

# Photoelectron Detachment and Solvated Electron Dynamics of the Cobalt(III) and Iron(III) Oxalato Complexes

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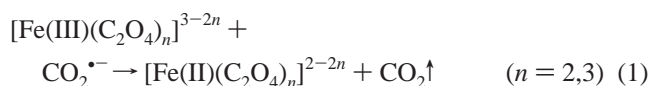
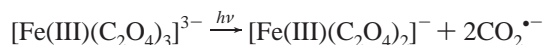
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The photochemical redox reaction kinetics of  $[\text{M(III)}(\text{C}_2\text{O}_4)_3]^{3-}$  [ $\text{M} = \text{Co}, \text{Fe}$ ] complexes have been reexamined and studied by time-resolved spectroscopy. The redox mechanisms of the two systems, Co and Fe, were found to be similar to each other, and solvated electrons were observed immediately after 266/267 nm photoexcitation. A reaction mechanism is proposed that involves photoelectron detachment as a primary process. The charge-transfer bands for both complexes, which had been attributed to ligand to metal charge-transfer (LMCT) transitions previously, are reassigned to charge transfer to solvent (CTTS) transitions.

## 1. Introduction

The photochemical behavior of the transition metal oxalato complexes has attracted considerable interest for a long period of time from both the fundamental science and the application points of view.<sup>1,2</sup> Ferrioxalate has received relatively more attention<sup>2</sup> ever since Parker suggested in 1953 that it is an efficient chemical actinometer.<sup>3</sup> Because radicals are generated after irradiation, ferrioxalate has also been used as a radical polymerization reaction initiator,<sup>4</sup> and, in recent years, ferrioxalate has found additional extensive use in environmental chemistry, which extends the limitation of Fenton oxidation due to its strong absorption from the UV to visible range and its ability to degrade organic pollutants by absorption of solar light.<sup>5</sup> In other applications, cobaltoxalate has been utilized in solar energy media that could photolyze water to produce hydrogen.<sup>6</sup>

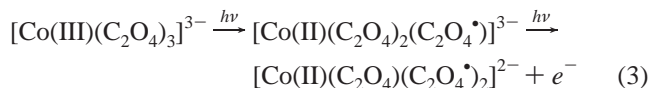
Numerous researchers have investigated the photochemical mechanism of ferrioxalate<sup>7–11</sup> and cobaltoxalate<sup>12–15</sup> systems by various techniques. The flash photolysis studies of ferrioxalate and cobaltoxalate complexes had been summarized by Stasicka et al.<sup>2</sup> and further discussed by Poznyak et al.<sup>16</sup> Although it has been a tendency to assume that a similar mechanism is operative for both complexes, the value of this assumption has not been confirmed because their photochemical mechanisms have not been clearly defined. The major debate until recently has been whether intramolecular or intermolecular electron transfer (ET) is the primary photoredox reaction.<sup>17</sup> Ultrafast structural studies performed by time-resolved X-ray absorption spectroscopy<sup>11,17,18</sup> combined with ultrafast optical studies and theoretical calculations have shed light on the operating photoredox mechanism of ferrioxalate. The ultrafast structure changes obtained using 400 nm excitation rejected the proposal of intramolecular electron transfer as the primary reaction and supported a mechanism where dissociation of an oxalate group occurs initially and the iron remains at the +3 oxidation state during the first steps of the photoredox reaction.<sup>11</sup>



Further experimental studies with 267 nm irradiation have shown that, in addition to the major primary dissociation process, ferrioxalate molecules undergo low quantum yield direct electron photodetachment and subsequently generate solvated electrons:<sup>18</sup>



The generation of electrons has also been proposed by Shagisultanova et al.<sup>19</sup> in their study of cobaltoxalate photolysis under low-temperature acidic conditions. However, these authors reported that the electron was formed by the secondary photoreduction of cobaltoxalate as a result of CW irradiation and subsequently the electron would reduce the acidic hydrogen ion to produce hydrogen radical. This electron formation mechanism had been further extended by Cordemans et al.<sup>13</sup> and is described in reaction 3.

