Photolysis of iron(III)-carboxylato complexes in aqueous atmospheric particles

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Motivation and background

Iron-complex photochemistry in the atmospheric aqueous phase

Iron is always present in concentration from ~10^{-9} (clouds) up to ~10^{-3} M (fog, particles). Iron sources are mainly mineral dust emissions. Iron complexes are very good absorbers in the UV-VIS actinic region → photo-chemically reactive through LMCT transitions. Fe-complex photolysis leads to radical production (see Fig.1). The photochemistry initiates radical chain reactions, which is related to the oxidizing capacity of the atmosphere. The Fe^{2+} budget is important for the Fenton-reaction, which can be a considerable in-situ OH source. Iron-complex photolysis modelling is currently only included in CAPRAM: oxalate is consumed through Fe-oxalate photolysis, which results in a net destruction of oxalate. This is a Contradiction to field measurements, where substantial amounts of oxalate are found. Other models don't include Fe-oxalato photolysis and over-predict oxalate. Laboratory studies of iron complex photolysis processes are therefore needed.
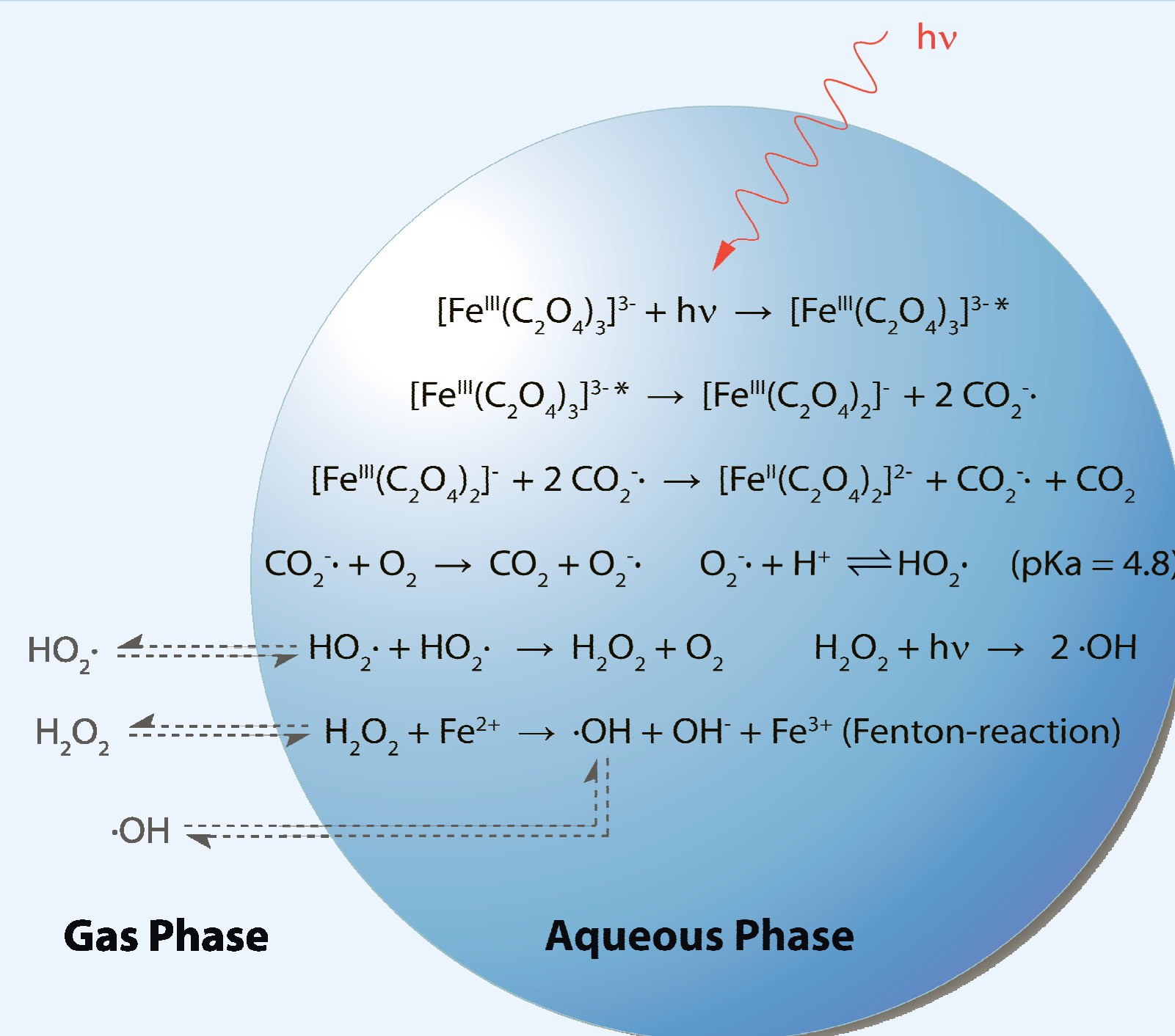

