PAUL SCHERRER INSTITUT

L. Iezzi , M. Reza, H. Finkenzeller , A. Roose ,T. Bartels-Rausch, R. Volkamer and M. Ammann

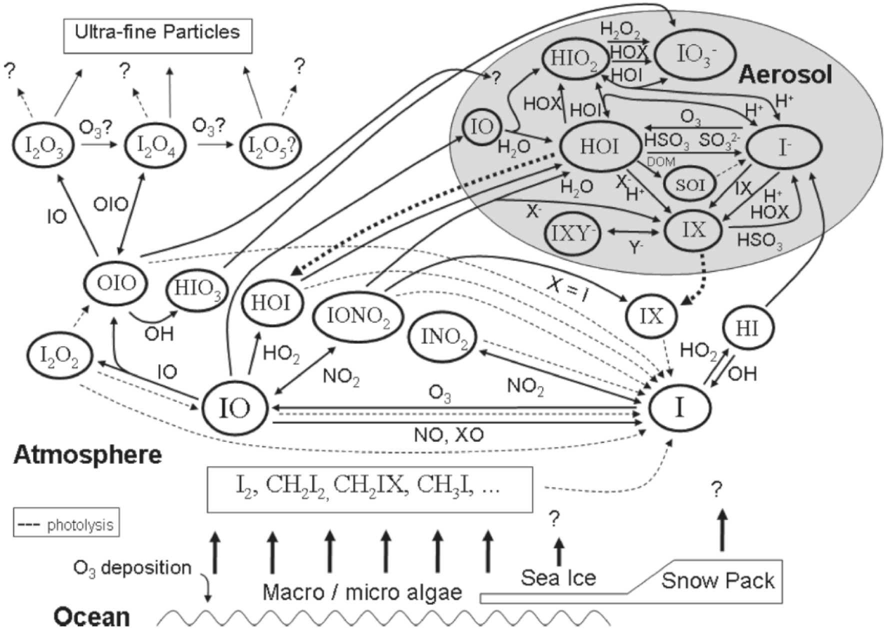
Iron(III)-carboxylate photochemistry induces iodate reduction

23.05.2022, EGU general assembly AS3.12, Halogens in the Troposphere

Iodine chemistry

Why Iodine?

Troposphere



Saiz-Lopez et al. 2012

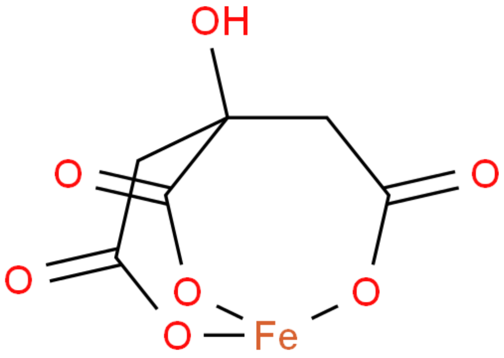
- Global important **sink for O_3**
- **lowers** the **HO_2/OH** radical ratio
- **enhances** the **NO_2/NO** ratio
- affects **Hg deposition**
- take part in **new particle formation**

Saiz-Lopez et al. 2012

- **Link** between **carbonyl compounds, ROS** and **iodine chemistry**
- Observed **ratios of I^-/IO_3^-** in aerosol particles and cloud droplets of the troposphere are **higher than expected**
- Observed **release of $I_{2(g)}$** from dust in the free troposphere

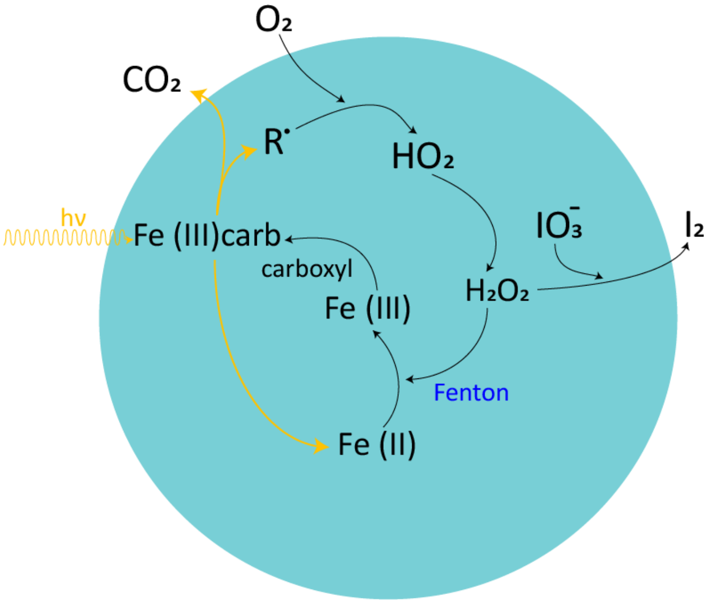
Corral Arroyo et al. 2019, Baker et al. 2021, Koenig et al. 2020, Koenig et al. 2021

