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IO radical yield from iodide oxidation by ozone on aqueous aerosol proxy surfaces

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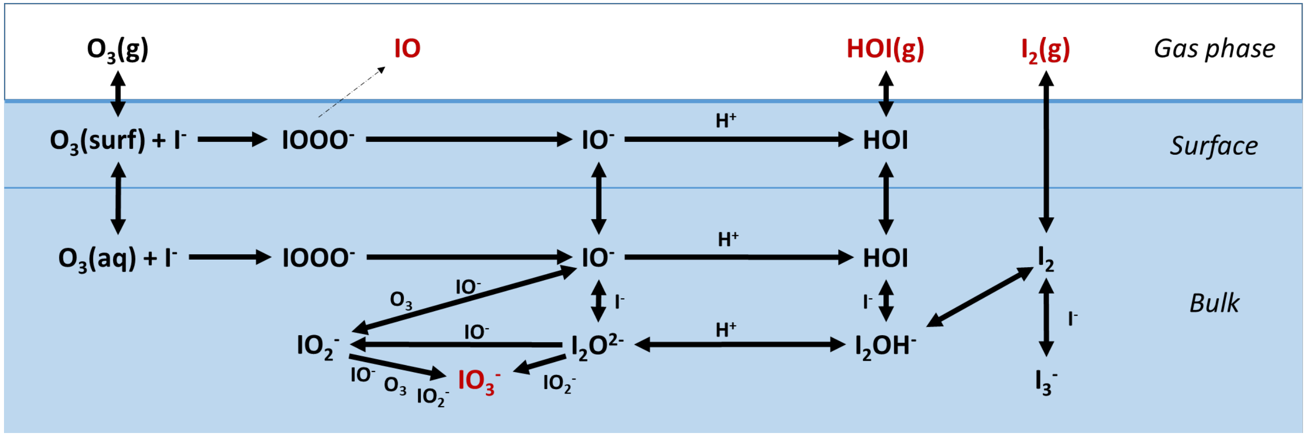
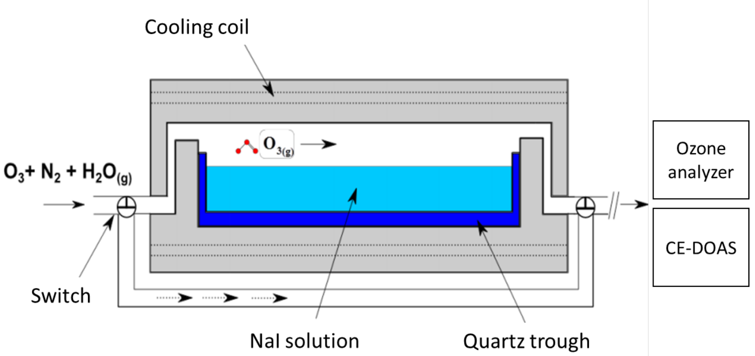
Oxidation of iodide

- Oxidation of iodide by ozone is a major iodine activation pathway at the ocean surface
- Recycling via the gas phase prevents iodine from being fully wet deposited in the troposphere
- Surprisingly large fraction of iodide of total particulate iodine in the troposphere AND the stratosphere
- Large turnover of iodide oxidation by ozone in the aerosol phase
- $I^-(aq) + O_3(aq) + H^+(aq) \rightarrow HOI(aq) + O_2$ $\quad k(298\ K) = 1.2 \times 10^9\ M^{-1}\ s^{-1}$
- Temperature dependence: Magi et al., 1997: 275 K – 293 K, large uncertainty for extrapolations to high solute strength und low temperatures
- IO radical formation demonstrated in one previous study (Sakamoto et al. 2009)



Saiz-Lopez et al., 2012; Carpenter et al., 2013; Sakamoto et al., 2009; Moreno et al., 2020; Koenig et al. 2020; Baker and Yodle, 2021; Koenig et al., 2021