$$[Fe^{III}(C_2O_4)_3]^{3-} + h\nu \rightarrow [Fe^{III}(C_2O_4)_3]^{3-*}$$
$$[Fe^{III}(C_2O_4)_3]^{3-*} \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + 2 CO_2^{-\cdot}$$
$$[Fe^{III}(C_2O_4)_3]^{3-} + 2 CO_2^{-\cdot} \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + CO_2^{-\cdot} + CO_2$$
$$CO_2^{-\cdot} + O_2 \rightarrow CO_2 + O_2^{-\cdot} \qquad O_2^{-\cdot} + H^+ \rightleftharpoons HO_2^{\cdot} \quad (pKa = 4.8)$$
$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad H_2O_2 + h\nu \rightarrow 2 \cdot OH$$
$$H_2O_2 + Fe^{2+} \rightarrow \cdot OH + OH^- + Fe^{3+} \text{ (Fenton-reaction)}$$

Gas Phase   **Aqueous Phase**

Figure 1: Photolysis of Fe(III)-oxalato complex as example, including subsequent reactions

Experimental

Measurement of overall Fe^{2+} quantum yield

- De-oxygenation with Argon-bubbling prior to photolysis, if desired
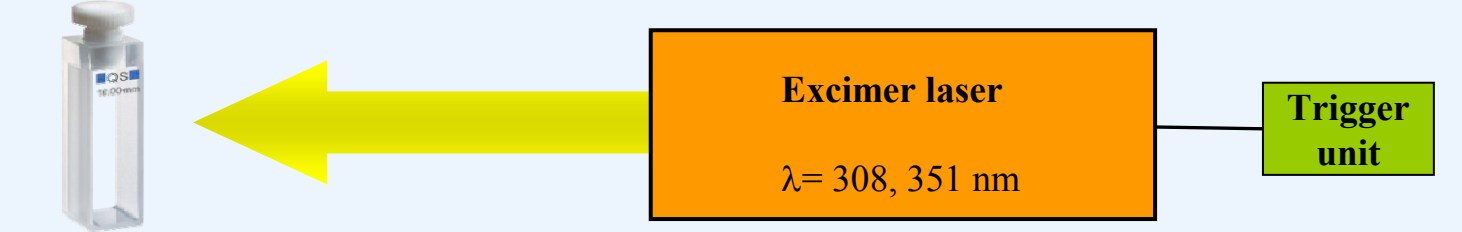
- Direct photolysis in quartz-cuvette
- Measurement of Excimer laser energy with calibrated pyro-electric sensor
- Mixing of photolysed aliquot with strong Fe^{2+} complexing agent Phenanthroline
- Formation of stable Fe^{2+}-complex between pH 2-9 ($[Fe(Phen)_3]^{2+}$) $\varepsilon_{\lambda = 510 nm} = 11\ 100\ l\ mol^{-1} cm^{-1}$
- Measurement of Fe^{2+}-complex absorbance with UV-VIS spectrometer
- Calculation of iron speciation with speciation program (Species, Visual Minteq)

