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Ferric chloride photochemistry in sulfuric acid droplets: Constraints on SO_2 oxidation by O_2

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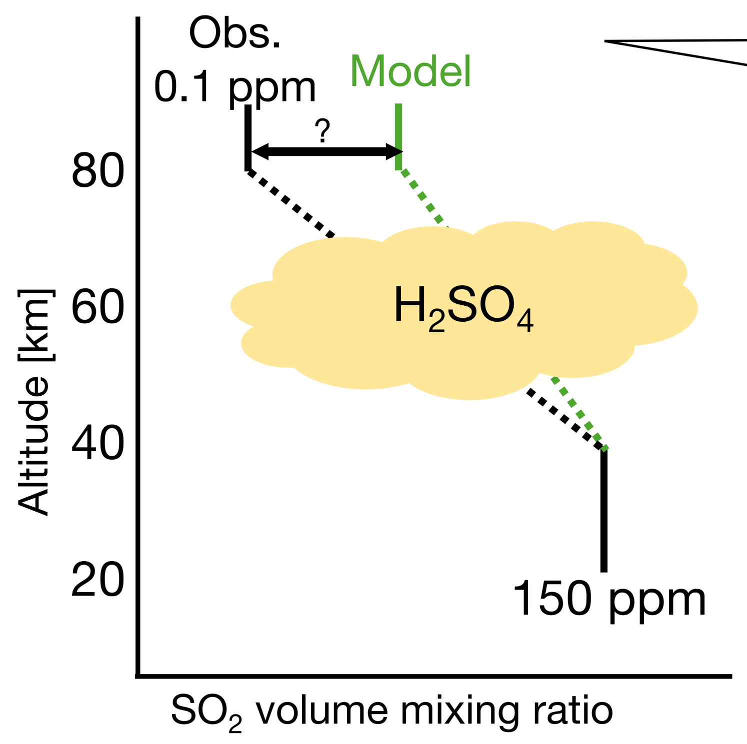
- $FeCl_3$-containing H_2SO_4 droplets exhibited a deviation from the equilibrium radius under 280 nm irradiation.
- Equilibrium speciation indicates that Fe–sulfate, rather than Fe–chloride, complexes dominate under the tested conditions.
- Assessing the dependence on Fe, SO_2, O_2, and UV will constrain the mechanism of the response.

1. Introduction

➤ SO_2 decrease in the H_2SO_4 cloud layer



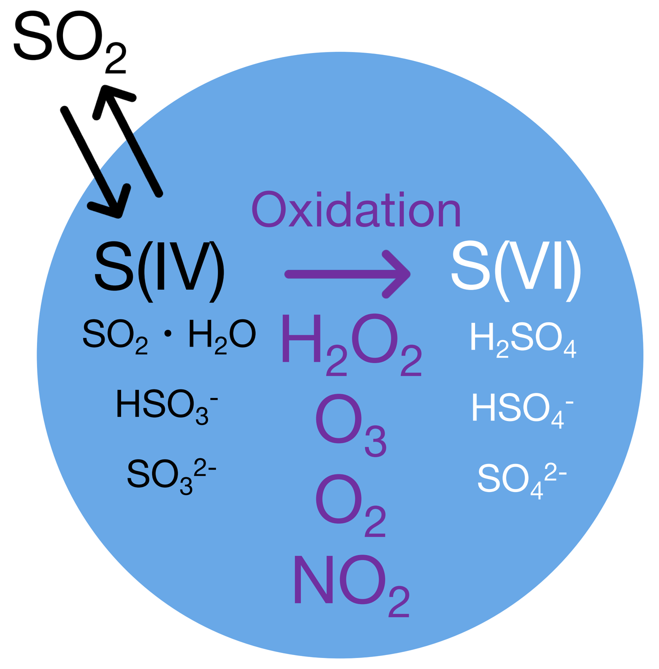
Gas phase sinks of SO_2
SO_2 + oxidants
SO_2 + hv

An additional cloud-layer SO_2 sink may be required to explain the observed depletion.