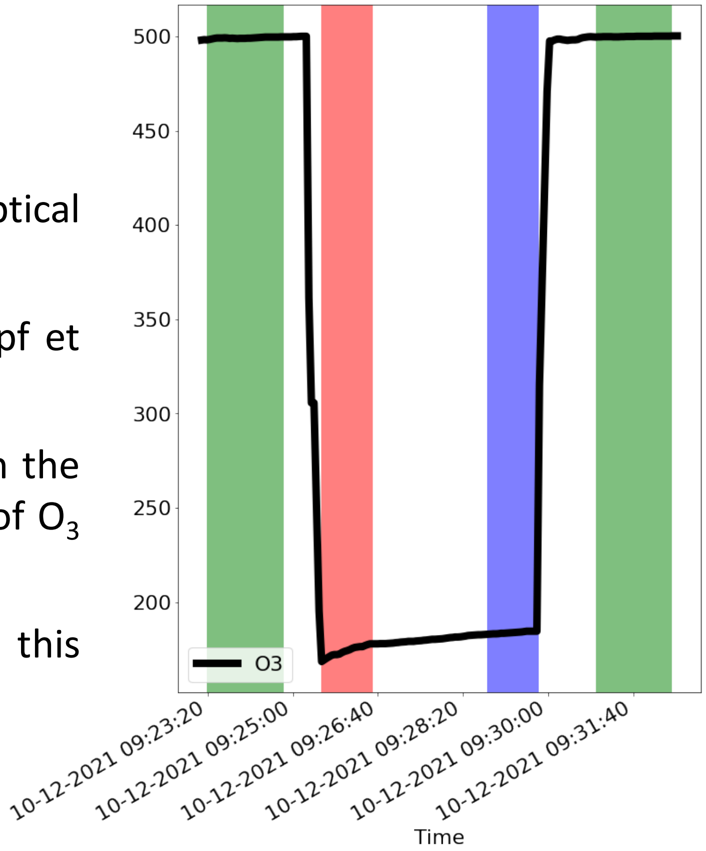
Trough experiment



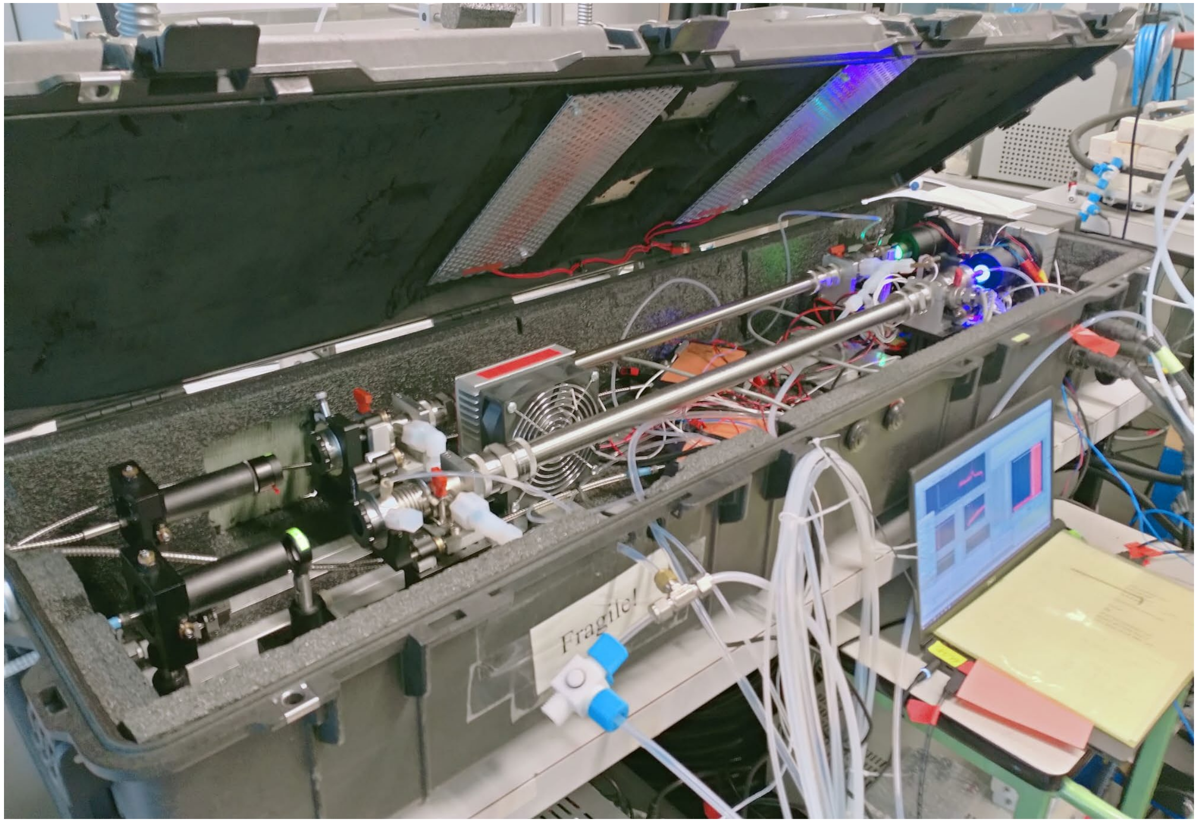
Based on Artiglia et al. 2017

$$\gamma_{X,obs} = \frac{4Q}{\omega_X S_{reactor}} \ln\left(\frac{[bypass]}{[trough]}\right)$$

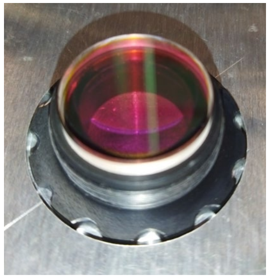
- UC Boulder Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS)
- Gas phase diffusion correction is treated using Knopf et al. (2007) algorithm
- Two different uptakes can be determined, initially in the reacto-diffusive kinetic regime, later a combination of O_3 and iodide diffusion
- The initial uptake coefficient (red) is used for this presentation.

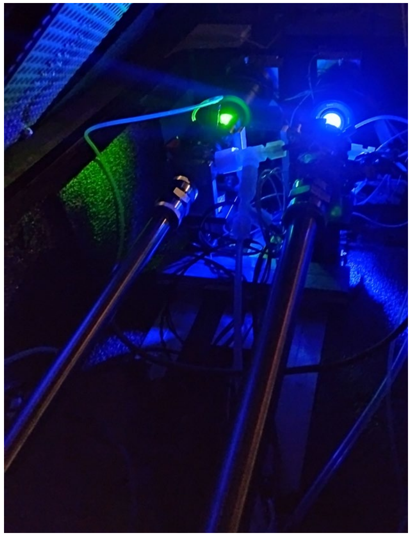


Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS)