Results and discussion
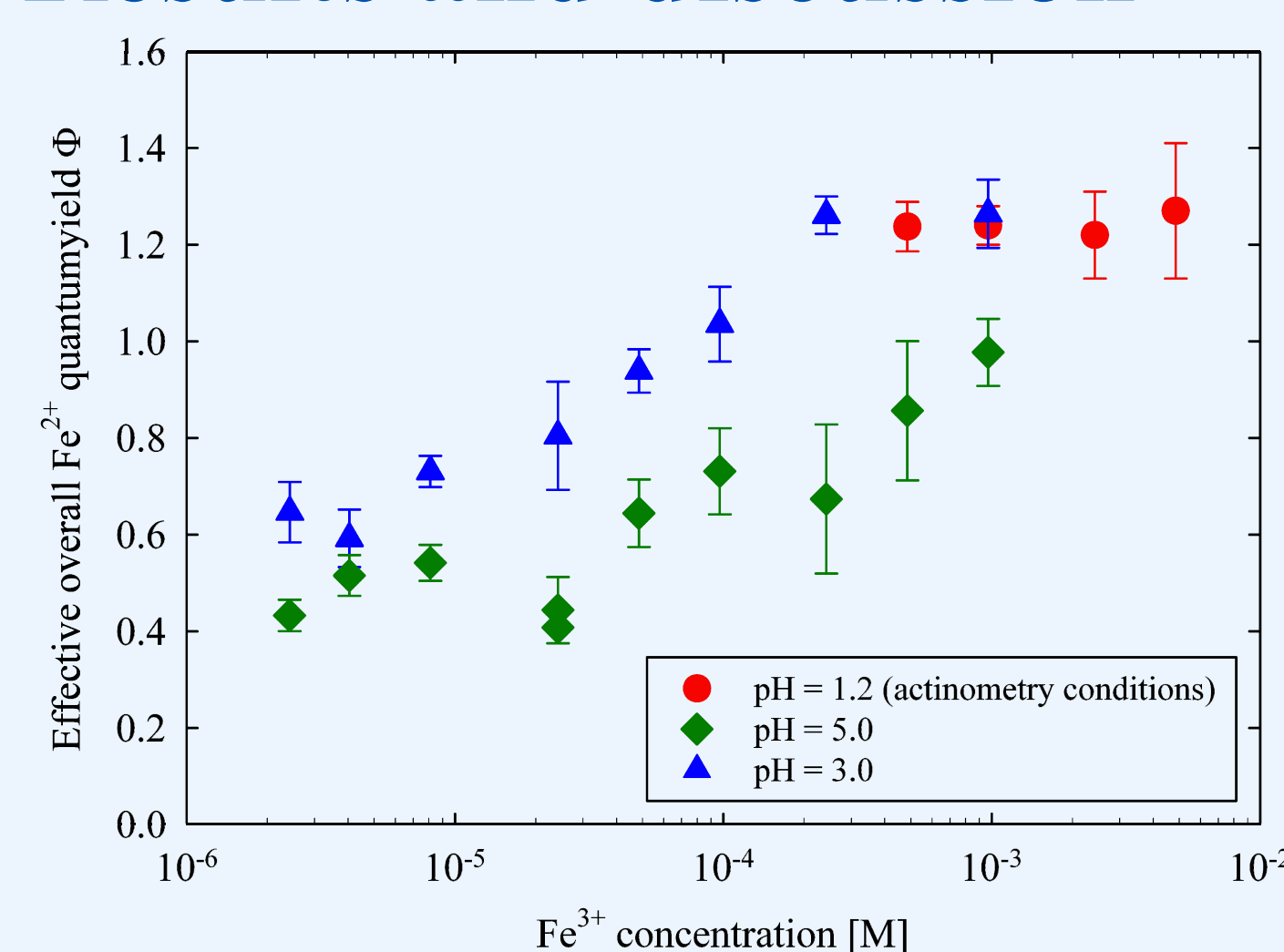
Photochemistry of Fe-oxalato complexes: Concentration dependence

From $6 \cdot 10^{-3}$ down to $5 \cdot 10^{-4}$ M and also at higher concentrations the overall quantum yield is independent of the initial Fe^{3+} concentration in agreement with other studies (Hatchard and Parker 1956, Nicodem 1983). In and above millimolar concentrations the Fe-oxalate system is reliably used as chemical actinometer. But there is a marked concentration dependence below $5 \cdot 10^{-4}$ M.

Two $CO_2^{-\cdot}$ can be produced per photon (see Fig. 1), one reacts instantly with Fe^{3+}, yields one Fe^{2+} and the other can subsequently react:

1. with another Fe^{3+} (secondary thermal reduction), yielding more Fe^{2+}, or

2. with itself, traces of oxygen

Lowering the concentration of Fe^{3+} could make reaction path 1. less effective (decrease of Φ) until the point where it is completely shut down and the overall quantum yield remains low.

