

Quantification of SO₂ Oxidation on the Surfaces of Acidic Micro-Droplets: Implication to the Ambient Sulfate Formation

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The Impact of Aerosol Particles on Human Life

Visibility



Jan 6, 2015

PM_{2.5} ~ 50-100 $\mu\text{g}/\text{m}^3$



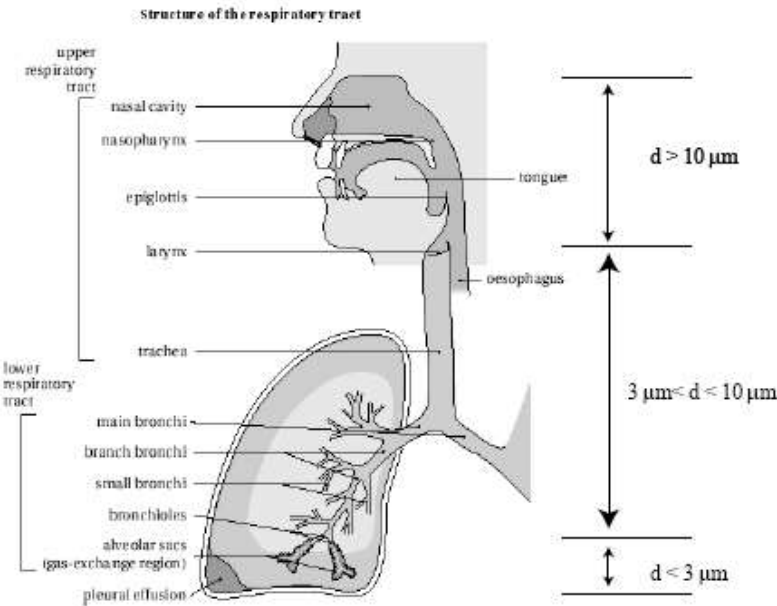
Jan 7, 2015

PM_{2.5} < 20 $\mu\text{g}/\text{m}^3$

The Impact of Aerosol Particles on Human Life

Health effect

The penetration of particles in the respiratory system

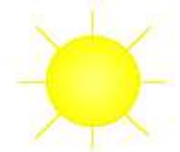


