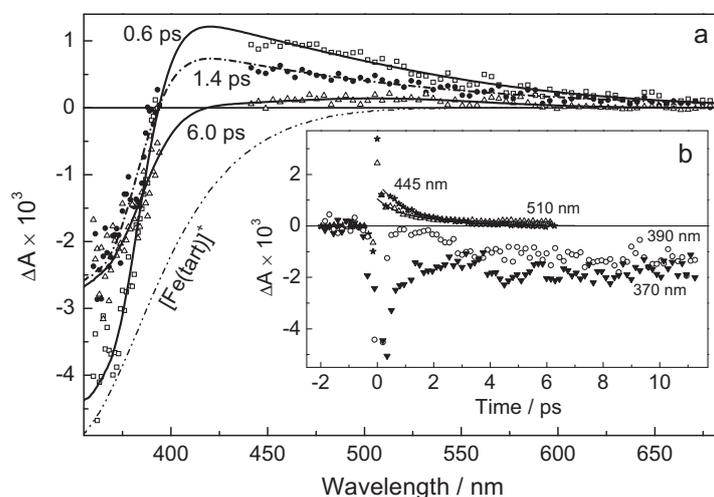
Complex	$\lambda_{\text{ex}}$ nm	$\tau_1$ ps	$\lambda_{\text{max}}(\tau_1)$ nm	$\tau_2$ ps	$\lambda_{\text{max}}(\tau_2)$ nm
[Fe(Cit)]	405	0.2	<440	1.4	≈450
	320	–	–	≈2	≈440
[Fe(tart)] <sup>+</sup>	405	0.4	<440	≈40	≈470
	320	≈1	<440	40 <sup>a</sup>	≈500

<sup>a</sup> Fixed value.



**Figure 4.** Femtosecond ( $\lambda_{\text{pump}} = 405$  nm) photolysis of [Fe(Cit)] complex ( $1.5 \times 10^{-2}$  M). (a) Kinetic curves of transient absorption change at different wavelengths. Solid lines: best two-exponential fit after reconvolution with the instrument response function. (b) Spectra at different times. (1) Spectrum at zero time (sum of amplitudes  $A_1(\lambda) + A_2(\lambda)$ ); (2) spectrum after the end of ultrafast process (amplitude  $A_2(\lambda)$ ).

Fe(III)-carboxylates depends rather weakly on excitation wavelength ( $\lambda_{\text{ex}}$ ) and is equal 1.25 for Fe(III)-oxalate ( $\lambda_{\text{ex}} = 260$ –365 nm [23]), ≈0.28 for Fe(III)-citrate ( $\lambda_{\text{ex}} = 366$  [22] and 436 [4] nm) and ≈0.4 for Fe(III)-tartrate ( $\lambda_{\text{ex}} = 313$  [24], 355 [15] and 366 [22,24] nm) complexes, accordingly. This fact indicates that the formation of the Fe(II) radical complex is taking place from the thermalized excited state of corresponding Fe(III)-carboxylate.



**Figure 3.** Femtosecond ( $\lambda_{\text{pump}} = 320$  nm) photolysis of [Fe(Tart)]<sup>+</sup> complex ( $5 \times 10^{-3}$  M). (a) Transient spectra at different time delay between probe and pump pulses together with inverted absorption spectrum of [Fe(Tart)]<sup>+</sup>. (b) Kinetic curves of transient absorption change at selected wavelengths. Solid lines: best two-exponential fit.

In this case the biphasic dynamics observed for Fe(III)–carboxylate complexes upon charge transfer (CT) band excitation could be explained by following mechanism [25]:

The first process with observed time constant  $\tau_1$  could be assigned to combination of an ultrafast vibrational cooling and solvent relaxation of Frank–Condon excited state to the thermalized one. This situation is typical for relaxation of Frank–Condon excited states of transient metal complexes in polar solvents exhibiting inertial solvation time about 100 fs [25]. One can expect that relaxation of the Frank–Condon excited state leads to some narrowing of absorption band due to vibrational relaxation [26] and blue shift of absorption maximum due to so-called dynamic Stokes shift [27] as indeed was observed experimentally (Figure 3a, b).

The thermalized excited state decays with time constant  $\tau_2$  by two processes – internal conversion to the ground state and formation of the long-lived Fe(II) radical complex. The competition of these processes determines the quantum yield of photolysis of Fe(III)–carboxylates.

#### 4. Conclusion

Femtosecond pump–probe technique was applied to investigate the photophysical properties of aqueous solutions of Fe(III) complexes with tartaric and citric acids. Biphasic dynamics of primary populated Frank–Condon excited state was observed. The shorter time constant is ascribed to vibrational cooling and solvent relaxation of Frank–Condon excited state and the second time constant is assigned to superposition of internal conversion to the ground state and formation of the long-lived Fe(II) radical complexes. The competition of these processes determines the quantum yield of photolysis of Fe(III)–carboxylates.

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