Figure 2: Dependence of overall Fe^{2+} quantum yield on initial Fe^{3+} concentration, Fe-oxalato flash photolysis at 308 nm, Fe:Ox = 1:10, Ar purged

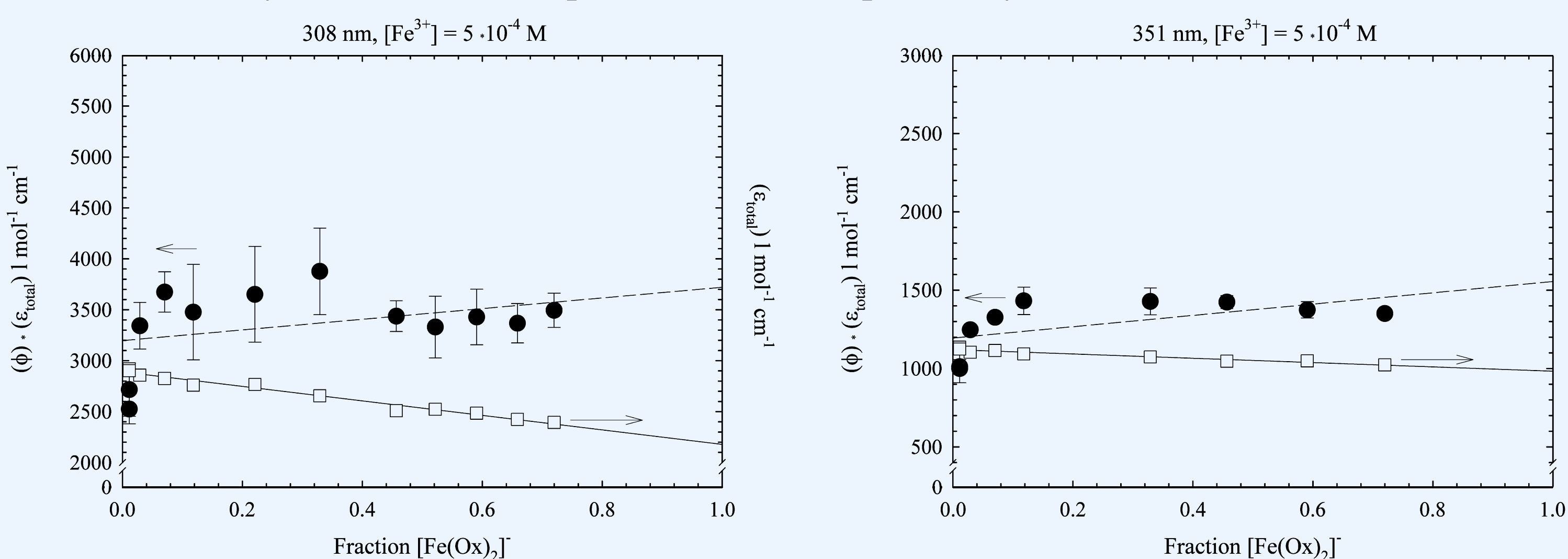### Photochemistry of Fe-oxalato complexes: Individual quantum yields

Figure 3: Product of overall quantum yields (Φ) and overall extinction coefficients (ε_{total}) of $[FeOx_2]^-$ and $[FeOx_3]^{3-}$ mixtures as a function of calculated $[FeOx_2]^-$, laser flash photolysis @ 308 and 351 nm, Ar purged