Significance of Atmospheric Particles: Climate and Chemical Reactions

Chemical Reactions

Reactants → Products

Indirect Radiative Forcing



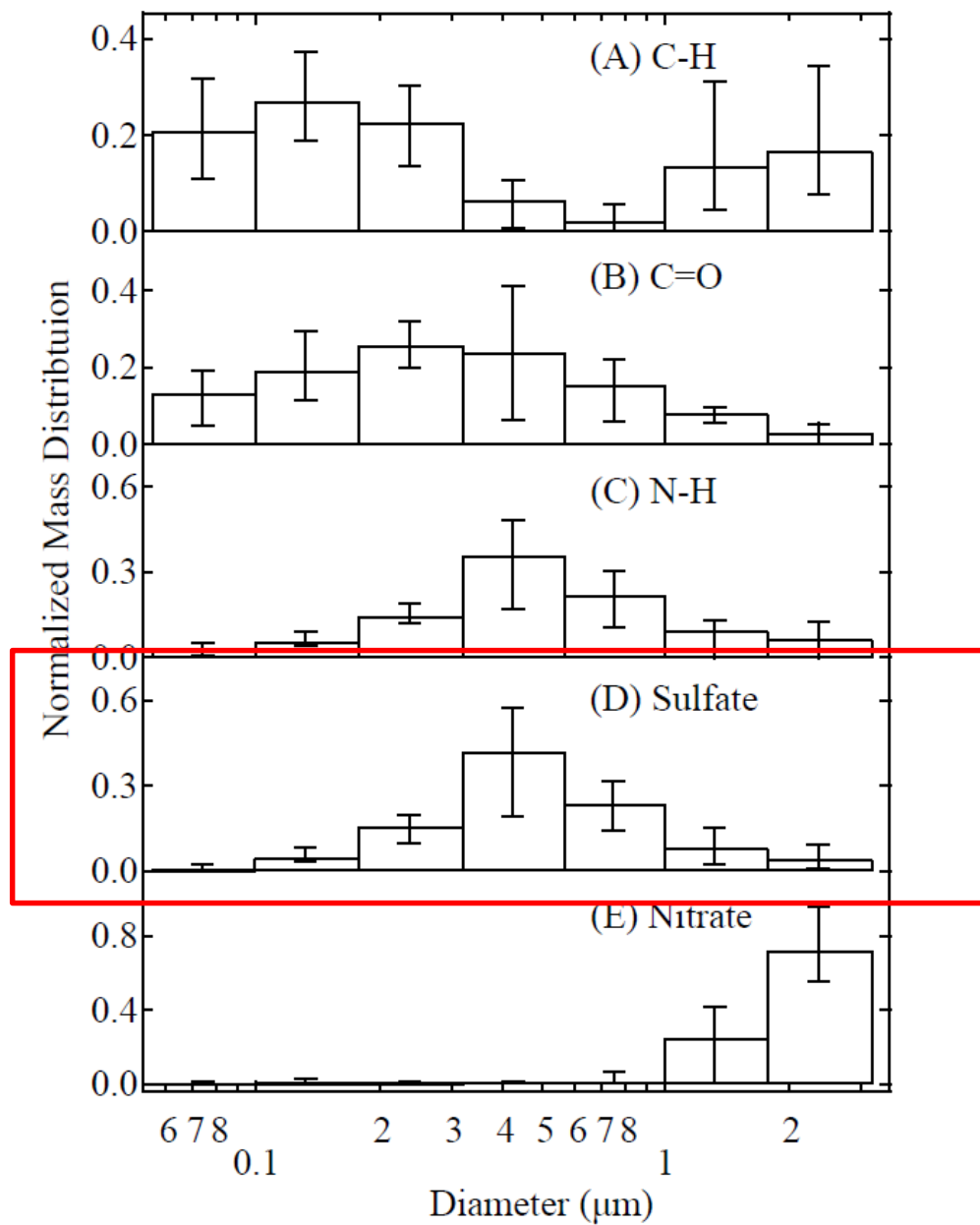
Direct Radiative Forcing



Biogenic Sources

Anthropogenic Sources

The mass fraction of selected functional groups



Taipei

SO₂(g) Oxidation in the Atmosphere

What we knew:

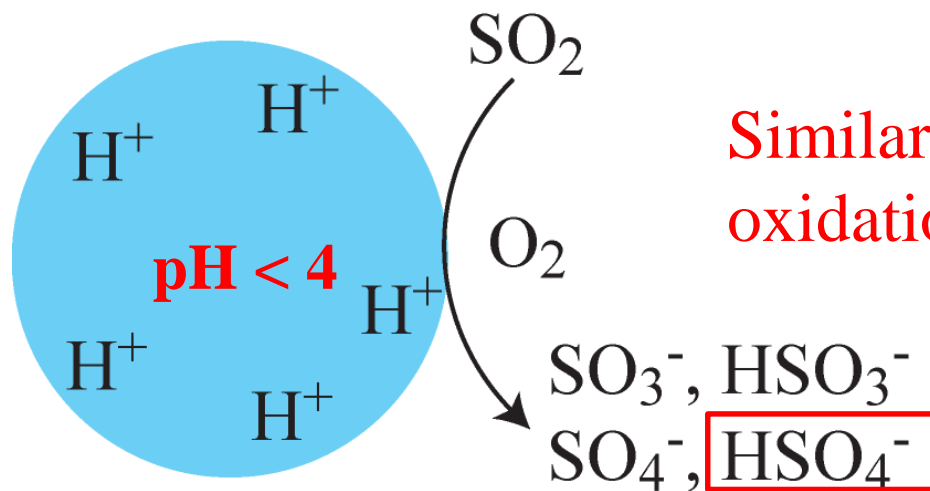
Gas phase: oxidation by hydroxyl (OH) radicals.

Yield is low

Aqueous phase: reactions of SO₂ with hydrogen peroxide (H₂O₂) and O₂ (catalyzed by Fe³⁺ and Mn²⁺ or uncatalyzed)

