Photolysis of iron(III)-organic complexes in cloud droplets and deliquescent particles

Christian Weller and Hartmut Herrmann

Leibniz-Institut für Troposphärenforschung, Permoserstr. 15, 04318 Leipzig, Germany (weller@tropos.de)

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-oxalato 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.

Values for Fe-oxalato complex quantum yields quite scattered in the literature (Fig. 2). All reported Fe-oxalato quantum yields are overall yields, they include secondary reactions (Fig. 1), no primary quantum yields are reported. Other ligands than oxalate might be also interesting, which implies a need for further laboratory investigations.
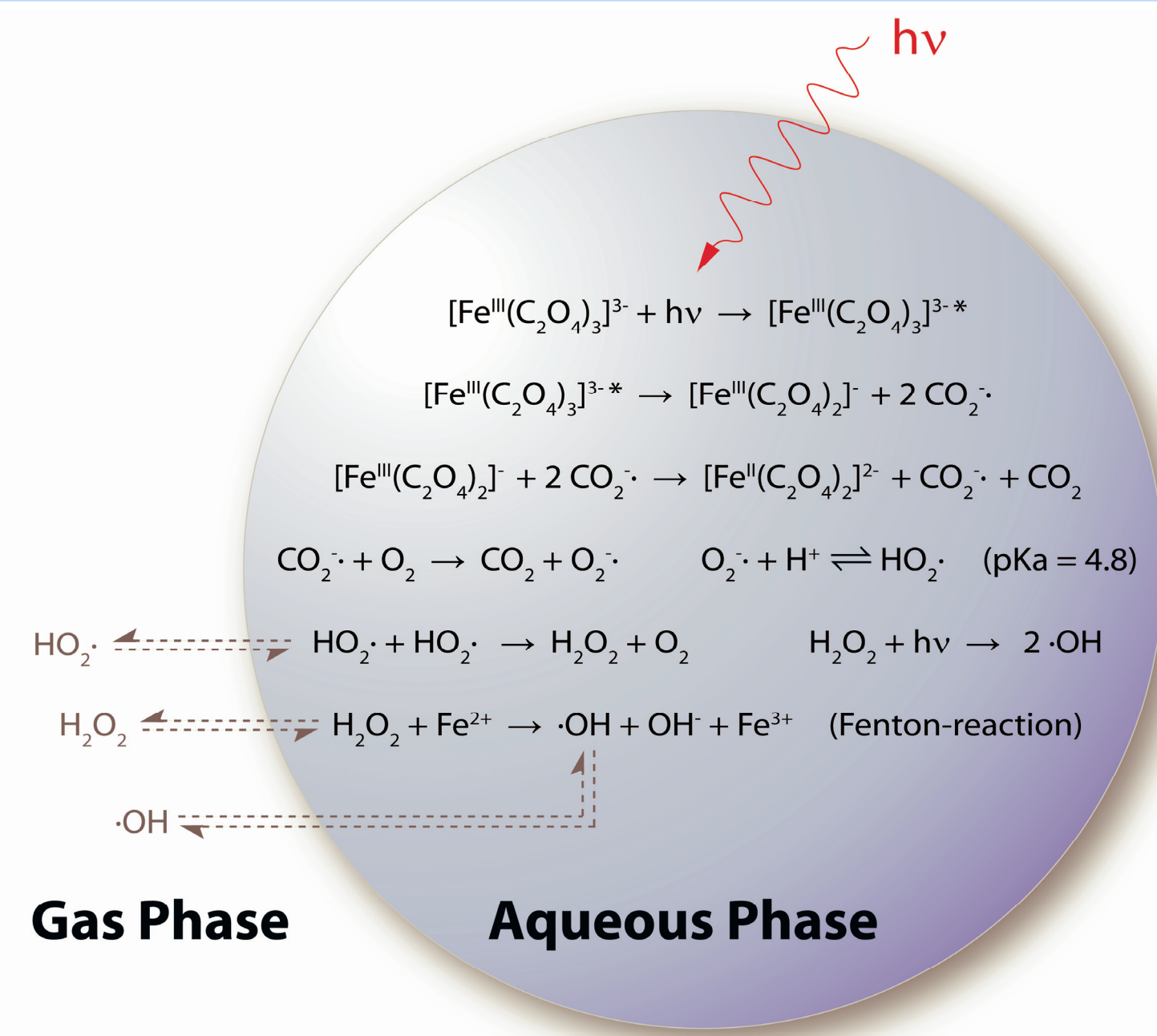