HYPOTHESIS

SO_2 uptake into sulfuric acid droplets

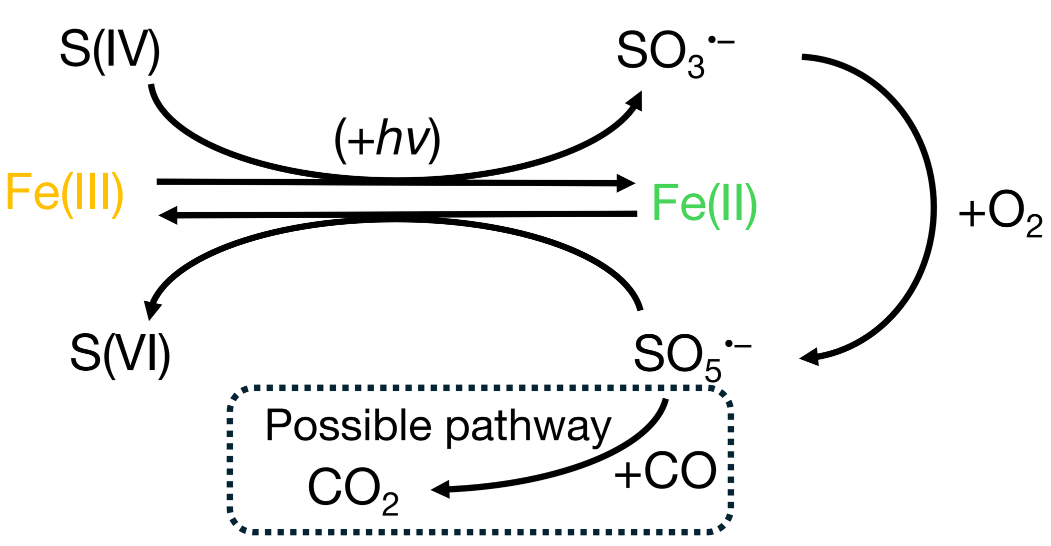
➤ SO_2 oxidation in cloud droplets



- SO_2 is less soluble when the acidity of solution is higher.
- Uptake of SO_2 is known to be facilitated by dissolved oxidants in droplets (pH 2-8).
- We previously measured the SO_2 oxidation by NO_2 in sulfuric acid droplets (pH < −1) by tracking the size increase due to uptake. [Ubukata et al., 2025]

➤ Fe ion catalyzed SO_2 oxidation by O_2

Can Fe photochemistry promote SO_2 oxidation by O_2 in sulfuric acid droplets?



[Rowland et al., 2002]

$[Fe(III) - SO_3]^+ \rightarrow Fe(II) + SO_3^{\bullet-}$

$[Fe(III) - SO_4]^+ \rightarrow Fe(II) + SO_4^{\bullet-}$

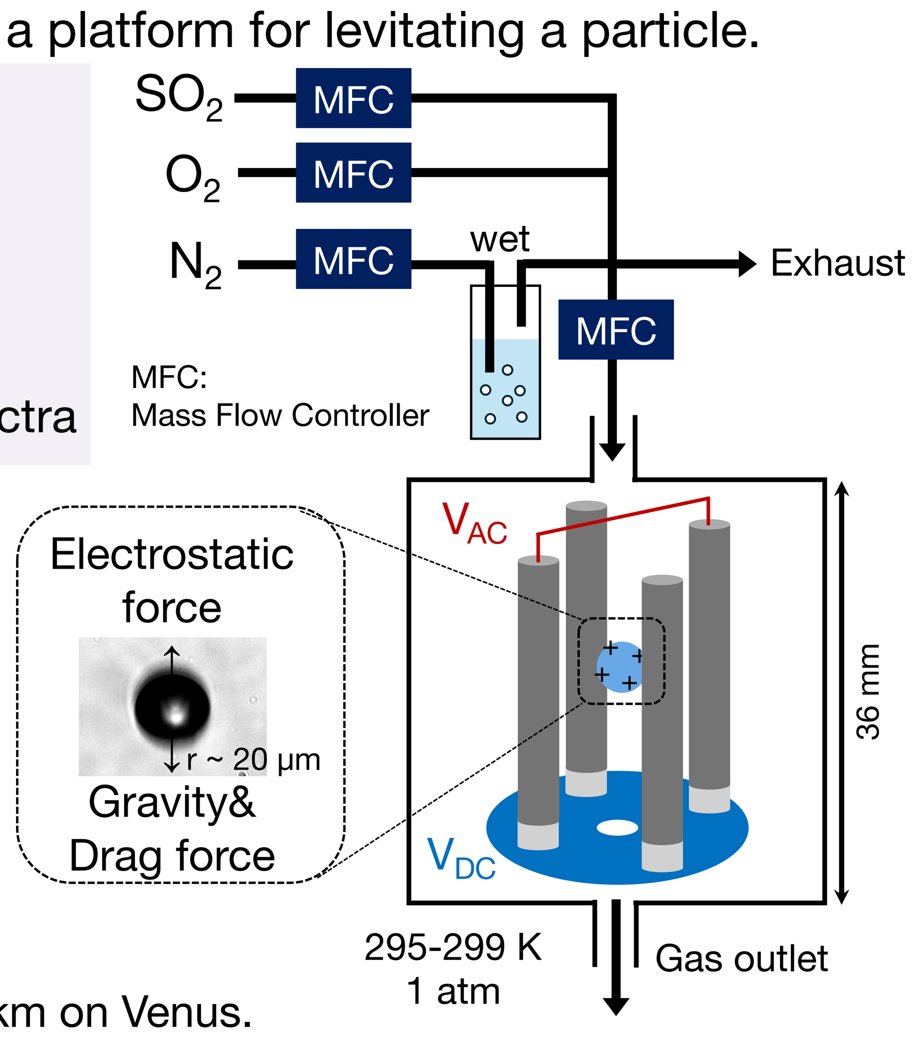
$[Fe(III) - Cl]^{2+} \rightarrow Fe(II) + Cl^{\bullet}$