Iron(III) carboxylate photochemistry



Fe(III)-citrate (Fe-cit)

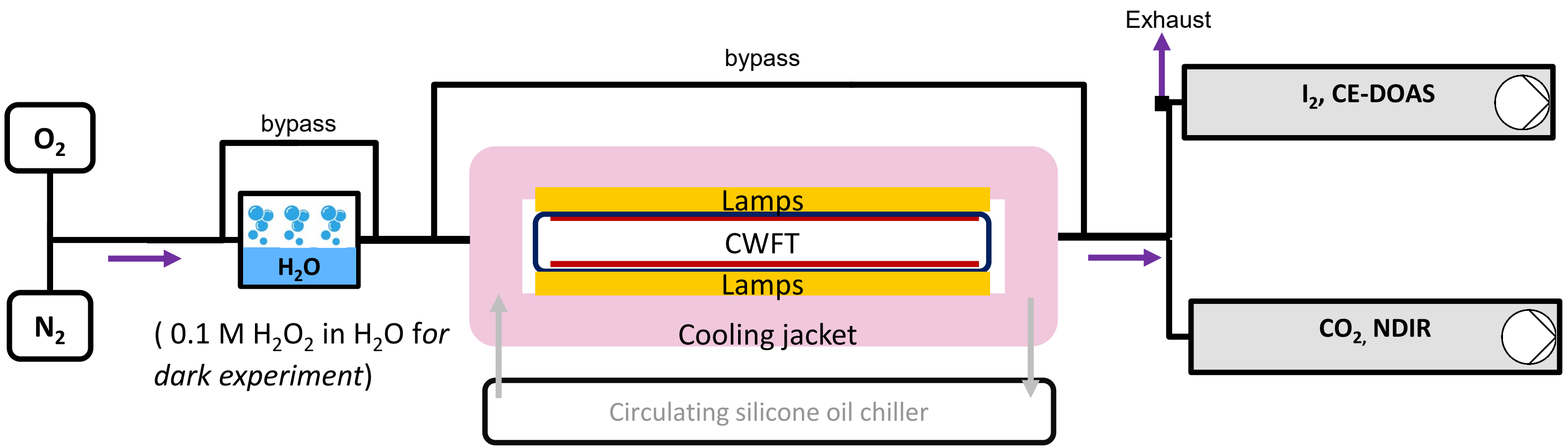
What is the role of Fe(III)-carboxylate photochemistry in the redox chemistry of iodine?



- Iron(III) carboxylate complexes $[Fe^{III}(OOCR)]^{2+}$ are well-known photoactive compounds and their photochemistry in **aqueous aerosol phase** represents:
- the main **sink for carboxylic acids**
- an important **source of** Reactive Oxygen Species (**ROS**)