UC Boulder CE-DOAS





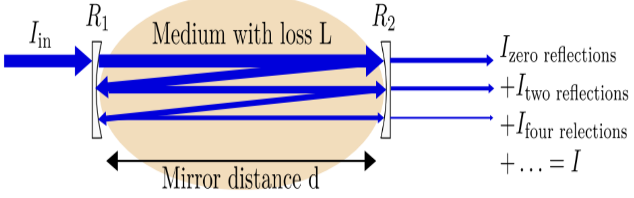


Figure 4.3: *Sketch of the light propagation through a CE-DOAS instrument.*

Dynamics of the reaction at the interface

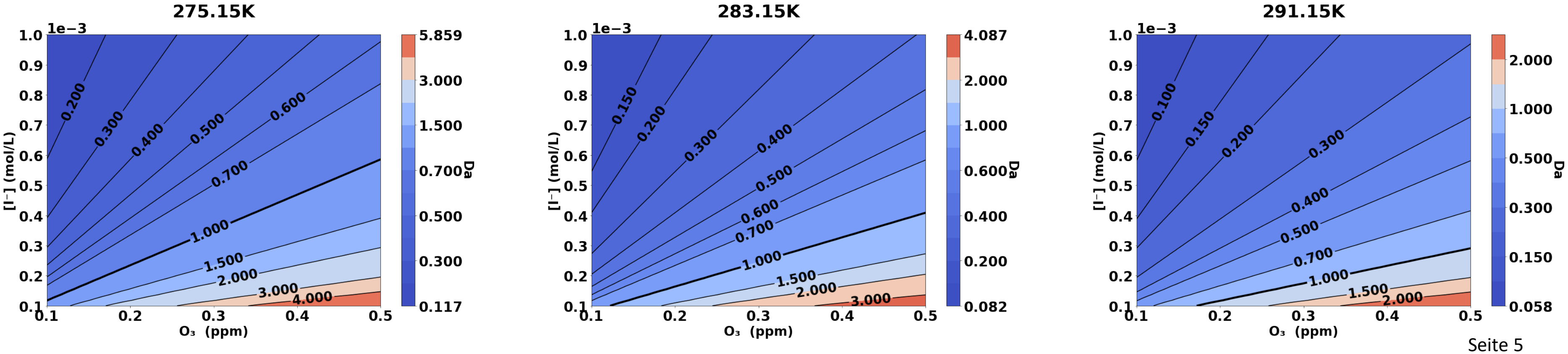
One can assess the liquid phase diffusion limitation by computing the Damköhler number:

$$Da_l = \frac{Reaction\,rate}{Diffusion\,rate} = \frac{\gamma_{O_3,theory}\,\omega_{O_3}[O_3]_g h_{film}}{4[I^-]_{ss} N_A D_{b,I^-}}$$

This number remaining below one for the majority of the experiments indicates that the diffusion limitation remains acceptable.

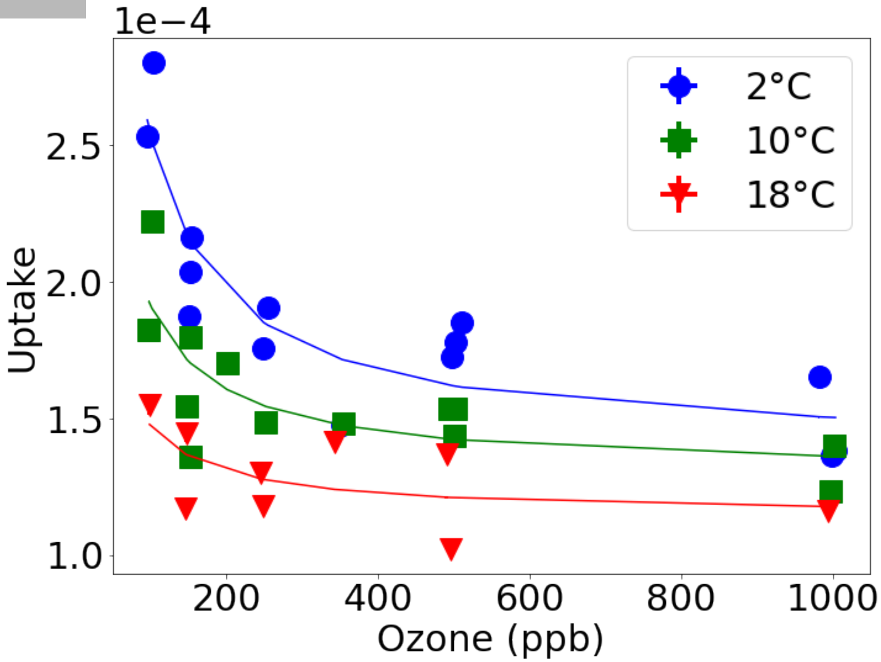
However we may still be affected by a slow supply of iodide from deeper layer. We therefore only use initial uptake values for further analysis.

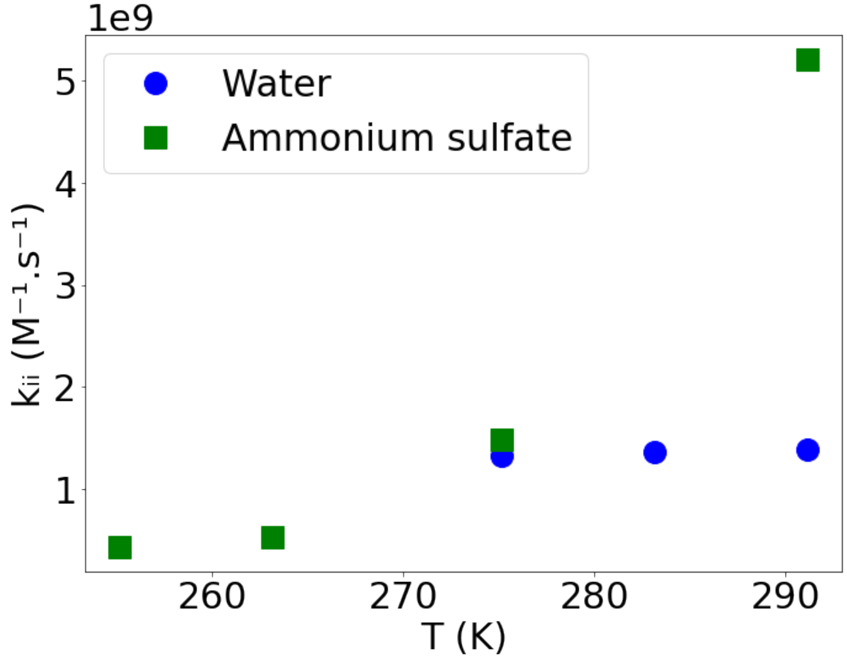
At lower T, the liquid phase diffusion limitation becomes stronger.