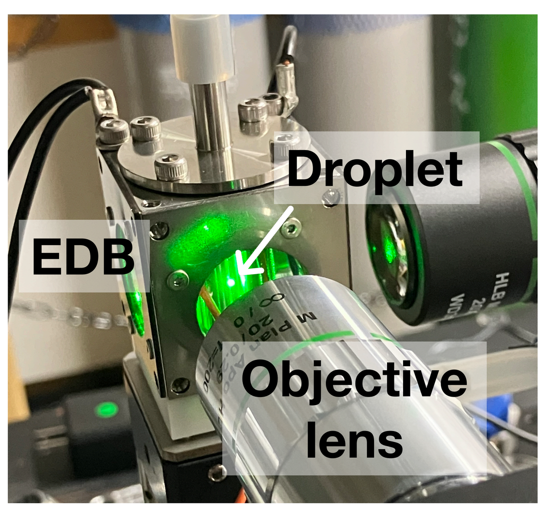
To interpret the photochemistry, we also constrain Fe speciation.

2. Method

EDB (electrodynamic balance) is a platform for levitating a particle.

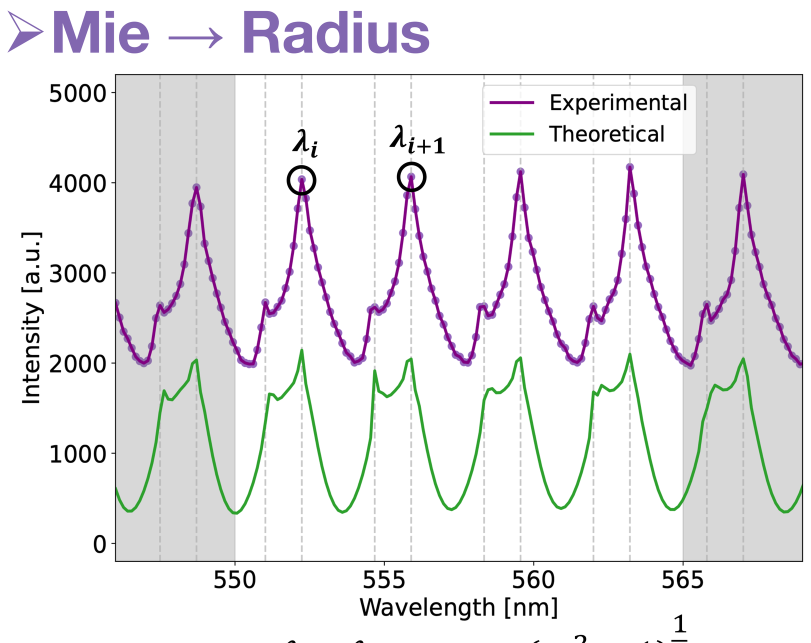
1. Flow SO_2 , O_2 and N_2 at certain concentration into the chamber
2. Irradiate with 280 nm UV light
3. Irradiate a white light for Mie spectra
4. Irradiate a 532 nm laser for Raman spectra





The room temperature corresponds to ~55 km on Venus.