Deguillaume et al. 2005, Weller et al. 2013

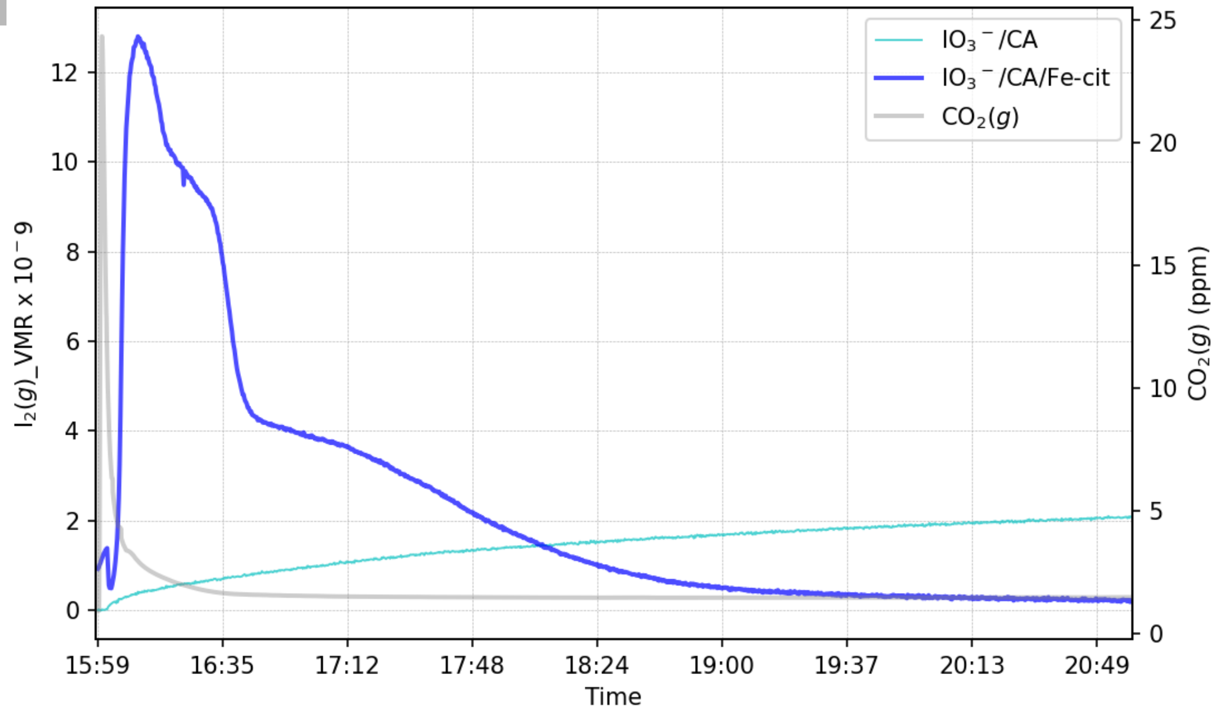
Coated Wall Flow Tube experiments (CWFT)



- RH (%) ≈ 88%
- Coating film: $NaIO_3$/Fe(III)-citrate/Citric Acid 1:10:100

Results_ UV-A light

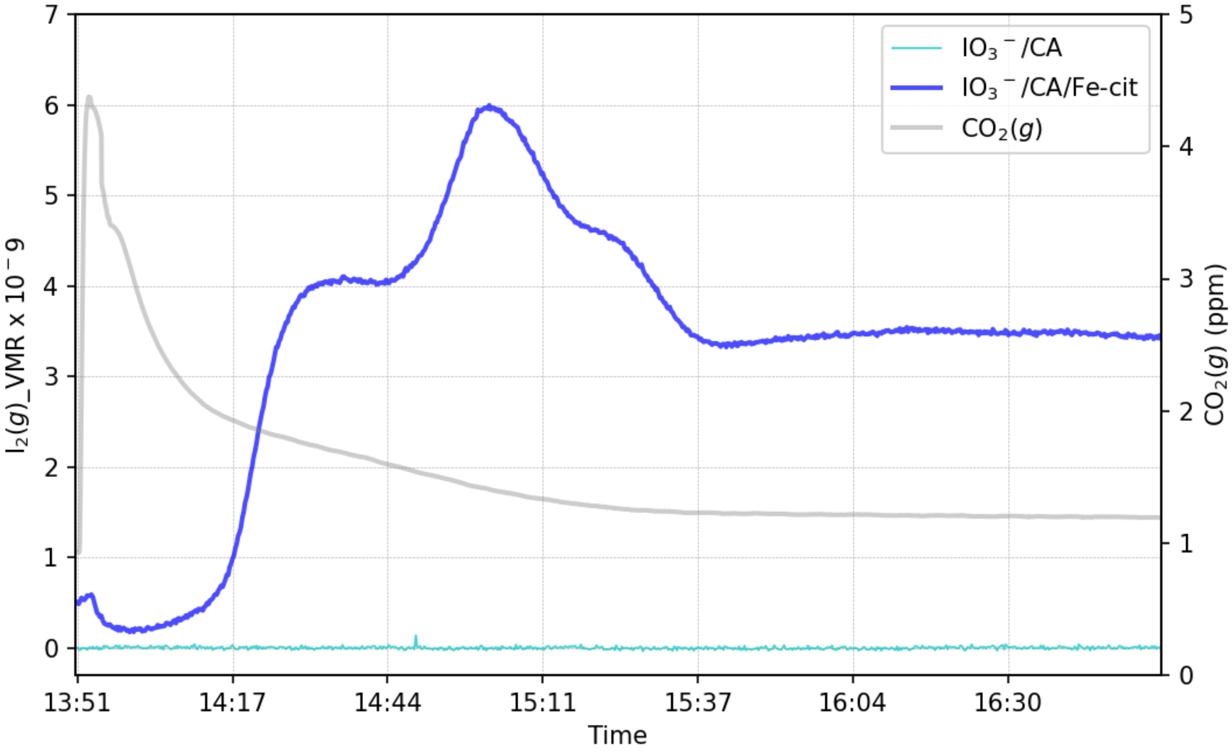
- Evolution of $I_{2\,(g)}$ which is produced in the CWFT upon **UV-A light irradiation**