Surface process dominating ozone loss

$$\gamma_{X,obs} = \Gamma_b + \Gamma_s = \frac{4H_X RT}{\omega_X}\sqrt{D_{b,X}[Y]_{aq}k_b^{II}} + \frac{4k_s[Y]_s K_{Lang} N_{max}}{\omega_X\left(1 + K_{Lang}[X]_g\right)}$$





For water (preliminary!!):

$$K_{Lang}(M^{-1}) = 1.75 \times 10^{-2} \exp\left(\frac{58.1(kJ/mol)}{RT}\right),$$

$$k_{II}(M^{-1}.s^{-1}) = 3.02 \times 10^{9} \exp\left(\frac{-1.88(kJ/mol)}{RT}\right)$$

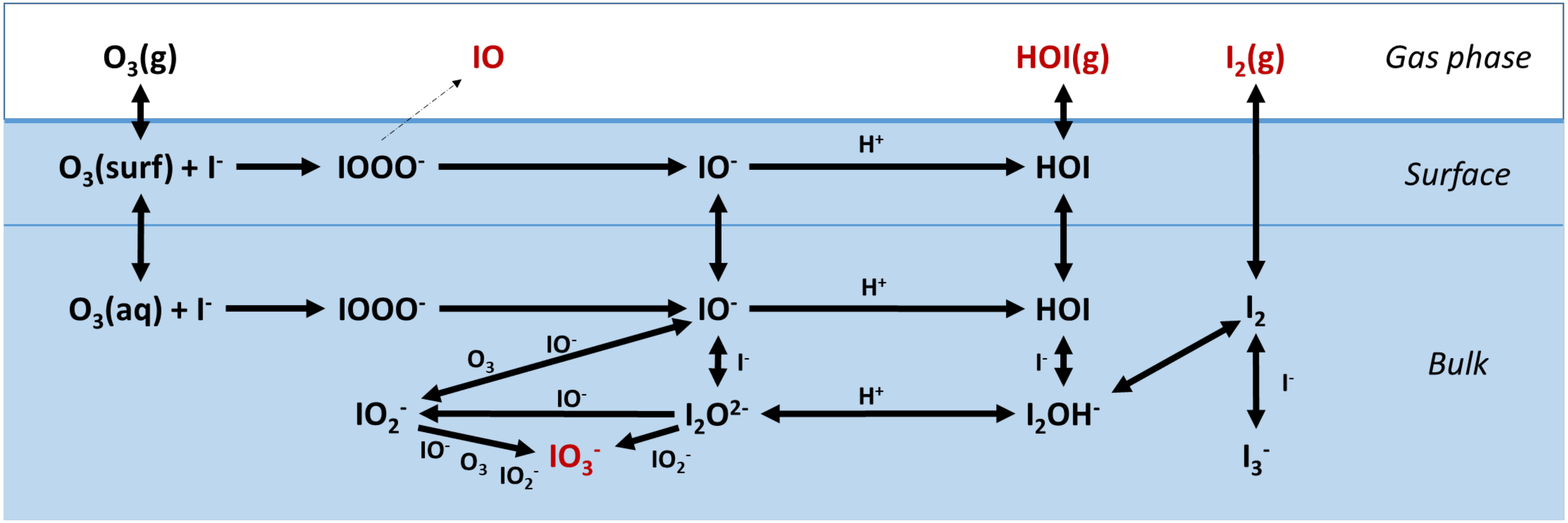
A pathway to IO radical formation?

Sakamoto et al. 2009 proposed a mechanism that leads to IO radical formation at the surface:

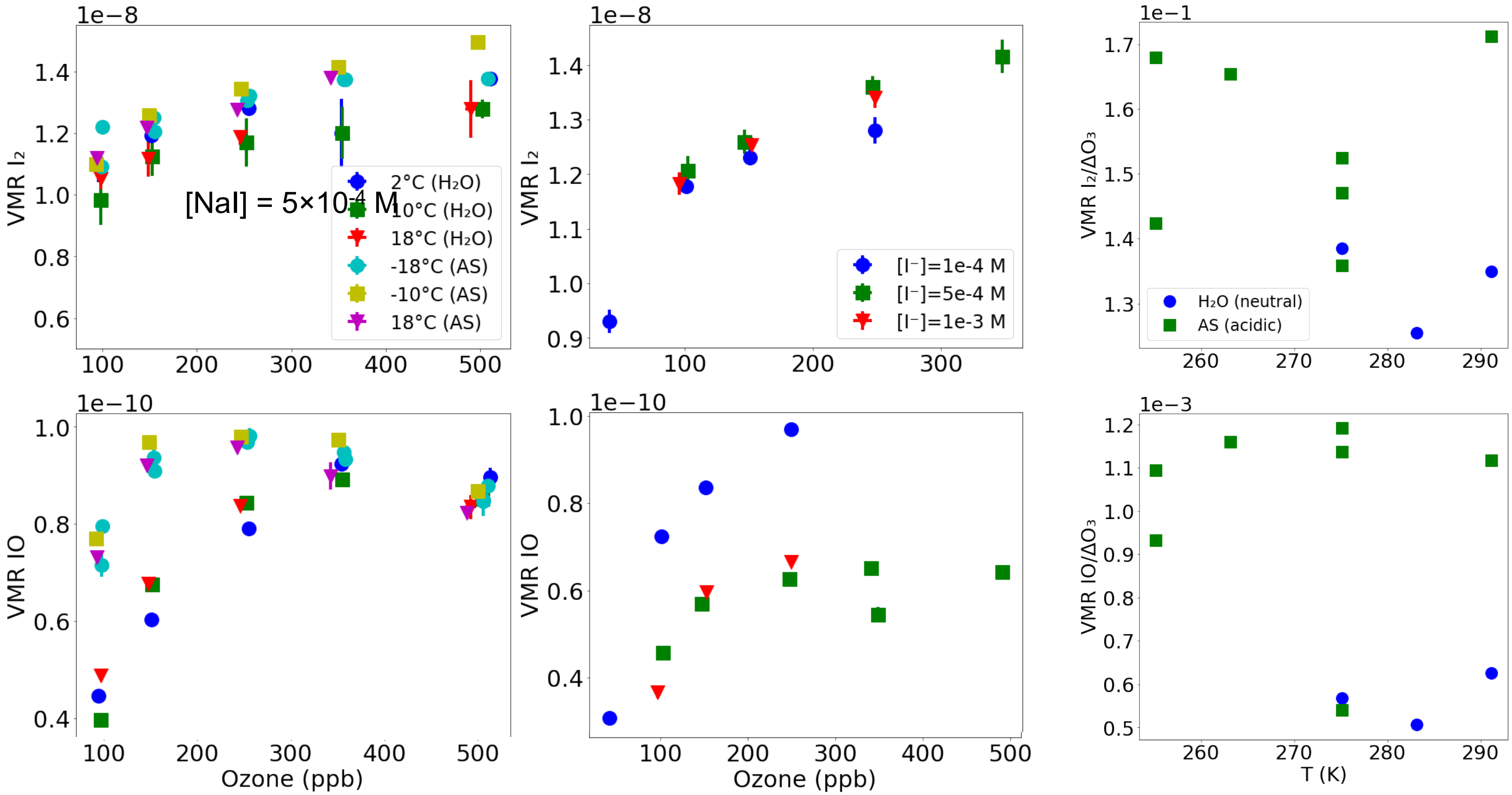
1. I_2(g) and IO(g), are released ([I_2(g)] > 100[IO(g)]) during the heterogeneous reaction of O_3(g) with KI(aq)