- Correlation of ε_{total} with $[FeOx_2]^-$ (Fig.3) and isosbestic point in Fig.4 indicate the correct species distribution
- Measured $\Phi \cdot \varepsilon_{total}$ do not correlate well with $[FeOx_2]^-$, the quantum yield seems mostly independent of $[FeOx_2]^-$ but shows a marked decline at a $[FeOx_2]^-$ content smaller than 5% at both photolysis wavelengths 308 and 351 nm
- Therefore it is concluded that the individual quantum yield contribution from the $[FeOx_3]^{3-}$ species must be lower than that of $[FeOx_2]^-$
- Because the solutions on the leftmost side of the plot are clearly dominated by $[FeOx_3]^{3-}$ with 99% bound iron, these individual quantum yields are assigned to $[FeOx_3]^{3-}$: $\Phi_{308nm} = 0.93 \pm 0.09$; $\Phi_{351nm} = 0.88 \pm 0.08$
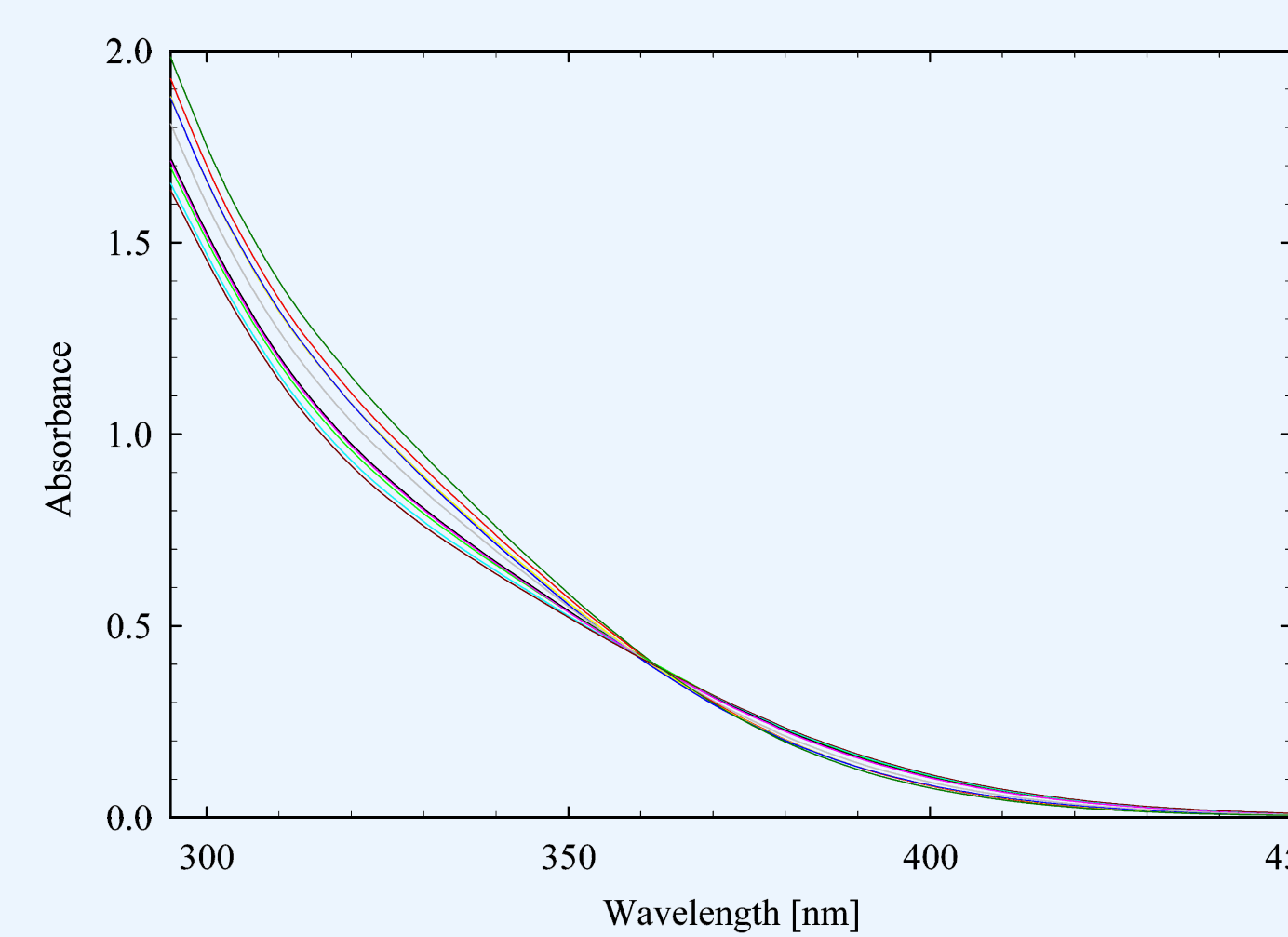
Figure 4: Absorption spectra of solutions with $FeOx_2$ and $FeOx_3$ species in different ratios, Fe:Ox = 1:3 - 1:10; pH = 2.4 − 5; I = 0.01 M; isosbestic point at 362 nm