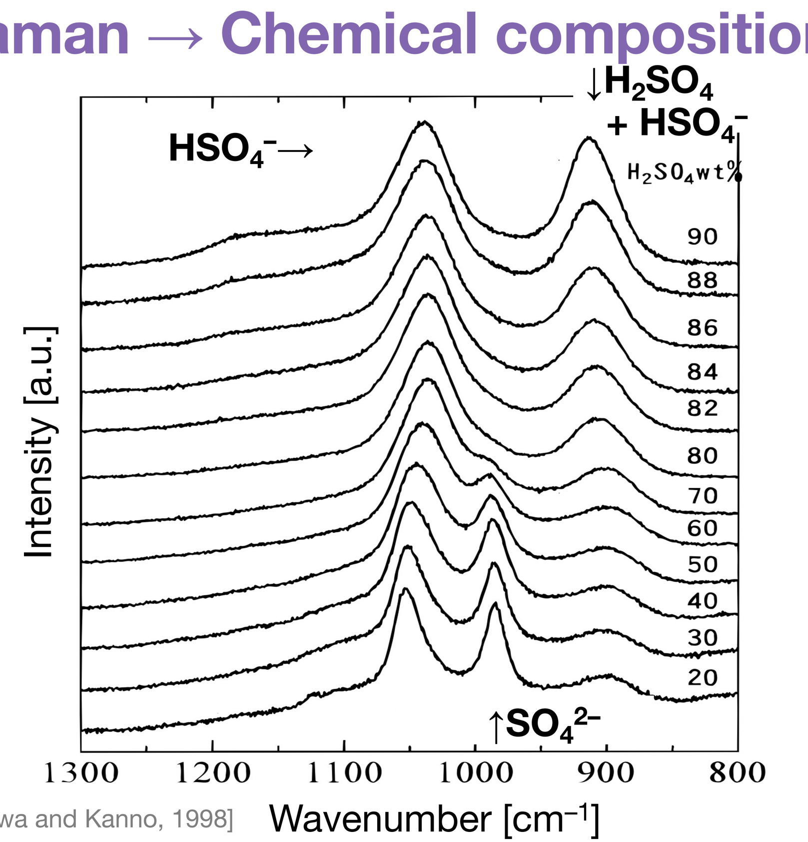
➤ Mie → Radius



$$r_i = \frac{\lambda_{i+1}\lambda_i}{\lambda_{i+1} - \lambda_i} \frac{\arctan(m^2-1)^{\frac{1}{2}}}{2\pi\,(m^2-1)^{\frac{1}{2}}}$$

r_i : Radius of a droplet
m : Refractive index of a droplet [Chýlek 1976]