2. IO(g) yields are independent of bulk pH between 2 and 11, whereas I_2(g) production is markedly enhanced at pH < 4

3. I_2(g) and IO(g) produced are directly proportional to [KI(aq)] up to 5 mM

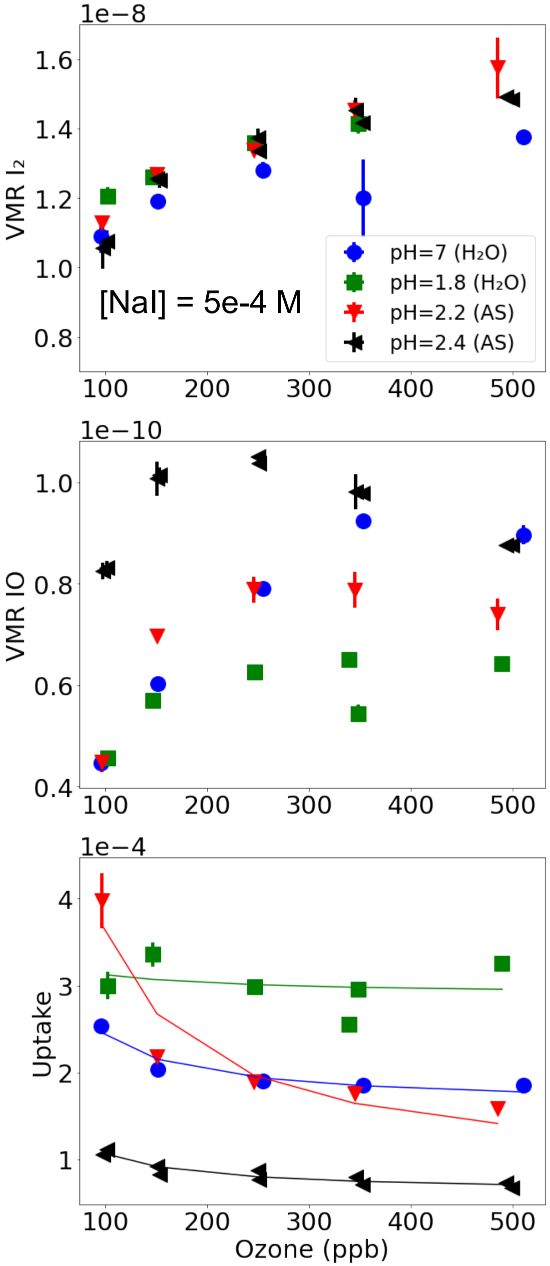


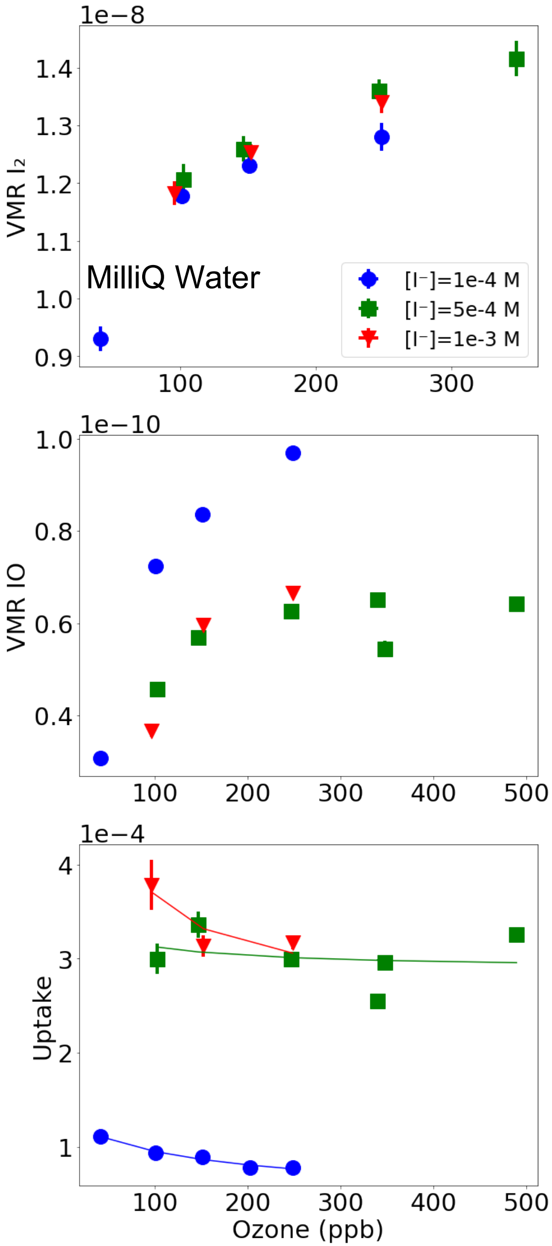
IO radical formation observed !