- $CO_{2(g)}$ measurement to track **Fe-cit photochemistry** due to ligand decarboxylation
- The initial peak of I_2 can be attributed to the complete photolysis of Fe-cit, which leads to high amounts of ROS
- IO_3^-/CA control experiment shows noticeable I_2 production though no known chromophore is present

Results_Visible light

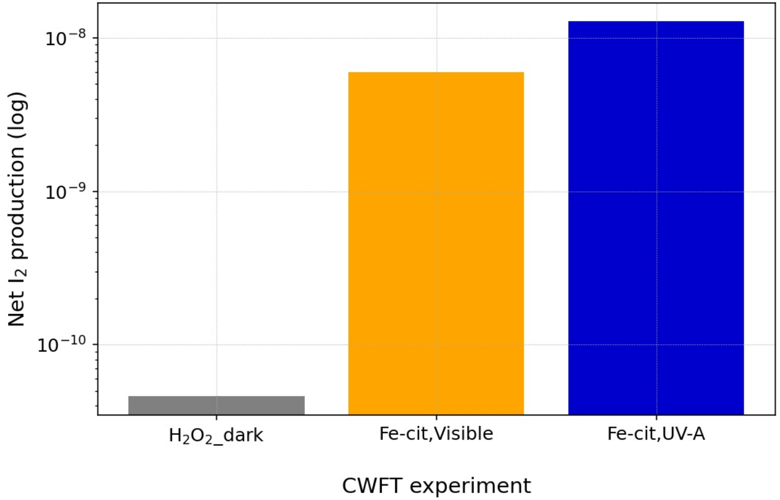
- Evolution of $I_{2\,(g)}$ which is produced in the CWFT upon **Visible light irradiation**

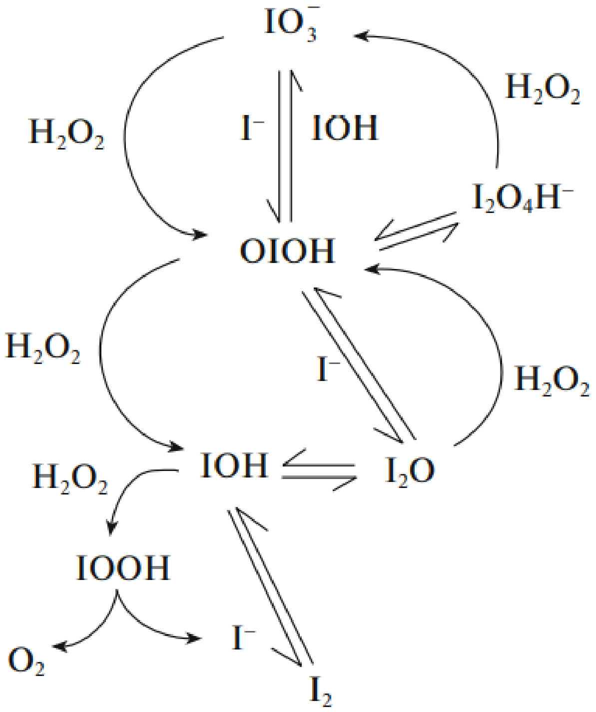


- $CO_{2(g)}$ measurement to track **Fe-cit photochemistry** due to ligand decarboxylation
- Visible light seems to be sufficient to reduce IO_3^- to I_2
- Induction period before I_2 is formed, followed by persistence long term production though photolysis in the visible should occur

Conclusion: take home messages

- Upon both UV-A and Visible irradiation, Fe-cit photochemistry **promotes iodate reduction**
- Time profiles suggest a **complex reductive mechanism**
- **Formation** and **photolysis** of **intermediate species** can occur
- **H_2O_2 is the key species?** Other actors may be relevant





Bray-Liebhafsky mechanism sketch, adapted from Schmitz and Furrow 2016

… model and further experimental studies need to be carried out in order to corroborate this hypothesis.