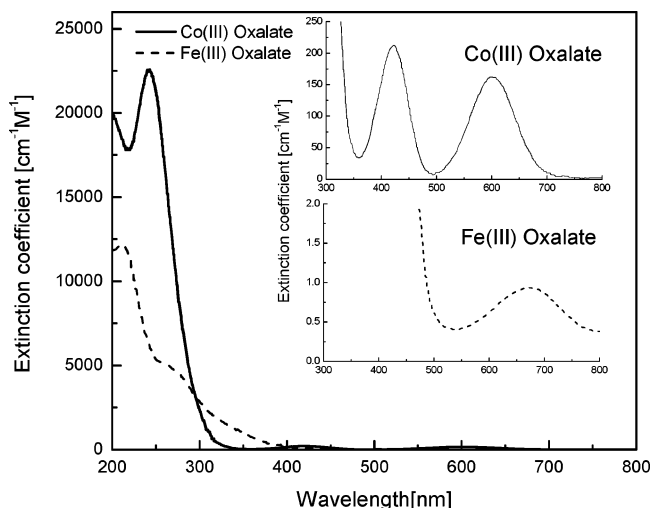


In this Article, the photochemical transients spectra and kinetics of cobaltoxalate have been investigated using 266 and 267 nm irradiation, and the results obtained are compared to the ferrioxalate transients formed under similar conditions. We have studied the similarities and differences between these two reactions in detail, and from the analysis of the data we draw the conclusions presented concerning the nature of the charge-transfer (CT) band and kinetics of the solvated electron.

## 2. Experimental Section

**2.1. Laser System.** The cobaltoxalate and ferrioxalate photoredox reaction experiments presented in this Article were conducted at room temperature using 100 fs, 0.3 mJ, 267 nm pulses (third harmonic of Ti: Sapphire) for the femtosecond to picosecond experiments and 266 nm pulses (fourth harmonic of the Nd:YAG) for the picosecond to microsecond experiments.

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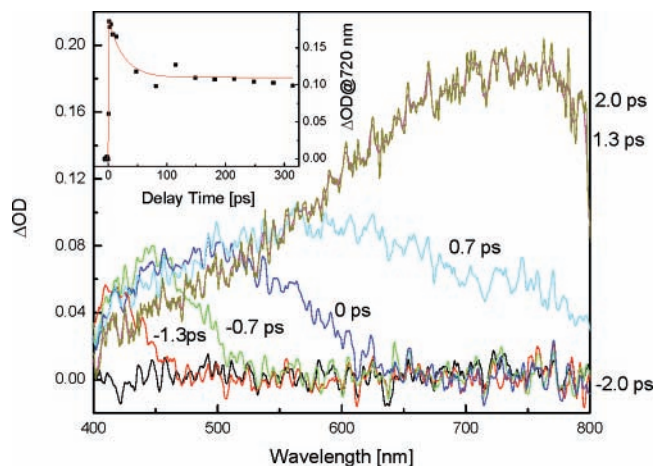
**Figure 1.** Absorption spectra of cobalt(III) oxalate (—) and ferrioxalate (---) in water. Inset: Enlarged absorption spectra from 300 to 800 nm.

**2.2. Materials and Absorption Spectra.** Ammonium ferrioxalate  $(\text{NH}_4)_3\text{Fe(III)(ox)}_3 \cdot 3\text{H}_2\text{O}$ , where  $\text{ox} = \text{C}_2\text{O}_4^{2-}$ , was purchased from Alfa Aesar, 98%, and used without further purification.  $(\text{NH}_4)_3\text{Co(III)(ox)}_3 \cdot 3.5\text{H}_2\text{O}$  was prepared according to the procedure described in ref 20 and purified repeatedly until its spectrum in water remained unchanged and all detectable impurities were removed. The percentage of oxalate group in cobalt(III) oxalate was analyzed and found to be  $59.6 \pm 1.3$ , which is in agreement with the theoretical value of 60.2. The absorption spectra, Figure 1, of  $[\text{Fe(III)(C}_2\text{O}_4)_3]^{3-}$  and  $[\text{Co(III)(C}_2\text{O}_4)_3]^{3-}$  show bands in the ultraviolet and visible regions. Ferrioxalate has two absorption bands with maxima at 210 nm ( $\epsilon = 1.2 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ) and 669 nm ( $\epsilon = 0.94 \text{ cm}^{-1} \text{ M}^{-1}$ ). Cobalt(III) oxalate has three broad absorption bands: (1) an intense absorption band with its maximum at 242 nm ( $\epsilon = 2.2 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ ), which has been attributed to the CT band; and (2) two weak bands with maxima at 422 nm ( $\epsilon = 218 \text{ cm}^{-1} \text{ M}^{-1}$ ) and 600 nm ( $\epsilon = 164 \text{ cm}^{-1} \text{ M}^{-1}$ ). The spectra and extinction coefficients of these bands are in agreement with the corresponding literature values.<sup>12,21,22</sup>