- Usually a straight line with a clear left and right intercept is expected, from which the individual Φ could be calculated
- Reasons for the nonlinear behavior of the product of Φ and ε_{total} are suspected to be the complex secondary radical reactions that take place after photoexcitation:
  - (i) It is likely that both $[FeOx_2]$ and $[FeOx_3]$ have a different initial photoreactivity
  - (ii) $[FeOx_2]$ and $[FeOx_3]$ have different redox potentials which would affect the reaction rate of the reducing radical $CO_2^{-\cdot}$ with them and contribute differently to the overall quantum yield
- $E^0(CO_2^{-\cdot}) = -1.85$ V (Surdhar 1989); according to (Bard 1985) the E^0 of solutions containing a lower excess of oxalate is higher (0.035 V) than in solutions dominated clearly by $[FeOx_3]^{3-}$ where $E^0 = 0.005$ V → Reaction of $CO_2^{-\cdot}$ with $[FeOx_2]^-$ should be favored
- Effects possibly counteract each other, influence of other unspecified side reactions possible

Photochemistry of Fe-carboxylato complexes

Table 1: Effective overall quantum yields of carboxylic acid iron-complexes obtained from excimer laser flash photolysis

System with Fe^{3+}	Φ attributed to individual complex (species contains > 95% Fe^{3+})	Effective overall Fe^{2+} quantum yield Φ			
		308 nm		351 nm	
		atm O_2	Ar	atm O_2	Ar
malonic acid[1]	$[Fe-(malonato)_2]^-$	0.024 ± 0.001	-	0.040 ± 0.003	-
tartronic acid	$[Fe-(tartronato)_2]^-$	0.79 ± 0.02	0.90 ± 0.02	0.78 ± 0.06	0.88 ± 0.02
succinic acid[2]	mixed species (1:1; 1:2)	0.24 ± 0.02	0.23 ± 0.02	0.16 ± 0.02	0.19 ± 0.02
tartaric acid	$[Fe-(tartrato)_2]^-$	0.62 ± 0.08	0.63 ± 0.09	0.75 ± 0.05	0.87 ± 0.02
	$[Fe-(tartrato)]^+$	0.60 ± 0.07	0.63 ± 0.07	0.57 ± 0.02	0.58 ± 0.02
glutaric acid	$[Fe-(glutarato)_2]^-$	0.021 ± 0.001	-	0.017 ± 0.002	-
pyruvic acid	$[Fe-(pyruvato)]^{2+}$	0.47 ± 0.07	0.63 ± 0.07	0.64 ± 0.02	0.76 ± 0.07
glyoxylic acid	$[Fe-(glyoxalato)_2]^-$	0.76 ± 0.05	1.21 ± 0.05	0.77 ± 0.06	1.06 ± 0.11
gluconic acid	$[Fe-(OH)_3(gluconato)_2]^{2-}$	0.076 ± 0.003	-	0.10 ± 0.03	-

366 nm (literature), Ar: [1] $\Phi = 0.027$ (Faust & Zepp 1993); [2] $\Phi = 0.13$ (Abrahamson 1994)