PAUL SCHERRER INSTITUT

Iron(III) carboxylate photochemistry

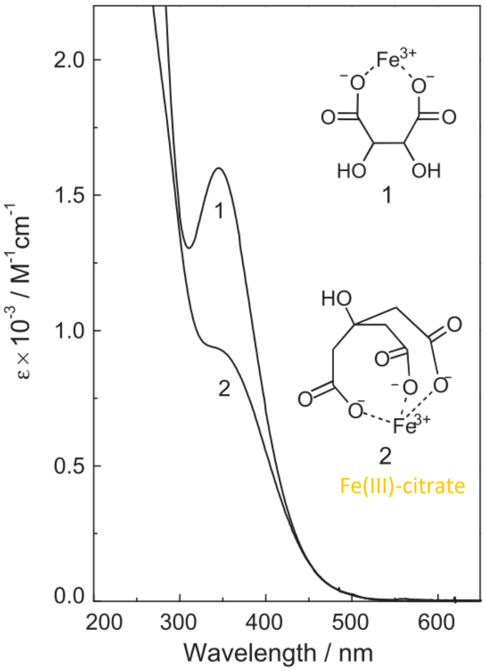


Figure 1. Absorption spectra and chemical structures of Fe(III) complexes with tartaric (1) and citric acids (2).

Pozdnyakov et al. 2012

- Iron(III) carboxylate complexes $[Fe^{III}(OOCR)]^{2+}$ are well-known photoactive compounds and their photochemistry in **aqueous aerosol phase** represents:

- the main **sink for carboxylic acids**

- an important **source of** Reactive Oxygen Species (**ROS**)

Deguillaume et al. 2005, Weller et al. 2013

$$Fe^{III}[(OOCCH_2)_2-C(OH)(OOC)] \xrightarrow{h\nu} Fe^{2+}_{(aq)} + (OOCCH_2)_2^{2-}-C(OH)(COO^\cdot)$$

$$(OOCCH_2)_2^{2-}-C(OH)(COO^\cdot) \rightarrow (OOCCH_2)_2^{2-}-C(OH)^\cdot + CO_2\uparrow$$

ROS

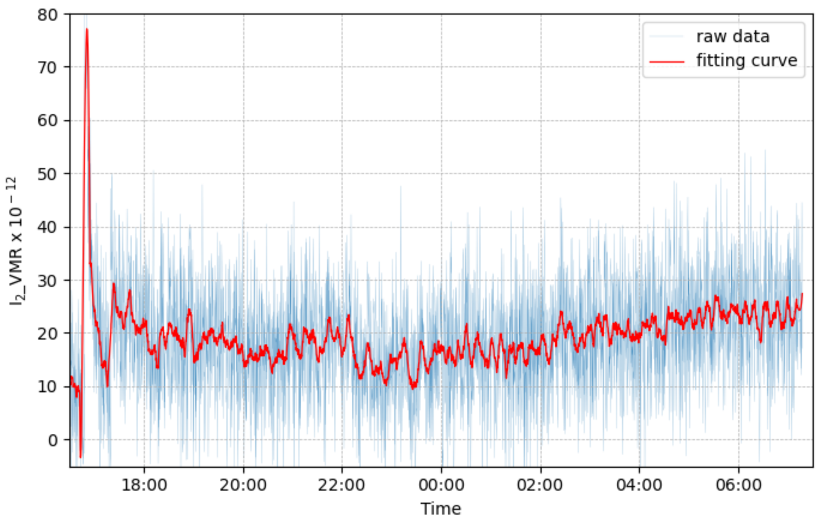
$$(OOCCH_2)_2^{2-}-C(OH)^\cdot + O_2 \rightarrow \boxed{HO_2^\cdot} + (OOCCH_2)_2^{2-}-C=O$$