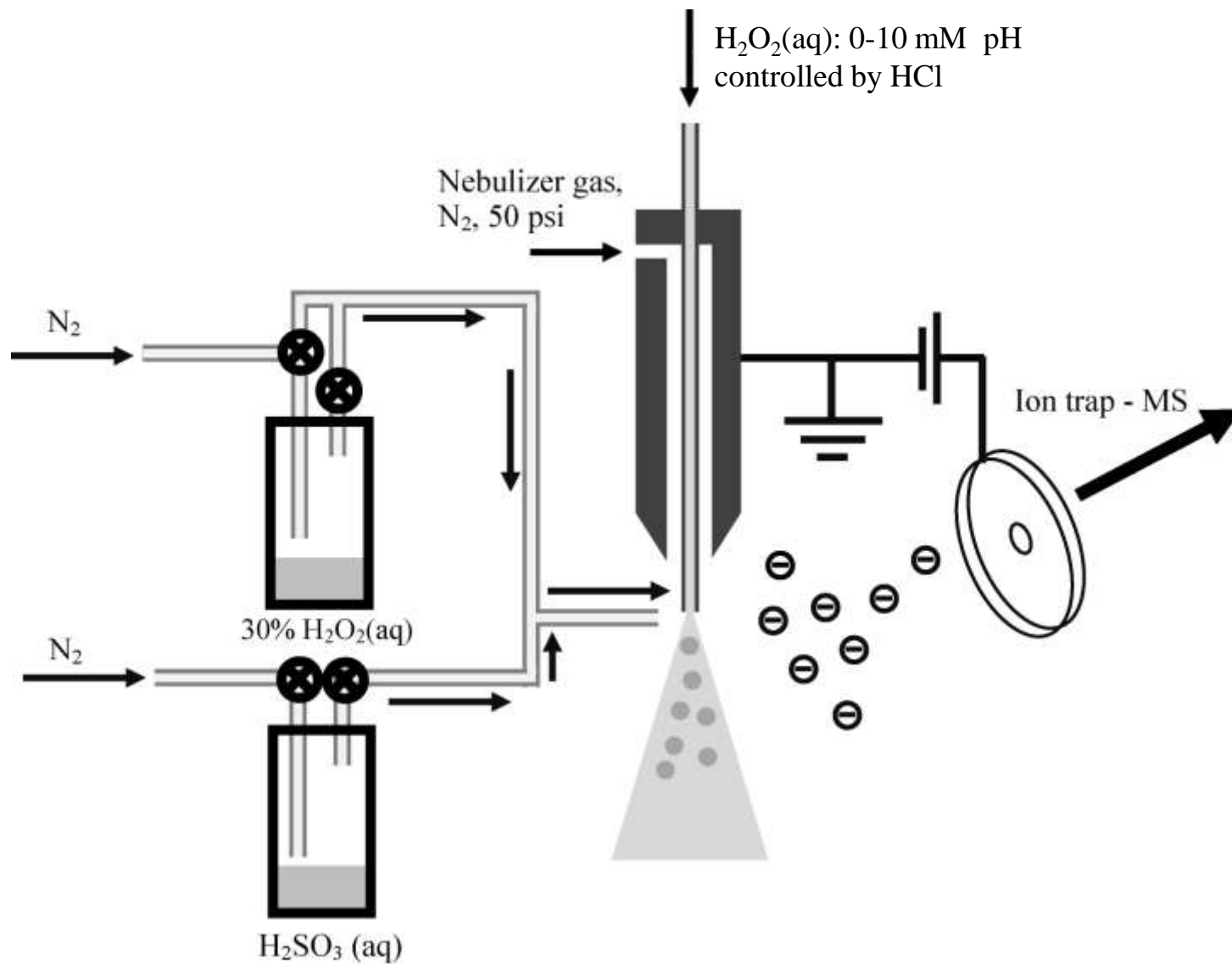
significant in cloud, 0.1-1g/m³-air

A new mechanism:

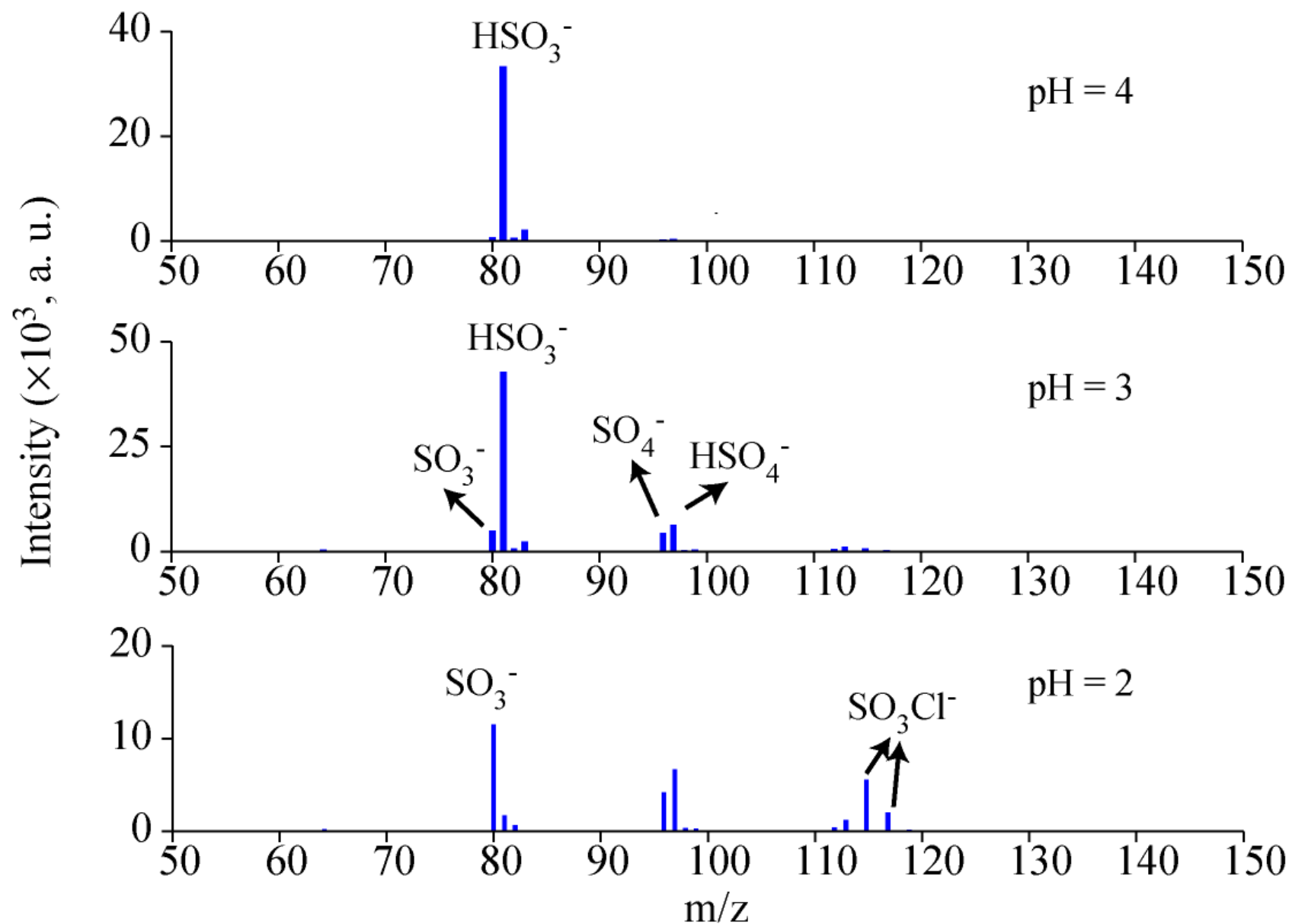


Similar to the uncatalyzed O₂ oxidation but different approach

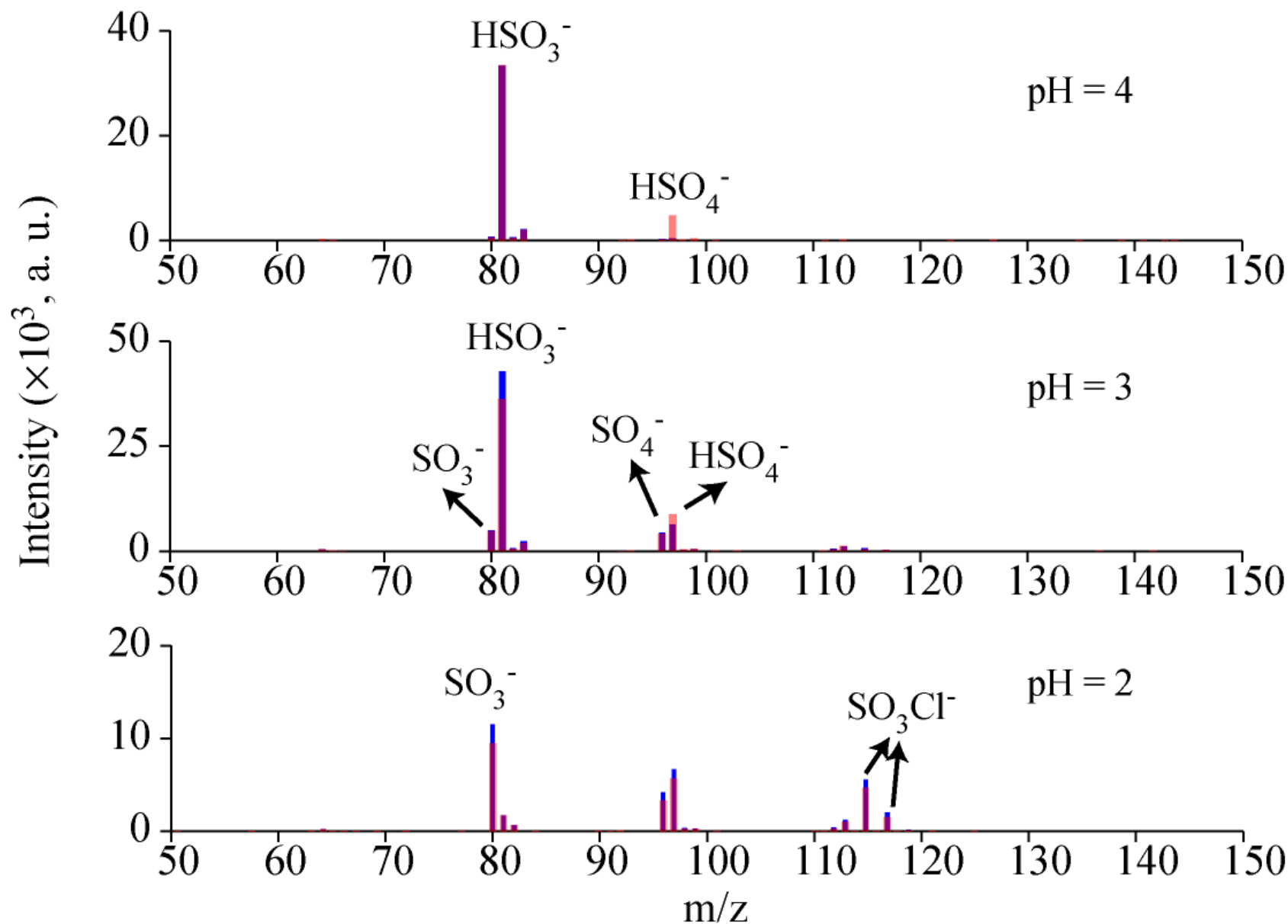
Experimental Setup