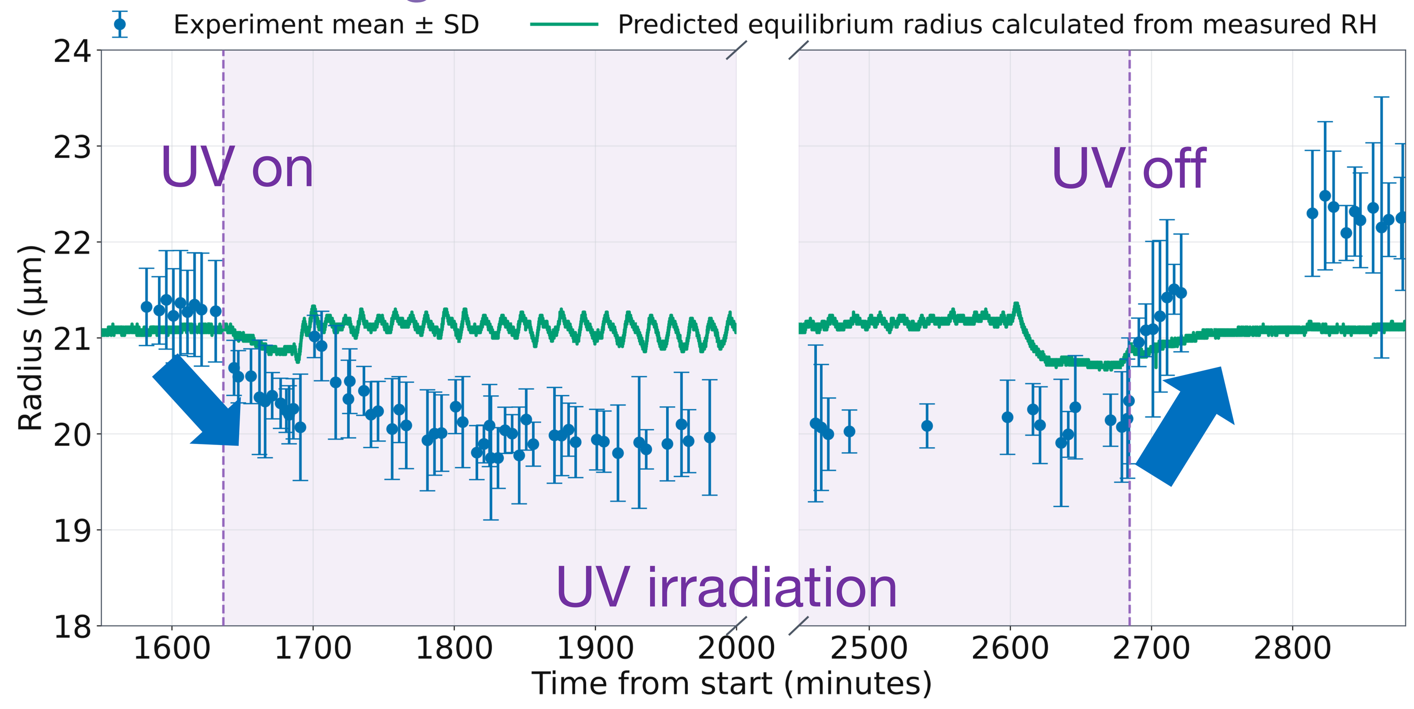
➤ Raman → Chemical composition



[Tomikawa and Kanno, 1998]

3. Results

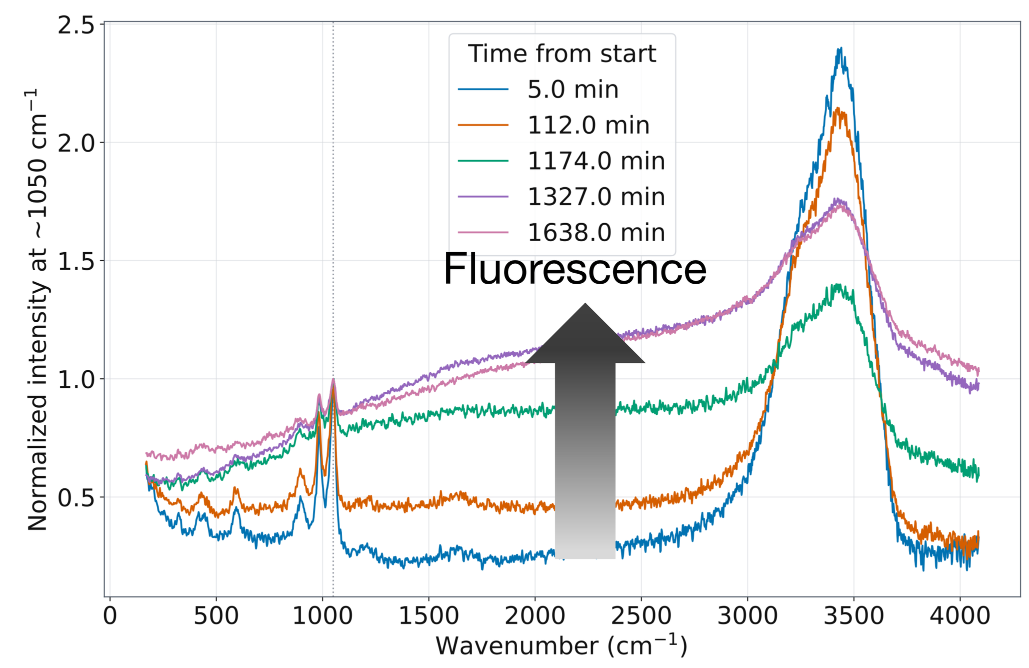
➤ Radius changes



N_2 Background
RH ~80%
110 ppm SO_2
870 ppm O_2
26 wt% H_2SO_4
0.2 mM $FeCl_3$

- Dilute H_2SO_4 and elevated O_2 conditions were used to enhance the detectability of SO_2 oxidation by increasing the uptake efficiency.
- Before UV irradiation, the droplet radius did not change.
- During UV irradiation, the radius decreased by ~1 μm from equilibrium radius.
- After UV was turned off, the radius increased above the equilibrium radius.