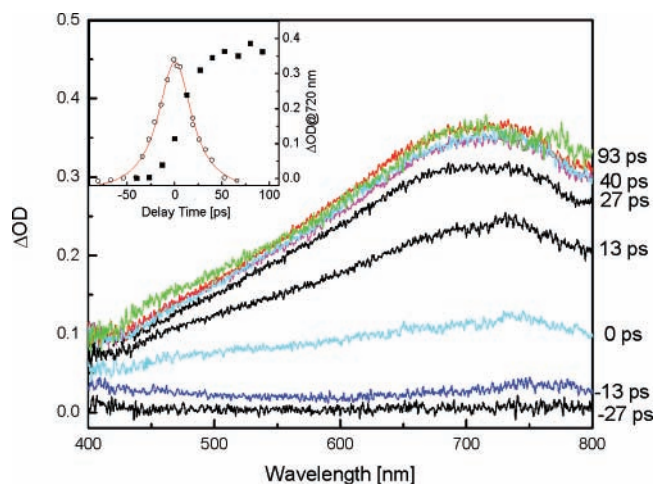
### 3. Results and Discussion

#### 3.1. Transient Absorption Spectra. 3.1.1. Cobalt(III) Oxalate.

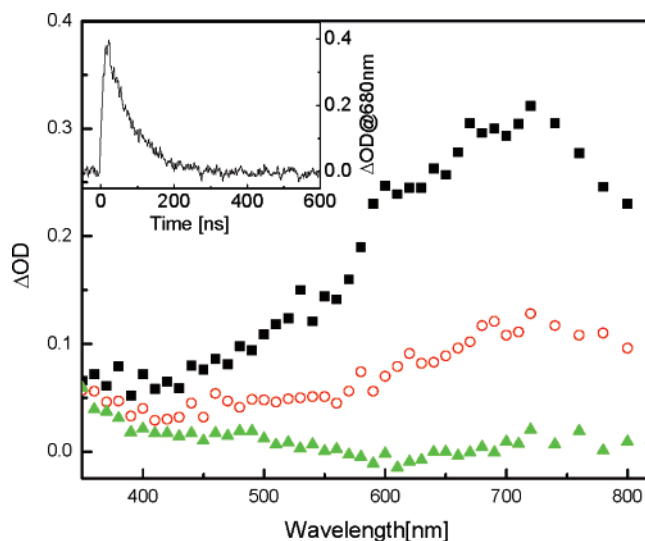
A 500–800 nm broad transient band with maximum at 720 nm was found to be formed immediately after 267 nm, 100 fs excitation of 1.0 mM cobalt(III) oxalate/water solution, Figure 2. Time zero is set as the time when the 267 nm pump pulse overlaps the 720 nm probe pulse. This band achieves its maximum intensity 1.3 ps after excitation followed by a partial decay with a lifetime of 25 ps, which reaches a plateau and remains constant for at least 300 ps. A continuous shift in the band maxima observed from  $-1.3$  to  $1.3$  ps is due to dispersion of the probe continuum. A very similar 500–800 nm band had also been detected after ps/ns and ns/ $\mu\text{s}$  266 nm excitations with formation times of about 45 ps, shown in Figure 3, and less than 10 ns, shown in Figure 4, respectively. These apparent formation times are due to the excitation pulse widths rather than depict the true formation lifetime. Further experiments described in this Article show also that the nature of this band is the same under both excitations; therefore, we attribute the 2 ps to 10 ns 500–800 nm transient bands to the same intermediate, which we shall show in this Article to be due to solvated electron in water. The absorbance of this transient depends



**Figure 2.** Femtosecond time-resolved transient absorption spectra of  $1.0 \times 10^{-3} \text{ M}$  cobalt(III) oxalate in water using 267 nm excitation. Inset: Transient optical density at 720 nm (■) and the fitting of transient absorption kinetics (—).