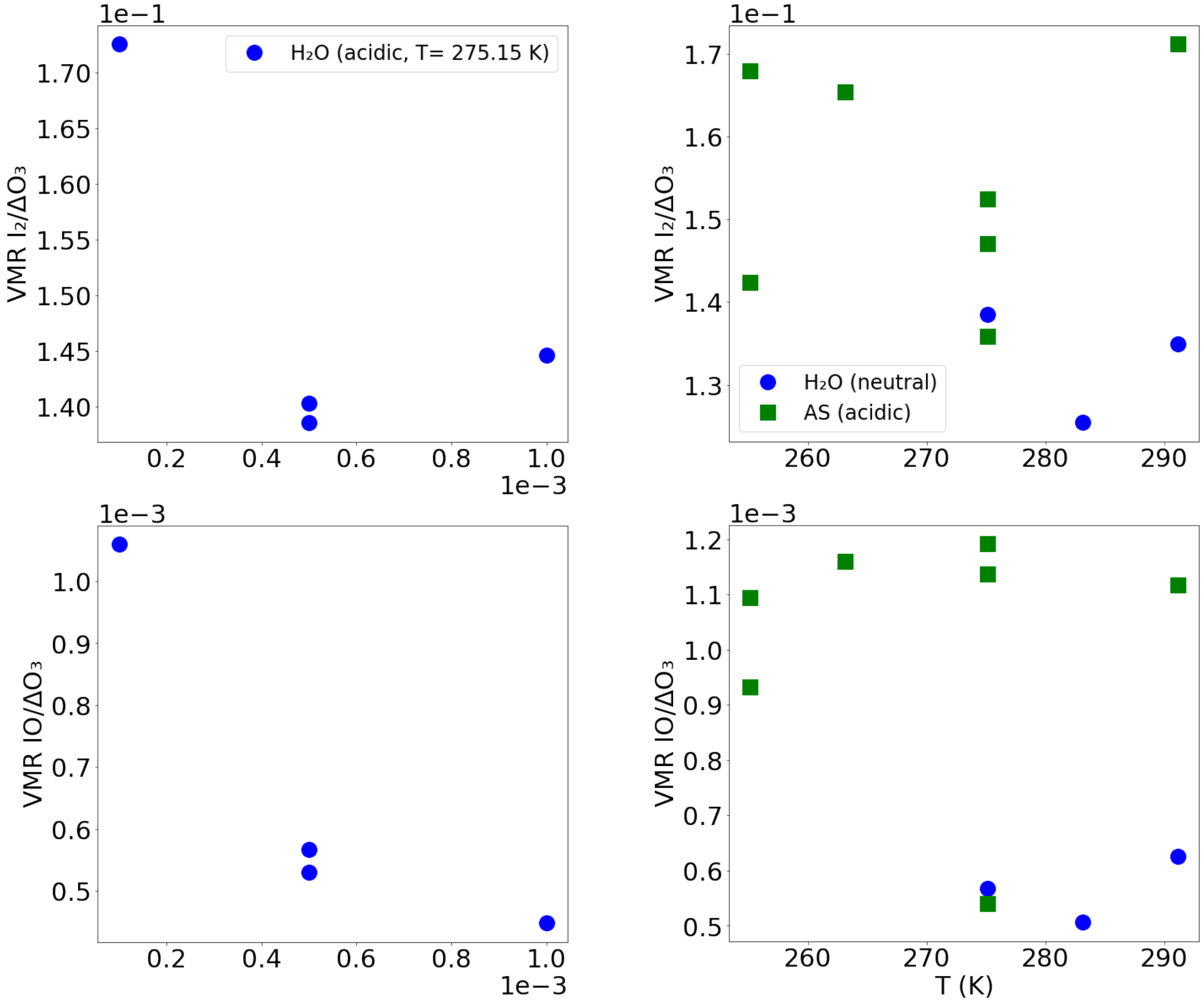


- $IO/I_2 \approx 1:100$, comparable to Sakamoto et al.
- O_3 uptake kinetics sensitive to T, but $IO/\Delta O_3$ not depending on T
- IO yield exhibits different sensitivity to solute strength or pH than I_2
- IO yield highest for lowest iodide concentrations
- I_2 recovery about 10% of O_3 lost