➤ Raman changes

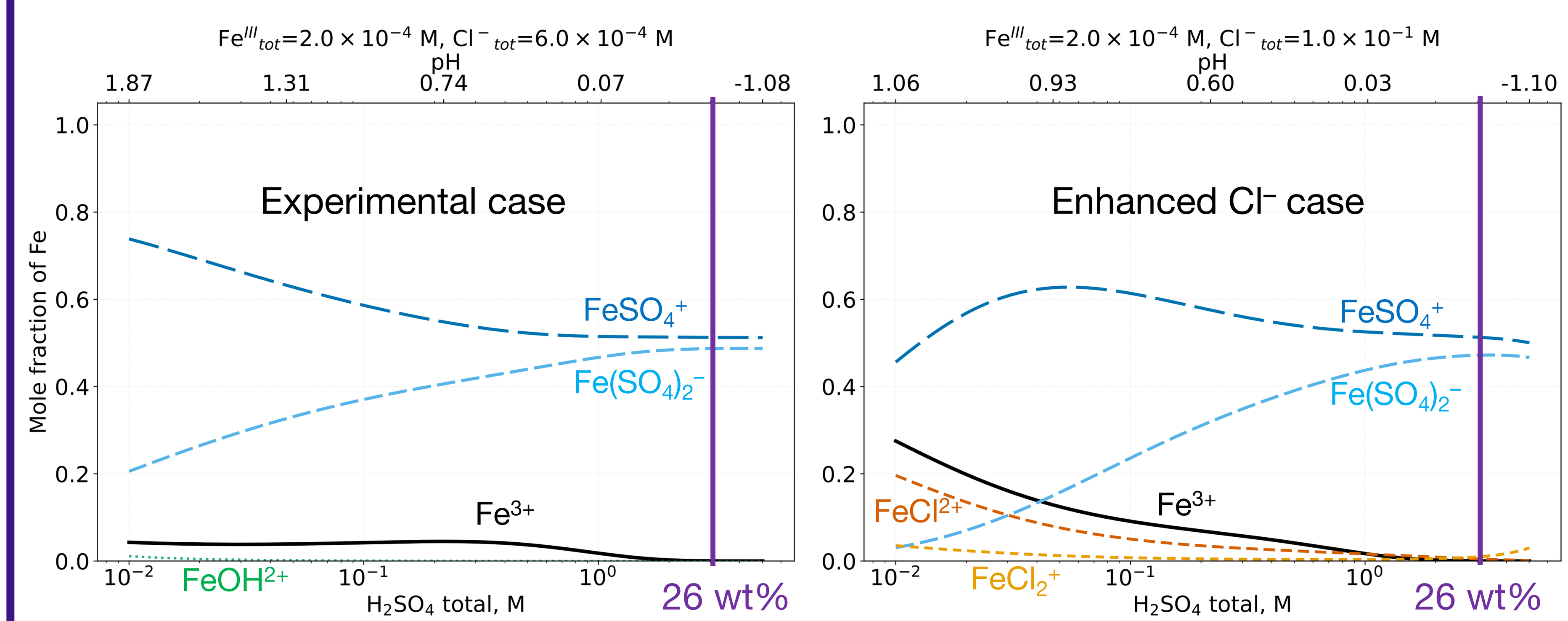


- New peaks were not detectable.
- The baseline of Raman spectra increased due to fluorescence.
- Usable Raman spectra could not be acquired after UV irradiation.

4. Discussion

UV heating alone is unlikely to explain the observed behavior. Changes in droplet composition or refractive index may contribute.

Speciation constrains which Fe complexes could initiate the photochemistry responsible for the observed response.



- Under our experimental conditions, Fe mainly forms sulfate complexes.
- Fe(III)–chloride complexes remain negligible even at [Cl⁻] = 0.1 M.
- At Venus-relevant Cl abundance, Fe(III) is predicted to occur mainly as sulfate complexes rather than Fe–Cl species.

5. Conclusion

- **Key finding**
  280 nm irradiation produced a clear non-equilibrium Mie response in $FeCl_3$-containing H_2SO_4 droplets with the SO_2 and O_2 flow.
- **Interpretation**
  The reason of the response remains uncertain; Fe-mediated SO_2 oxidation by O_2 is one of the possible pathways.
- **Mechanistic implication**
  Fe speciation calculations favor Fe–sulfate over Fe–chloride complexes under the tested conditions, suggesting that the relevant Fe photochemistry may differ from that expected from the $FeCl_3$ precursor.
- **Next step**
  To identify the reaction mechanism, Fe-free / O_2-free / SO_2-free controls and product-resolved Raman measurements are required.

References & Acknowledgments

- Ubukata et al. (2025) ACS Earth and Space Chemistry
- Rowland et al. (2002) Journal of Photochemistry and Photobiology A: Chemistry
- Chýlek (1976) Journal of the Optical Society of America.
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