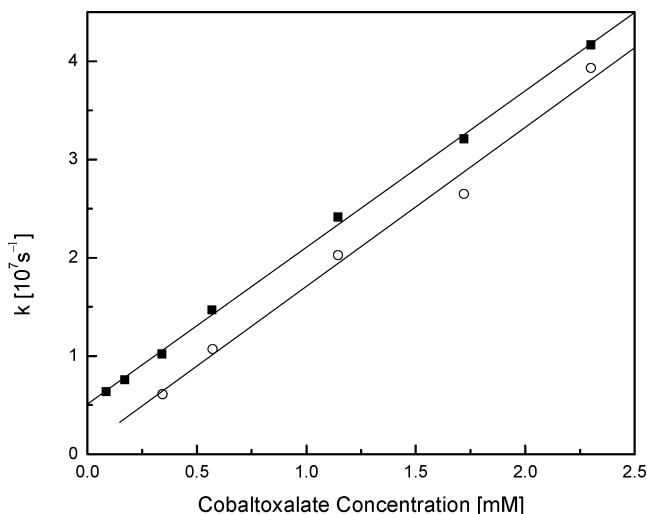


**Figure 3.** Picosecond transient absorption spectra of  $1.0 \times 10^{-3} \text{ M}$  cobalt(III) oxalate in water using 266 nm excitation. Inset: Transient kinetics at 720 nm (■) and the 45 ps pulse width (○).

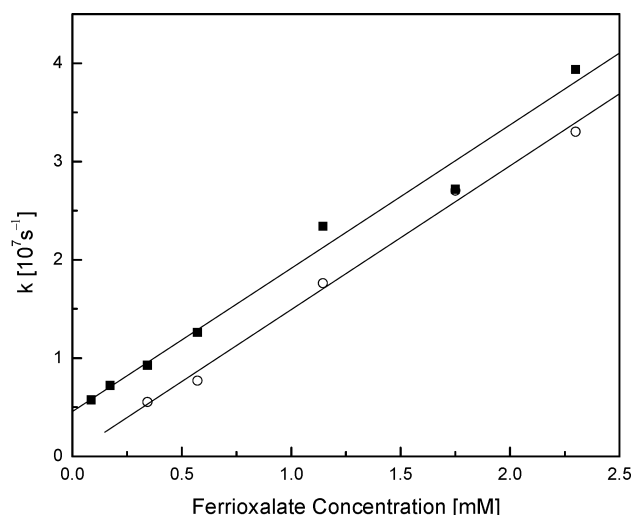


**Figure 4.** Transient absorption spectra of  $5.7 \times 10^{-4} \text{ M}$  cobalt(III) oxalate in water using 266 nm excitation at different delay times: 20 ns (■), 100 ns (○), and 500 ns (▲). Inset: Transient kinetics at 680 nm.

linearly on excitation intensity; therefore, the 266/267 nm photolysis was performed by a single-photon process. The nanosecond decay kinetics of the 500–800 nm transient band



**Figure 5.** The decay rate constant at 680 nm versus concentration of cobaltoxalate with bubbling nitrogen (○) and in air (■).

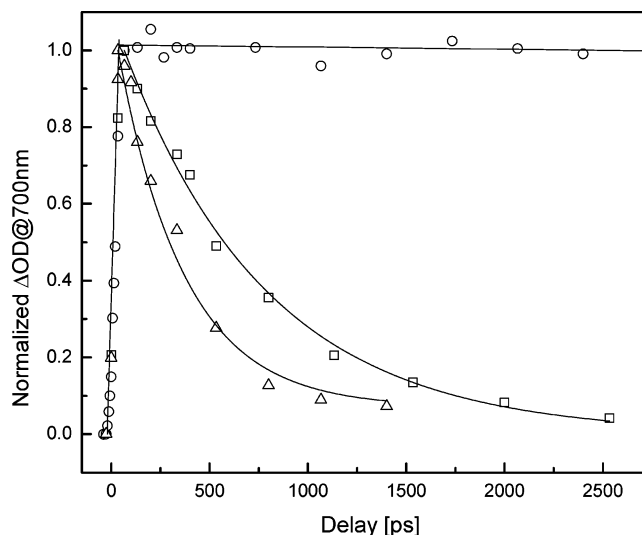


**Figure 6.** The decay rate constant at 680 nm versus concentration of ferrioxalate with bubbling nitrogen (○) and in air (■).

was found to be dependent on the concentration of cobaltoxalate. This dependence is clearly shown in Figure 5 where the decay rate constant is plotted as a function of the cobaltoxalate concentration.