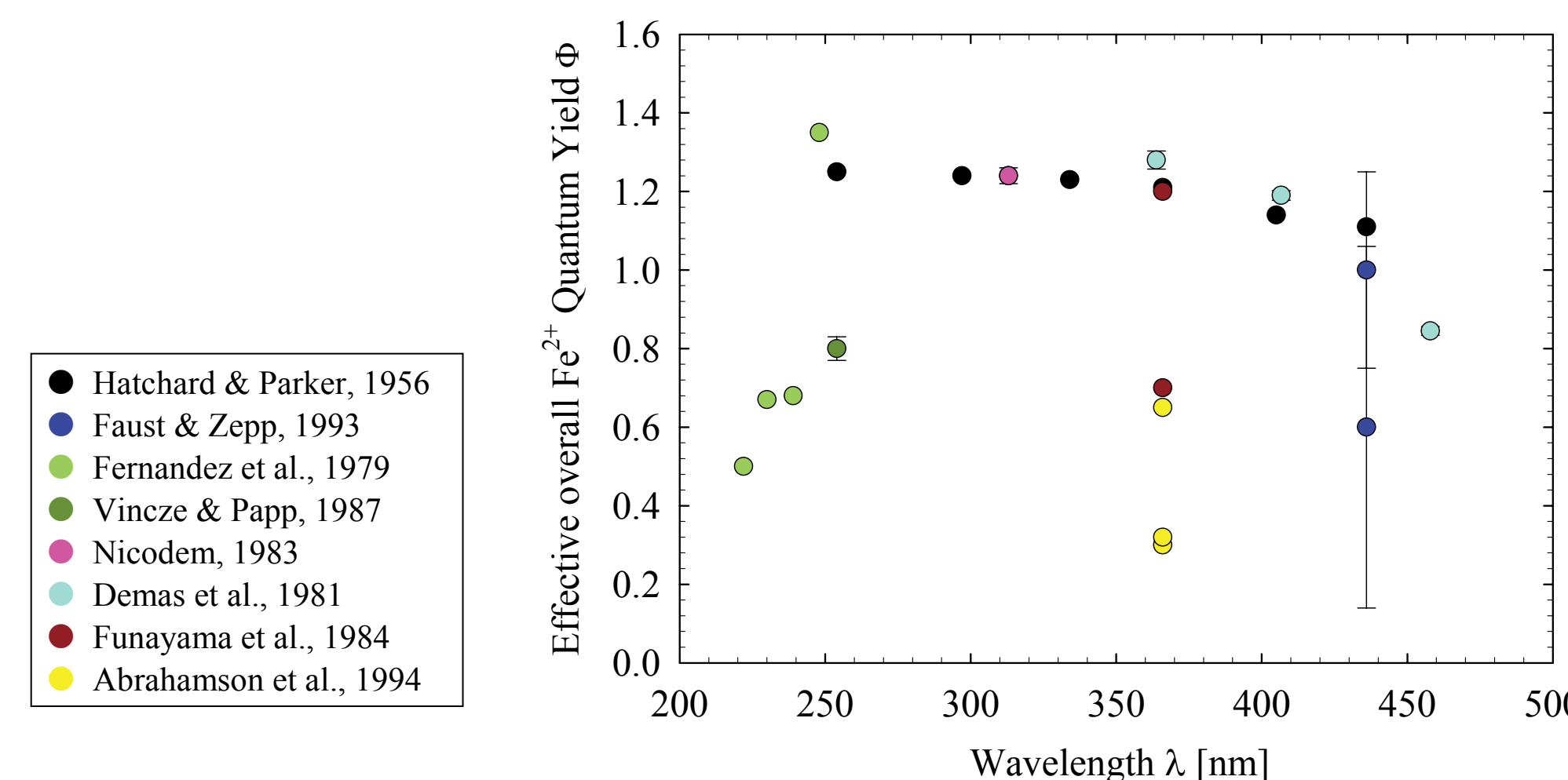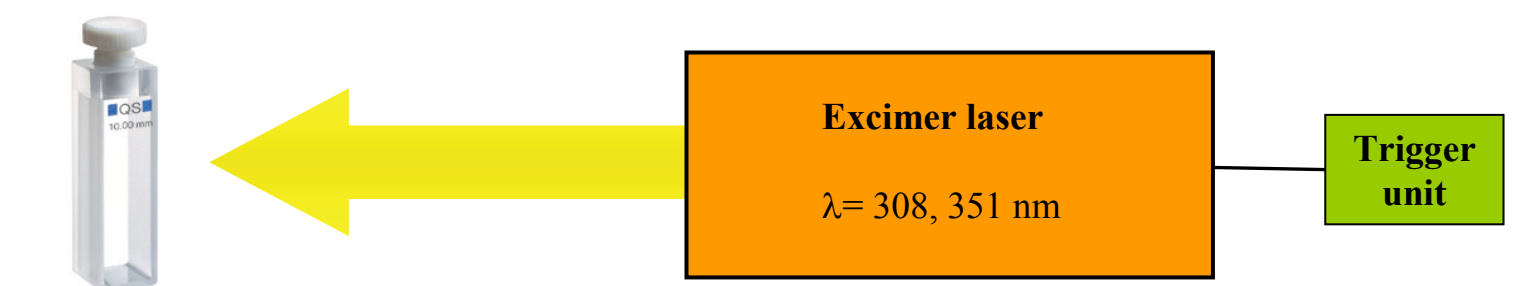**Figure 1:** Photolysis of Fe(III)-oxalato complex as example, including subsequent reactions