- The quantum yields can differ up to one order of magnitude among different ligands.
- Higher quantum yields with ligands that have keto-groups (glyoxalate, pyruvate) compared to the other carboxylic acids
- In all cases $\Phi_{argon} > \Phi_{oxygen}$ → indicates the dependence of most Φ on secondary reactions involving reducing radicals
- In case of malonic, glutaric, tartronic, tartaric, pyruvic, gluconic and glyoxalic acid the quantum yields could be attributed to individual complexes with known stoichiometry whereas the value for succinic acid was measured in a mixture of complexes
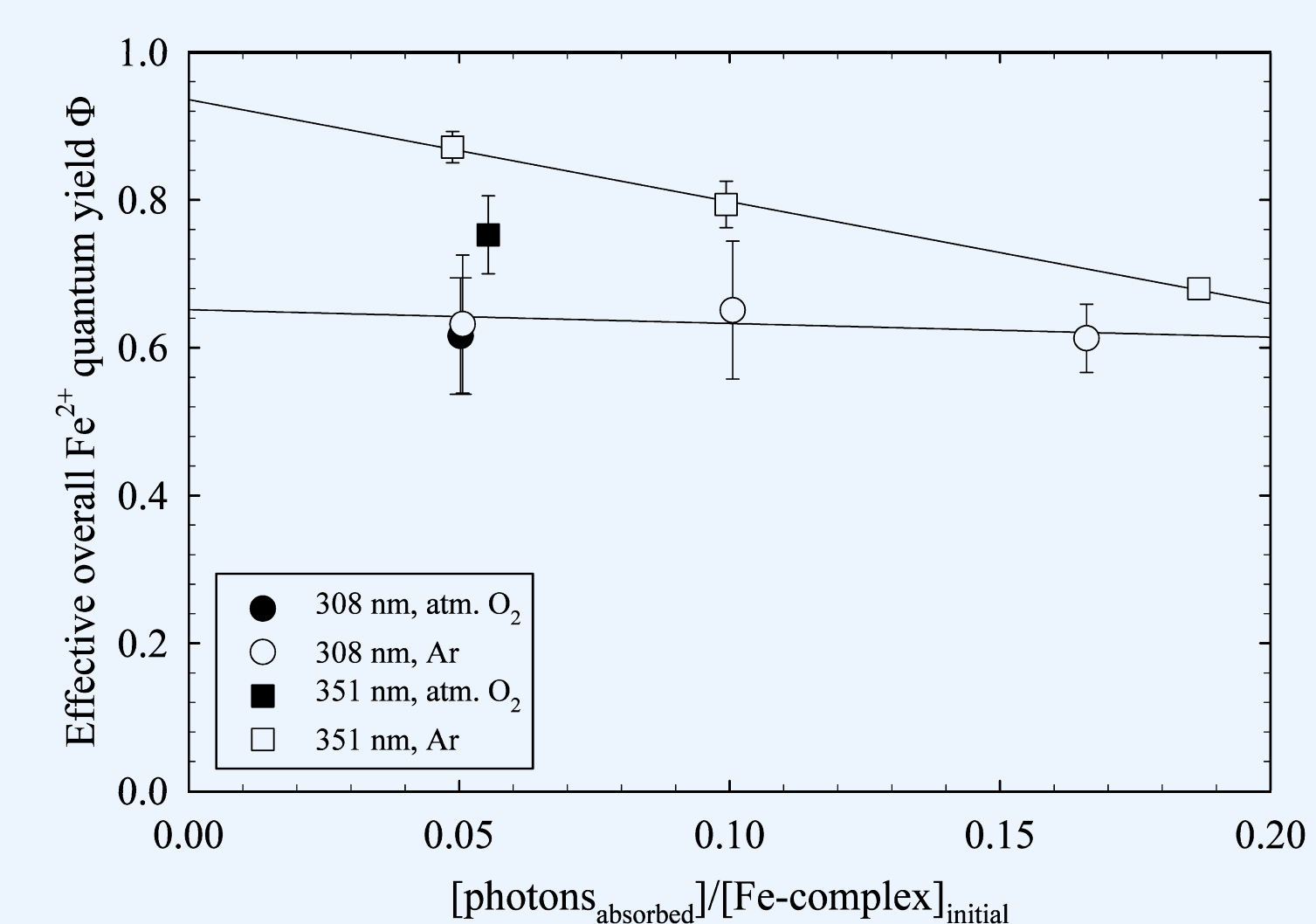

Figure 5: Wavelength & energy dependence of quantum yields $[Fe-(tartrato)_2]^-$ complex photolysis

- $[Fe-(tartrato)_2]^-$ Quantum yields are higher at 351 nm compared to 308 nm (Fig.5)
- Furthermore they are insensitive to dissolved oxygen at 308 nm and are not affected by a change in excitation energy
- The opposite is the case at 351 nm where a dependence on dissolved oxygen and excitation energy is seen
- This indicates a different reaction mechanism after excitation at different wavelengths
- For comparison (see Table 1) the quantum yields of the 1:1 Fe-tartrato complex are similar to those of the 1:2 complex at 308 nm and invariable with respect to dissolved oxygen and wavelength

- Values for Fe-malonato and succinato complexes at 308 and 351 nm are in the same range compared to literature values at 366 nm (Tab. 1).

Conclusions and Outlook

- Quantum yields of atmospherically relevant carboxylic acid complexes with iron other than oxalic are sufficiently high to play a role
- In atmospheric aqueous systems always mixture of suitable ligands → most likely formation of mixed ligand complexes, but studies on speciation needed
- In dilute solutions of Fe-oxalate (cloud water!) not all off the produced carboxyl radicals might ultimately lead to reduction of Fe(III)-species, this is important for the reduced iron budget
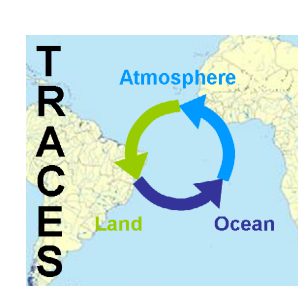
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