**3.1.2. Ferrioxalate.** A similar 500–800 nm transient absorption band and kinetics behavior have been observed for ferrioxalate,<sup>18</sup> and the intensity of this band is close to that observed for cobaltoxalate. The formation lifetime of this band was measured to be 1.3 ps by pump/probe ultrafast spectroscopy, while its decay was found to be biexponential. The short-lived component was measured to have a 17 ps lifetime, and the long component lifetime was determined to be concentration dependent with 30 and 130 ns decay lifetimes at 2.3 and 0.57 mM, respectively; see Figure 6.

**3.2. Solvated Electron Absorption Spectra.** The 500–800 nm transient absorption band generated with 266 or 267 nm excitation is practically the same in shape, width, and spectral range as the solvated electron band reported in the literature.<sup>23–25</sup> Furthermore, the formation kinetics of the 500–800 nm band that are measured are in agreement with the reported time-resolved spectra and formation kinetics for solvated electrons.<sup>23,25</sup> The inset of Figure 2 also shows a fast decay of 25 ps, which is due to the cage recombination of the photodetached electron with the cobaltoxalate complex. Such fast solvated



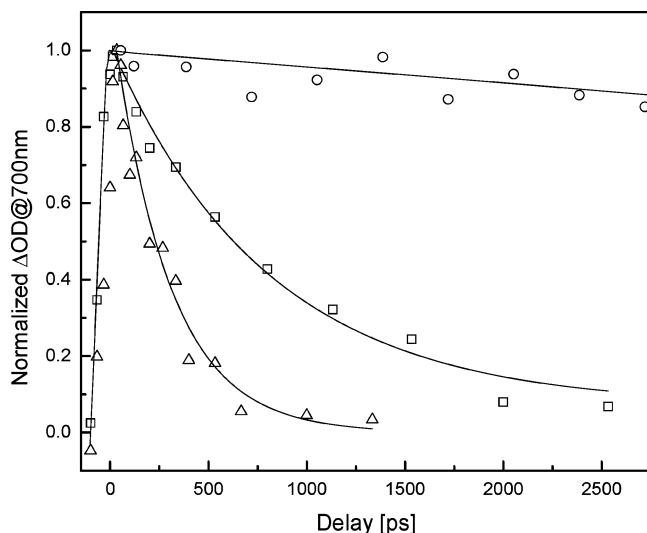
**Figure 7.** Picosecond kinetics of solvated electron absorption band at 700 nm from cobaltoxalate in water under various added  $\text{KNO}_3$  concentrations (○, 0 M; □, 0.1 M; and △, 0.2 M) excited with 266 nm pulses. The cobaltoxalate concentration was  $1.0 \times 10^{-3}$  M. The reaction rate constants were  $1.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  with 0.1 M  $\text{KNO}_3$  and  $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  with 0.2 M  $\text{KNO}_3$ .

electron recombination has been observed with decay lifetimes of 17 ps in ferrioxalate/water solution<sup>18</sup> and 13 ps in aqueous hydroxide solution.<sup>26,27</sup> It is known that intense 267/266 nm femtosecond and picosecond pulses generate electrons from pure water by a multiphoton process. To avoid electron generation from water, we used weak 267 nm femtosecond pulses and made certain that these pulses did not generate solvated electrons in pure water. The ionization potential of water<sup>28</sup> is  $I_p(\text{H}_2\text{O}) = 12.59 \text{ eV}$ , and the energy of a 267 nm photon is 4.64 eV, whose energy is by far too low to ionize water by one photon process. Photoelectron spectroscopy studies on hydrated electron cluster anions have shown that the photoelectric threshold is  $\sim 3.25 \text{ eV}$  for the hydrated electron in bulk water solution, which also corresponds to the solvation energy of the electron in water.<sup>29</sup> Even when we consider this solvation energy, there is still not sufficient energy for one-photon excitation, and the two-photon process is deficient by  $\sim 0.06 \text{ eV}$ .