Figure 2: Literature overview of Fe-oxalato quantum yields
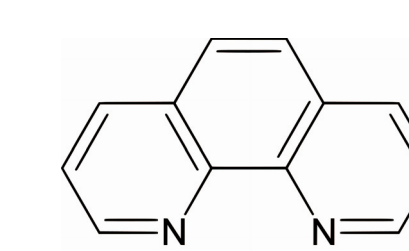
Experimental

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
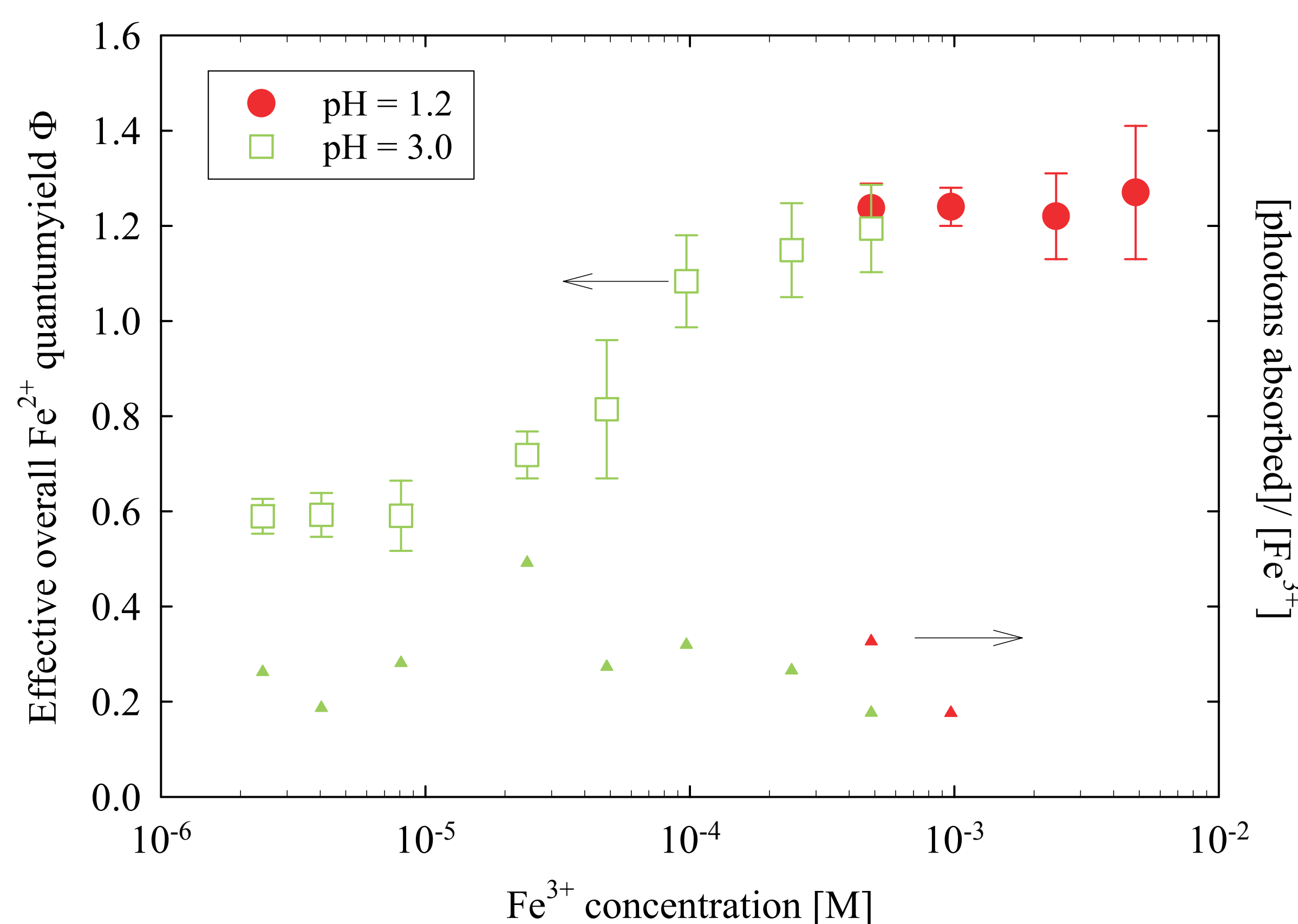
Photochemistry of Fe-oxalato complexes