$$HO_2^\cdot + HO_2^\cdot \rightarrow \boxed{H_2O_2}$$

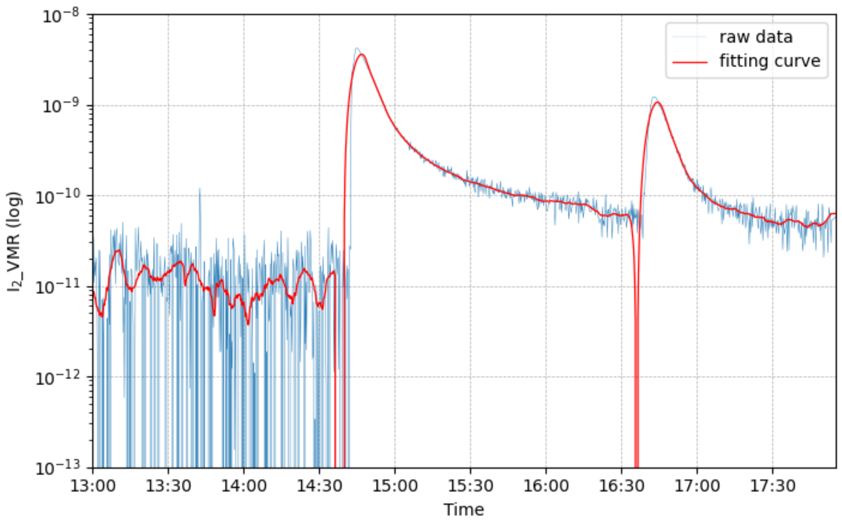
Dou et al. 2021

H2O2_dark_Results

- 23.08



- 10.09

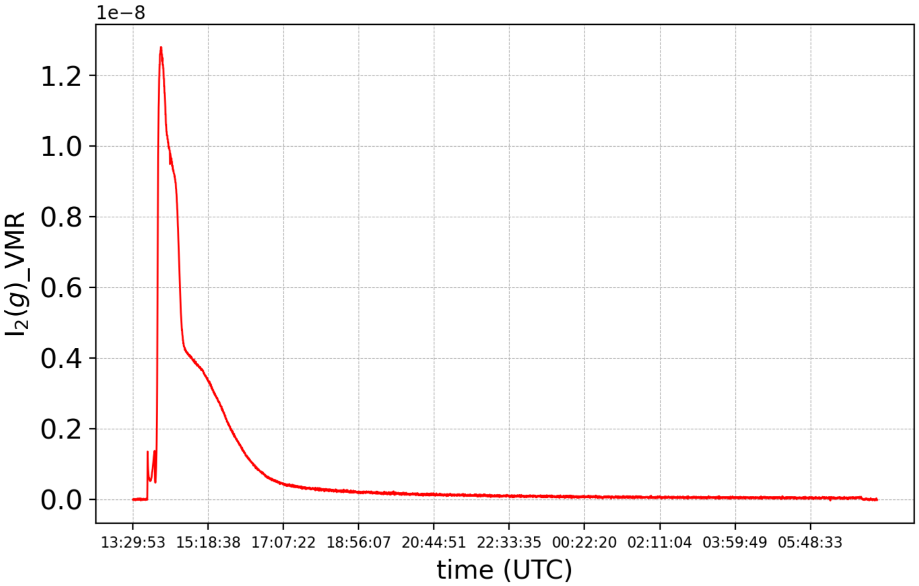


Experimental conditions

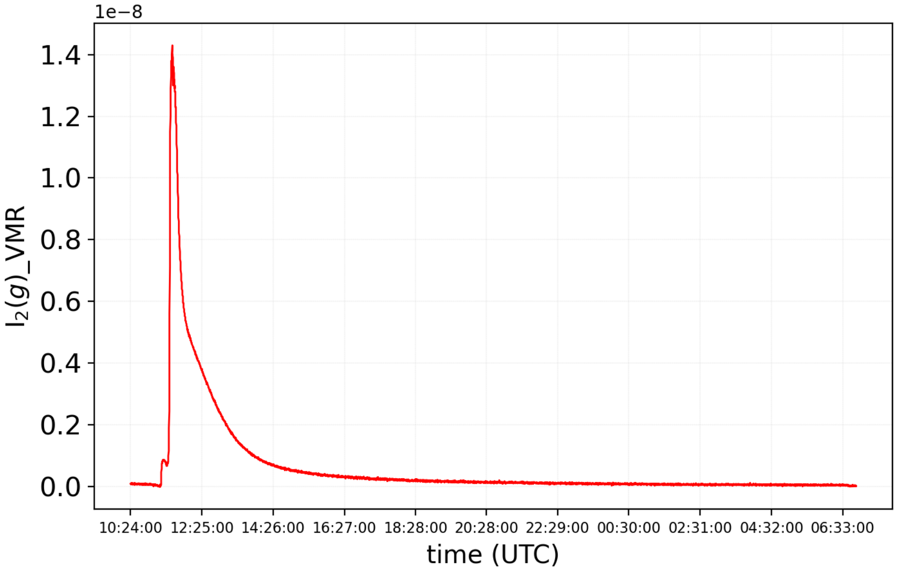
- $NaIO_3$/ Fe-cit/CA (M/M) = (0.001:0.01:0.1)
- Injected solution= 800 µL
- N_2=1 l/min;
- O_2= 0.4 l/min
- RH(%) ~ 88