**3.3. Electron Scavenging.** To ascertain the existence of solvated electrons in the  $\text{M(III)(ox)}$  solutions after excitation, we performed electron quenching experiments using 0.1–0.2 M  $\text{NO}_3^-$  that has been used widely as an effective electron quencher.<sup>30,31</sup>

**3.3.1. Cobaltoxalate.** The picosecond to nanosecond time-resolved solvated electron reaction data with and without  $\text{KNO}_3$  are shown in Figure 7. The reaction rate constant of the electron with the cation  $\text{K}^+$  reaction is small;<sup>23</sup> therefore, the effect of  $\text{K}^+$  was ignored when we evaluated the electron scavenger/solvated electron reaction rate. The lifetime of the 500–800 nm band was determined to be more than 3.7 ns without electron scavenger addition to the  $\text{Co(III)(ox)}$  solution. The intensity of this band was found to decrease significantly within 300 ps after nitrate was added to the solution. The decay lifetime of the 500–800 nm band was also found to depend upon the concentration of the nitrate added to the solution, corresponding to 0.79 ns at 0.1 M and 0.29 ns at 0.2 M  $\text{NO}_3^-$ . The bimolecular quenching constant derived from those results was determined to be  $(1.4–1.5) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

**3.3.2. Ferrioxalate.** We have obtained similar electron scavenging results for the solvated electron/nitrate reaction in ferrioxalate water solution, and these data are shown in Figure



**Figure 8.** Picosecond kinetics of solvated electron absorption band at 700 nm from ferrioxalate in water under various added  $\text{KNO}_3$  concentrations (O, 0 M; □, 0.1 M; and △, 0.2 M) excited with 266 nm pulses. The ferrioxalate concentration was  $3.3 \times 10^{-3}$  M. The reaction rate constants were  $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  with 0.1 M  $\text{KNO}_3$  and  $1.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  with 0.2 M  $\text{KNO}_3$ .

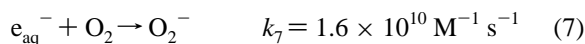
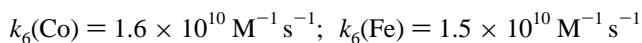
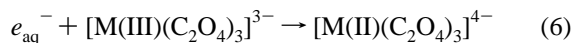
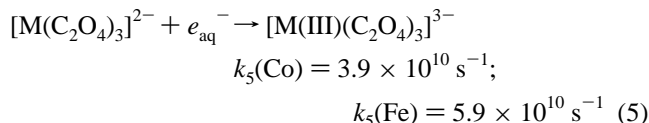
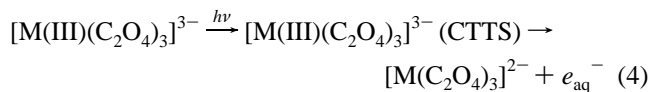
8. The quenching constant derived from the decay lifetime of the transient absorption at 700 nm was calculated to be  $(1.3\text{--}1.8) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ .

The solvated electron kinetic data are summarized in Table 1. The bimolecular quenching reaction constants obtained in both cobaltoxalate and ferrioxalate solution agree with the literature value of  $(0.9\text{--}2.2) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  reported for the solvated electron/nitrate reaction.<sup>30,31</sup> The good agreement of both spectra and quenching constant with the previously published results<sup>23,25,30,31</sup> indicates that the observed absorption band at 500–800 nm is due to solvated electrons in water.

**3.4. Photoelectron Detachment Mechanism.** Solvated electrons were generated by photoelectron detachment from a  $\text{M(III)(ox)}$  anion by 267 nm, 4.64 eV, pulses. Charge transfer to solvent (CTTS) theoretical and experimental studies have been performed<sup>32</sup> and have also been applied specifically to ferrocyanide and other charge-transfer systems.<sup>25,33</sup> However, to our knowledge, the ionization potentials of cobaltoxalate and ferrioxalate in solution are not known. The ionization potentials for  $\text{Co(III)}$  and  $\text{Fe(III)}$  atoms are reported to be  $I_p(\text{Co}) = 7.86$  eV and  $I_p(\text{Fe}) = 7.87$  eV, respectively.<sup>34</sup> Taking into account the solvation energy of the electron in water, 3.25 eV, the difference of 4.62 eV between these two values is therefore the minimum energy needed to excite the  $\text{M(III)(ox)}$  molecule to the CTTS state. This indicates that it is possible for one 267 nm photon, 4.64 eV, to excite the cobaltoxalate or ferrioxalate molecule to the metastable CTTS 4.64 eV state, which subsequently yields a detached electron.