Figure 3: Dependence of overall Fe^{2+} quantum yield on initial Fe^{3+} concentration, Fe-oxalato flash photolysis at 308 nm, pH = 3, Fe:Ox = 1:10, triangles show ratio of absorbed photons to $[Fe^{3+}]$

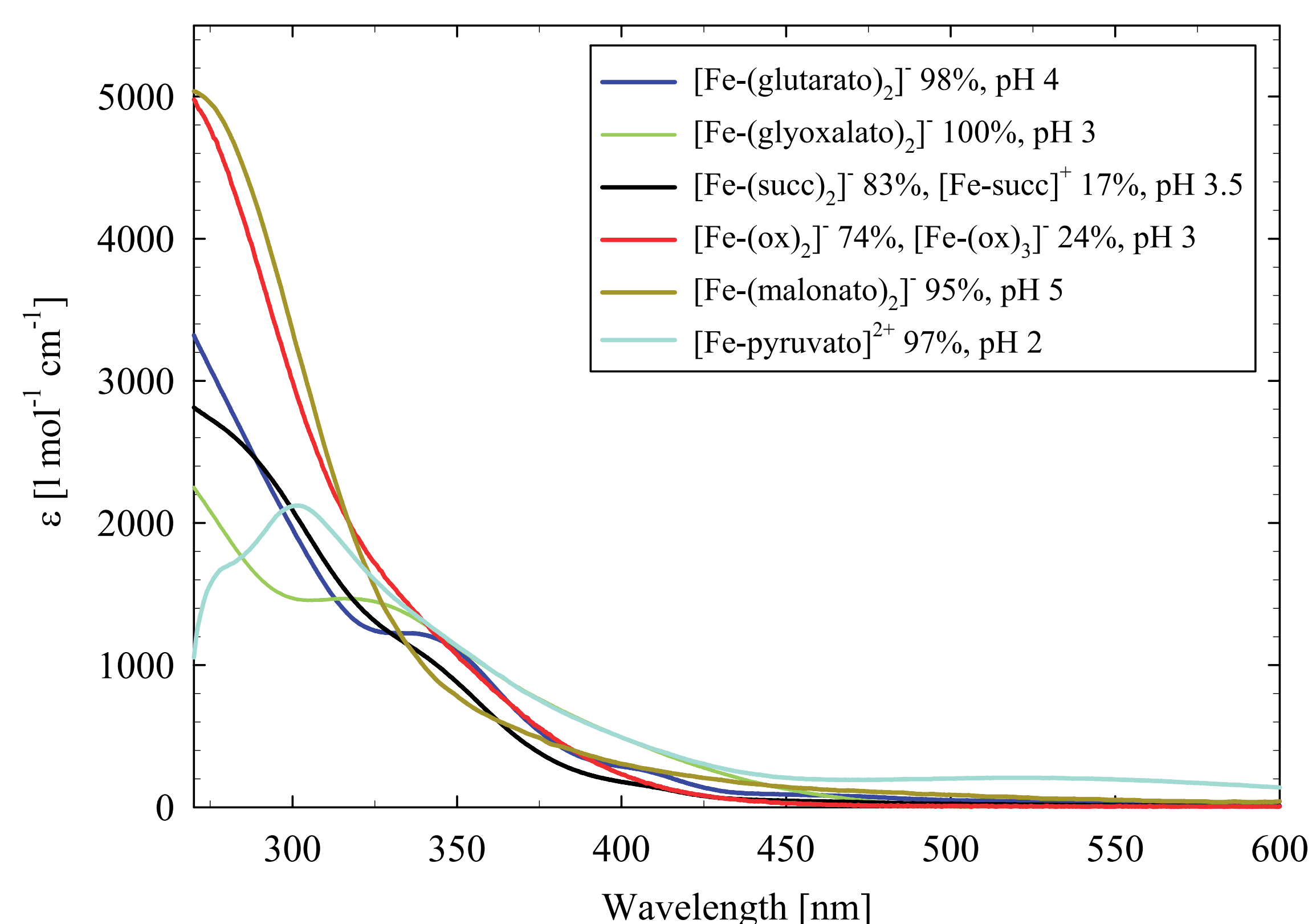**Photochemistry of Fe-carboxylato complexes**