UV-A light results_with Fe-cit

- 13.09

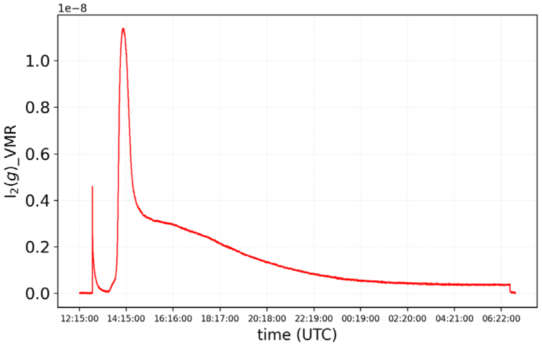


- 31.08

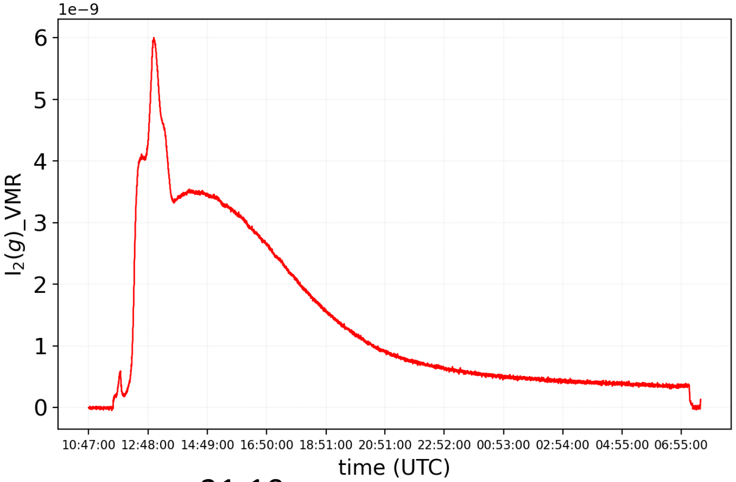


VIS light results_with Fe-cit

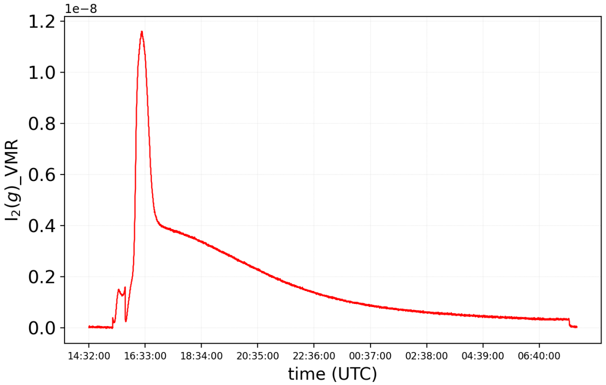
- 30.08



- 14.09

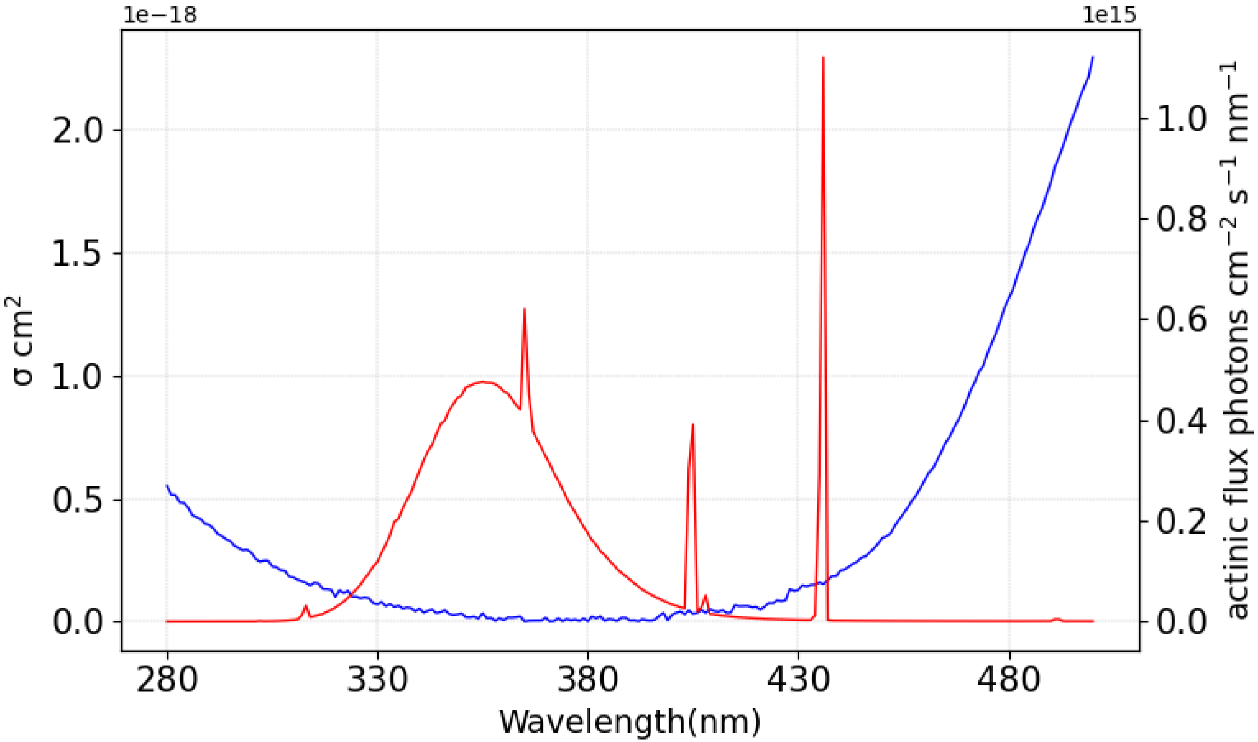


- 21.10