The solvated electron, which is known to have a high redox potential ( $E^0 = \sim -2.7$  V (NHE)),<sup>35</sup> may react with the parent  $\text{M(III)(ox)}$  and initiate the photoreduction of  $\text{M(III)}$  to  $\text{M(II)}$  according to reaction 6. Assuming the decay of the 500–800 nm band is due to the solvated electron/ $\text{M(III)(ox)}$  reaction, the reaction rate constants derived from the decay lifetime are estimated to be  $1.6 \times 10^{10}$  and  $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for electron/cobaltoxalate and electron/ferrioxalate reaction, respectively. These values agree well with the  $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  reaction constant of the electron/cobaltoxalate reaction reported in ref 23. The decay dependence on concentrations is also in agreement with reaction 6, which shows that the electron reacts with  $\text{M(III)(ox)}$  to generate  $\text{M(II)(ox)}$ . We have studied also the effect of oxygen on the decay lifetime of the electron transient band

by performing experiments with bubbling nitrogen and in air. These results depicted in Figures 5 and 6 show that oxygen also reacts with solvated electrons, reaction 7, and decreases the lifetime of the 500–800 nm transient band. Using the concentration of oxygen at room temperature, which is about 8.6 mg/L, the reaction constant for the electron/oxygen reaction is estimated to be  $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , which is in agreement with the  $2.16 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  value of ref 23. We propose, therefore, that the kinetic scheme of the reaction path for solvated electron generation and decay in  $\text{M(III)(ox)}$ /water solution is:



Data presented in the next section show that reaction 4 that generates the electron has a much lower quantum yield than the dissociation reaction 1.

**3.5. Charge Transfer to Solvent (CTTS) Band.** The intense absorption bands in the UV region of both cobaltoxalate and ferrioxalate have been attributed previously to the ligand to metal charge-transfer (LMCT) band,<sup>22</sup> which led to the proposal of intramolecular electron-transfer mechanisms.<sup>7</sup> However, in our recent studies of ferrioxalate solution using both 400 and 267 nm excitations, we found that dissociation of the metal ligand bond precedes intramolecular ET<sup>11,17,18</sup> and the photoreduction of  $\text{Fe(III)}$  is due to intermolecular rather than intramolecular ET. The mechanism shown in reaction 1, which involves dissociation as the primary photochemical process of  $\text{Fe(III)(ox)}$  followed by intermolecular ET, was substantiated by time-resolved EXAFS and UHF and DFT calculations.<sup>11,17,18</sup> EXAFS spectra obtained from  $-20$  ps (non-excited) to 140 ps after excitation allowed us to measure the  $\text{Fe-O}$  bond length at various times after excitations. These bond lengths were used to determine the structure of the  $\text{Fe(ox)}$  complex and conclude that the iron remains in the  $\text{Fe(III)}$  oxidation state; however, a  $\text{C}_2\text{O}_4^{2-}$  group is cleaved. DFT and UHF calculations also favor the intermolecular ET primary process mechanism over intramolecular ET. Those recent optical and X-ray experimental results and quantum chemistry calculations challenge the previous assignment of the strong absorption band to a LMCT band: Is intramolecular ET fast, and is the so-called CT band a real LMCT band? The observation of the 500–800 nm solvated electron absorption band has led us to reconsider the CT assignment and advance the possibility that it belongs to a charge transfer to solvent (CTTS) band.

The solvated electron band has also been observed in our previous studies where we used 400 and 355 nm to excite ferrioxalate/water solutions.<sup>18</sup> When intense 400 nm femtosecond pulses were used to excite the ferrioxalate complex in water, a broad absorption band was formed by a two-photon process in the 500–800 nm region. The shape, width, and spectral range of this band correspond very well with the published solvated electron spectra in water. However, these lower than 4.64 eV

**TABLE 1: Decay Lifetime of Solvated Electron at Various KNO<sub>3</sub> Concentrations**

KNO <sub>3</sub> concentration	0.1 M		0.2 M	
	lifetime [s]	$k(\text{NO}_3^-/\text{e}^-)$ [ $\text{M}^{-1} \text{s}^{-1}$ ]	lifetime [s]	$k(\text{NO}_3^-/\text{e}^-)$ [ $\text{M}^{-1} \text{s}^{-1}$ ]
ferrioxalate ( $C = 3.3 \times 10^{-3} \text{ M}$ )	$7.9 \times 10^{-10}$	$1.3 \times 10^{10}$	$2.9 \times 10^{-10}$	$1.8 \times 10^{10}$
cobaltoxalate ( $C = 1.0 \times 10^{-3} \text{ M}$ )	$7.3 \times 10^{-10}$	$1.4 \times 10^{10}$	$3.4 \times 10^{-10}$	$1.5 \times 10^{10}$