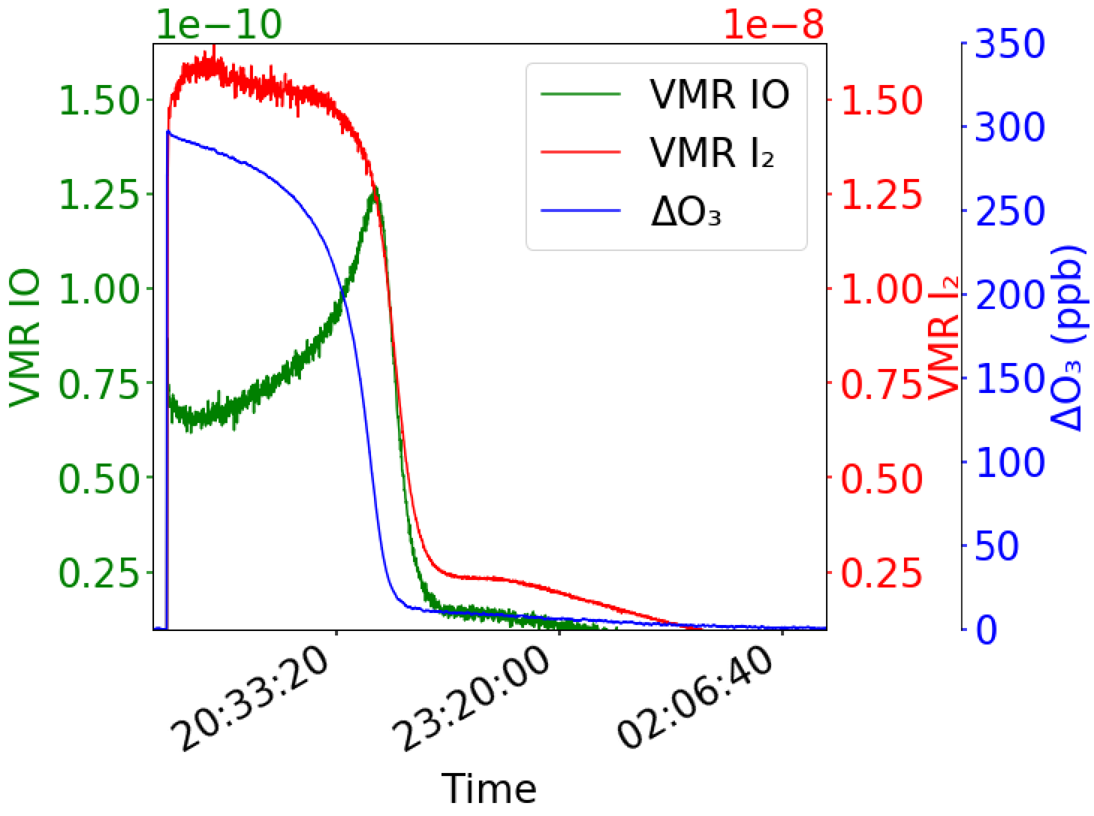
A pathway to IO radical formation?






1e−1
H₂O (acidic, T= 275.15 K)
VMR I₂/ΔO₃
1.70
1.65
1.60
1.55
1.50
1.45
1.40
0.2
0.4
0.6
0.8
1.0
1e−3
1e−1
1.7
1.6
1.5
1.4
1.3
VMR I₂/ΔO₃
H₂O (neutral)
AS (acidic)
260
270
280
290
1e−3
VMR IO/ΔO₃
1.0
0.9
0.8
0.7
0.6
0.5
0.2
0.4
0.6
0.8
1.0
1e−3
1e−3
VMR IO/ΔO₃
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
260
270
280
290
T (K)

Running iodide into depletion



[NaI] = 5×10^{-4} M in MilliQ water, O_3 = 350 ppb

- IO yield increases with increasing O_3 left
- IO decreases in parallel with I_2
- Secondary reaction in the aqueous or gas phase?
- I_2(g) + O_3(g) a factor of 100 too slow
- Aqueous phase source? Wall reaction ?

Iodide oxidation: take home messages

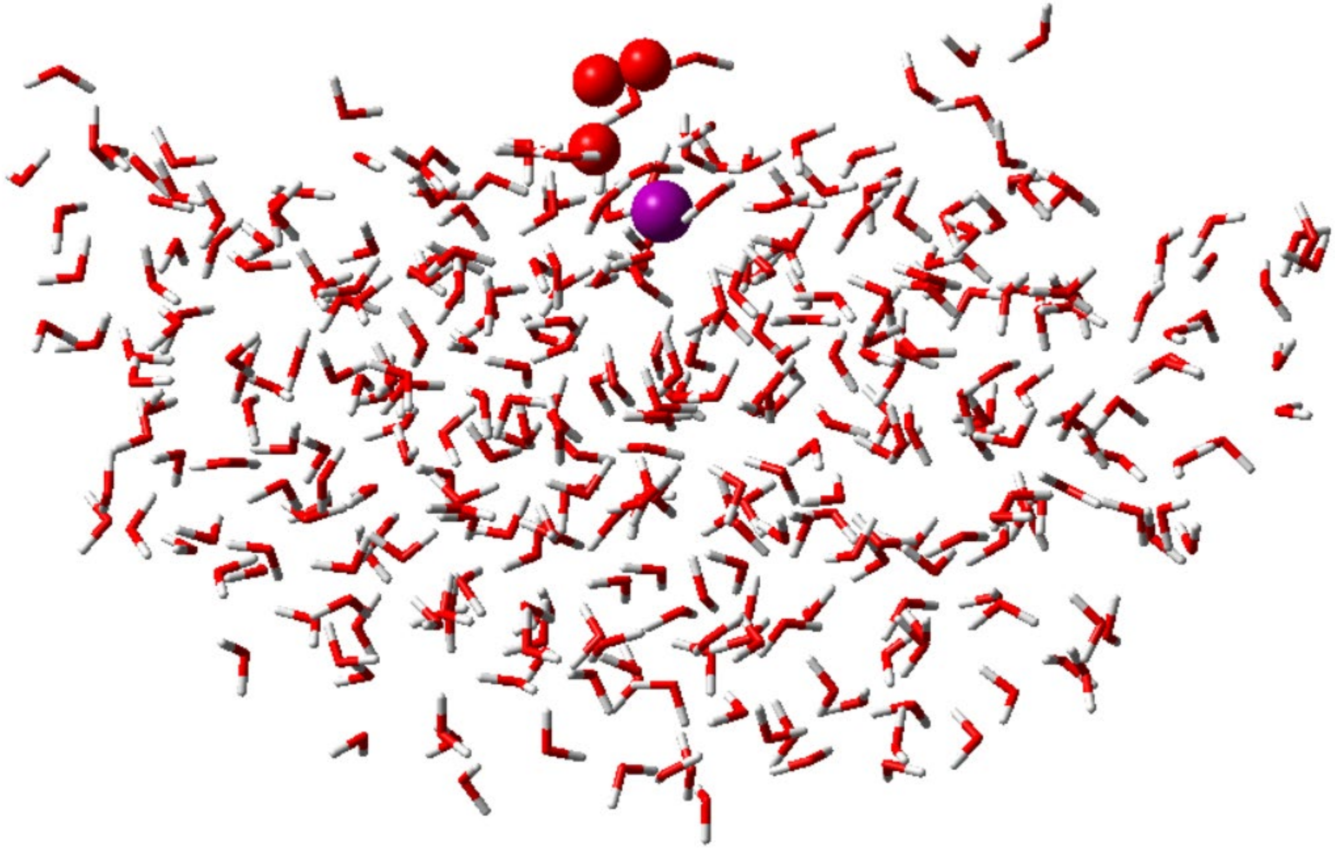
- The mixing ratio dependence of the uptake coefficient of ozone to iodide solutions indicate a surface reaction contributing to ozone loss, especially at low temperature. Impact of liquid phase diffusion limitations require attention.
- I_2(g) is the dominant gas phase product under the experimental conditions, the full iodine budget awaiting clarification.
- The bulk reaction rate coefficient of ozone with iodide decreases with temperature, consistent with earlier experiments (final values coming up).
- IO radical formation was observed. Its formation exhibits dependence on pH and temperature, and is inversely proportional to the iodide concentration.
- Some aspects of IO formation are consistent with a surface process as suggested by Sakamoto et al. (2008), but other aspects indicate secondary reactions at least contributing in part.