I2_photolysis rate

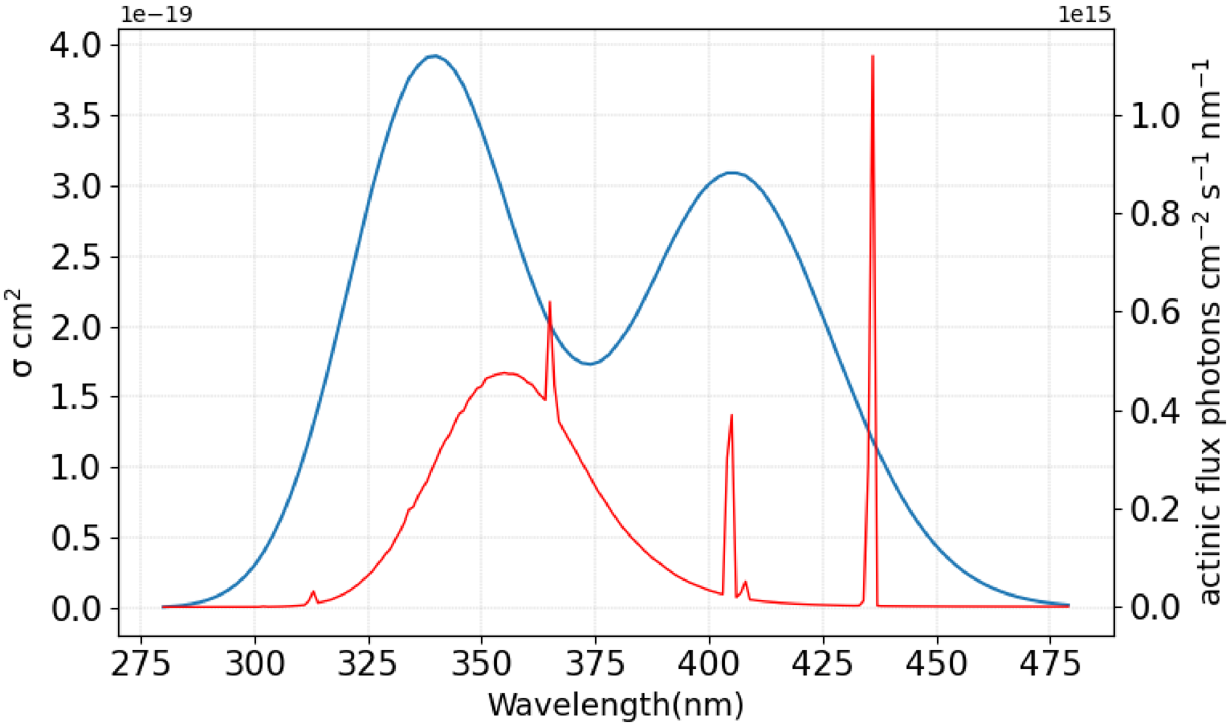
$J_{I_2}=8.61*10^{-4}\ s^{-1}$



http://satellite.mpic.de/spectral_atlas/cross_sections/

I2_photolysis rate

$J_{HOI}=6.03*10^{-3}\ s^{-1}$



http://satellite.mpic.de/spectral_atlas/cross_sections/

Visible lamps spectra