**TABLE 2: Extinction Coefficients of M(III)(ox)<sup>a</sup>**

material	CTTS band ( $\lambda_{\text{max}}$ )	extinction coefficient ( $\epsilon$ ) [ $\text{cm}^{-1} \text{M}^{-1}$ ]		
ferrioxalate	210 nm	$4.8 \times 10^3$ (1)	$8.4 \times 10^2$ (2)	$1.7 \times 10^2$ (3)
cobaltoxalate	242 nm	$1.6 \times 10^4$ (1)	$4.6 \times 10^1$ (2)	$1.4 \times 10^2$ (3)

<sup>a</sup> Excitation wavelength: (1) 267 nm, (2) 355 nm, (3) 400 nm.

energy pulses were able to generate the solvated electron transient absorption band only by a two-photon process and not by a single-photon process. As expected, only two 400 or 355 nm photons have sufficient energy to excite a M(III)(ox) molecule to a CTTS state, 4.64 eV; however, one 266 or 267 nm photon has sufficient energy to do so.

The above assignment to a CTTS band is also supported by comparing the absorption extinction coefficient at 267 and 400 nm for both cobaltoxalate and ferrioxalate, which are summarized in Table 2. Those data show that both molecules have a much higher extinction coefficient at 267 nm than at 400 nm, 100 and 30 times for cobaltoxalate and ferrioxalate, respectively. The 267 nm band is close to the 242 nm absorption peak of the “charge-transfer” band especially for cobaltoxalate. The 400 nm pulses excite the molecule to levels that belong to the 420 nm visible absorption band, which has been attributed to ligand field (LF) transition.<sup>22</sup> Here, we also note that the absorption spectrum of ferrioxalate, Figure 1, shows a shoulder around 267 nm in the intense CT band. This may be explained by attributing the 267 nm to the overlap of the tail of 210 nm CT band and the LF 400 nm band of ferrioxalate. Under this assumption, we can generate the solvated electrons from ferrioxalate/water solution using one photon 267 nm excitation, but not with one 400 nm photon excitation.

We have estimated the quantum yield of the solvated electron formation by comparing the intensity of the transient absorption bands of M(III)(ox) [ $M = \text{Co}, \text{Fe}$ ] and ferrocyanide solutions at 680 nm under the same experimental conditions. Using the quantum yield of ferrocyanide, which is reported to be about 1,<sup>31</sup> we determined the quantum yield for the photodetachment of an electron from ferrioxalate and cobaltoxalate to be about 0.05–0.10. The quantum yield of M(II)(ox) formation has been measured to be 0.7–1.2.<sup>3,12</sup> The higher quantum yield for the generation of Fe(II)(ox) than electron is due to the efficient dissociation of  $[\text{Fe}(\text{III})(\text{C}_2\text{O}_4)_3]^{3-}$ , shown in reaction 1, to produce  $[\text{Fe}(\text{III})(\text{C}_2\text{O}_4)_2]^-$  and  $\text{CO}_2^{\bullet-}$ , which reacts with the parent molecule to reduce Fe(III) to Fe(II).

In summary, we assign the UV charge-transfer transition to the CTTS band instead of the LMCT band for the following reasons: (1) There is no direct observation for intramolecular ET, but solid evidence of solvated electron generation; and (2) solvated electron could not be formed within the LF band but easily formed within the CTTS energy range.

#### 4. Conclusion

The UV charge-transfer bands of  $[\text{M}(\text{III})(\text{C}_2\text{O}_4)_3]^{3-}$  [ $M = \text{Co}, \text{Fe}$ ] complexes are assigned to CTTS transitions. We observed that excitation in the CTTS band with 266 or 267 nm laser pulses induces photoelectron detachment and the generation of solvated electrons in  $[\text{M}(\text{III})(\text{C}_2\text{O}_4)_3]^{3-}$  complexes.

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