Theory is needed to understand better!!

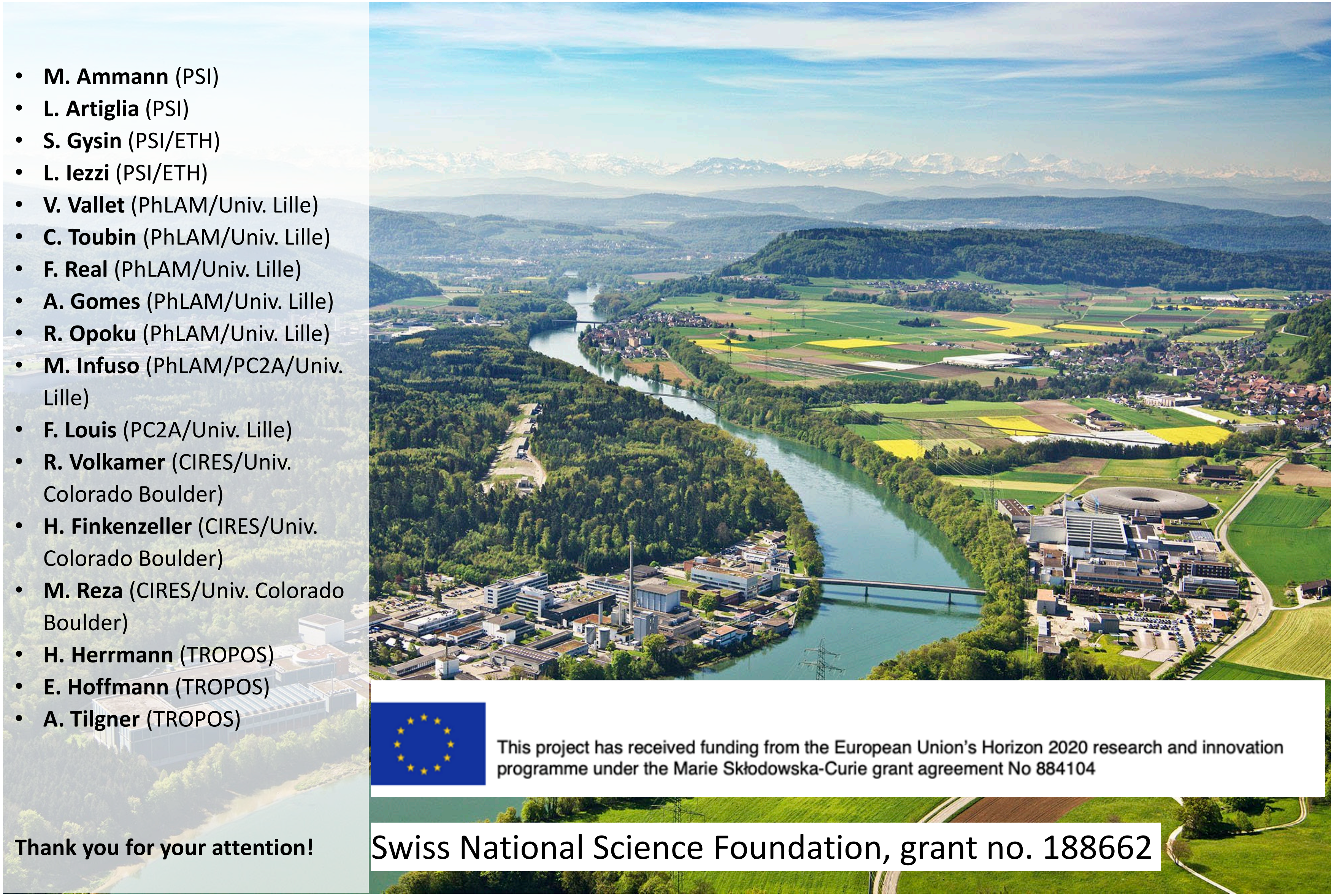
Roose et al., EGU22-4762, room 1.34 on Friday, 27 May 2022, 14:31 CEST

ONIOM QM/MM investigation of iodide oxidation by ozone on an aqueous particle

https://meetingorganizer.copernicus.org/EGU22/EGU22-4762.html



Acknowledgements



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