Figure 4: UV-VIS absorption spectra of carboxylic acid iron-complexes, composition of experimental solution

Extinction coefficients for Fe-carboxylato complexes are in a similar range (Fig. 4). The Fe-pyruvato complex has highest extinction coefficients in the visible range.

Quantum yield measurements in the literature are scarce, 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). The quantum yields can differ up to one order of magnitude among different ligands. Higher quantum yields are measured with ligands that have keto-groups (glyoxalate, pyruvate) compared to the other carboxylic acids with the exception of oxalate.

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 Fe3+ concentration in agreement with other studies (Hatchard and Parker 1956, Nicodem 1983). In and above milimolar concentrations the Fe-oxalate system is reliably used as chemical actinomter. 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^{III}, yields one Fe^{2+} and the other can subsequently react:

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

2. with itself, traces of oxygen, impurities in the solution

Lowering the concentration of Fe^{III} 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 constant at ~ 0.6. The fact that the lower limit is 0.6 (~ half of quantum yield at high concentrations) supports this explanation.

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	Effective overall quantum yield Φ		
		308 nm	351 nm	366 nm (literature)
malonic acid	$[Fe-(malonato)_2]^-$	0.023 ± 0.01	(0.09) n = 2	0.027 (Faust and Zepp 1993)
succinic acid	mixed	0.17 ± 0.01	0.18 ± 0.01	0.13 (Abrahamson 1994)
glutaric acid	$[Fe-(glutarato)_2]^-$	0.023 ± 0.001	-	-
pyruvic acid	$[Fe-(pyruvato)]^{2+}$	0.28 ± 0.03	0.42 ± 0.02	-
glyoxalic acid	$[Fe-(glyoxalato)_2]^-$	0.46 ± 0.02	0.55 ± 0.01	-

In case of malonic, glutaric, pyruvic 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 (solution composition given in legend of Fig. 4). No difference in quantum yields between 308 and 351 nm is noticed with succinic acid but values of malonic, pyruvic and glyoxalic acid are higher at 351 nm, this might be due to a difference in the electronic transitions at higher wavelengths.

Conclusions and Outlook

- 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

- Quantum yields of atmospherically relevant carboxylic acid complexes with iron other than oxalic are sufficiently high to play a role
- Out of the investigated compounds, $[Fe-(glyoxalate)_n]^m$ complexes have the highest stability constants and high quantum yields → hot candidate
- In atmospheric aqueous systems always mixture of suitable ligands → most likely formation of mixed ligand complexes, but studies on speciation needed

References

Abrahamson et al. (1994) *Inorg. Chim. Acta, 226*, 117-127
Demas et al. (1981) *J. Phys. Chem., 85* (19), 2766
Faust & Zepp (1993) *Environ. Sci. Technol., 27*, 2517-2522
Fernandez et al. (1979) *J.Photochem., 11*, 69
Funayama et al. (1984) *Kag. Kog. Ron., 10* (4), 534
Hatchard & Parker (1956) *Proc. R. Soc. Lond., Ser. A, 235*, 518
Nicodem (1983) *J. Photochem., 21* (3), 189
Vincze & Papp (1987) *J. Photochem., 36* (3), 289

Acknowledgements