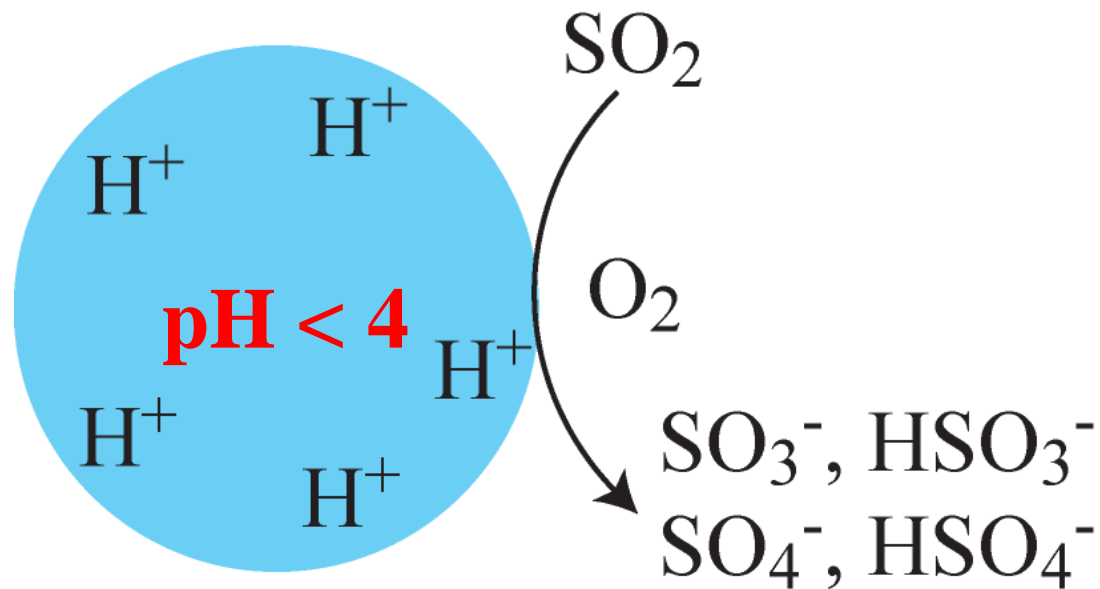
Results-HCl(aq) exposed to SO₂(g)



Results-HCl(aq) exposed to SO₂(g)+H₂O₂(g)



Results-HCl(aq) exposed to SO₂(g)

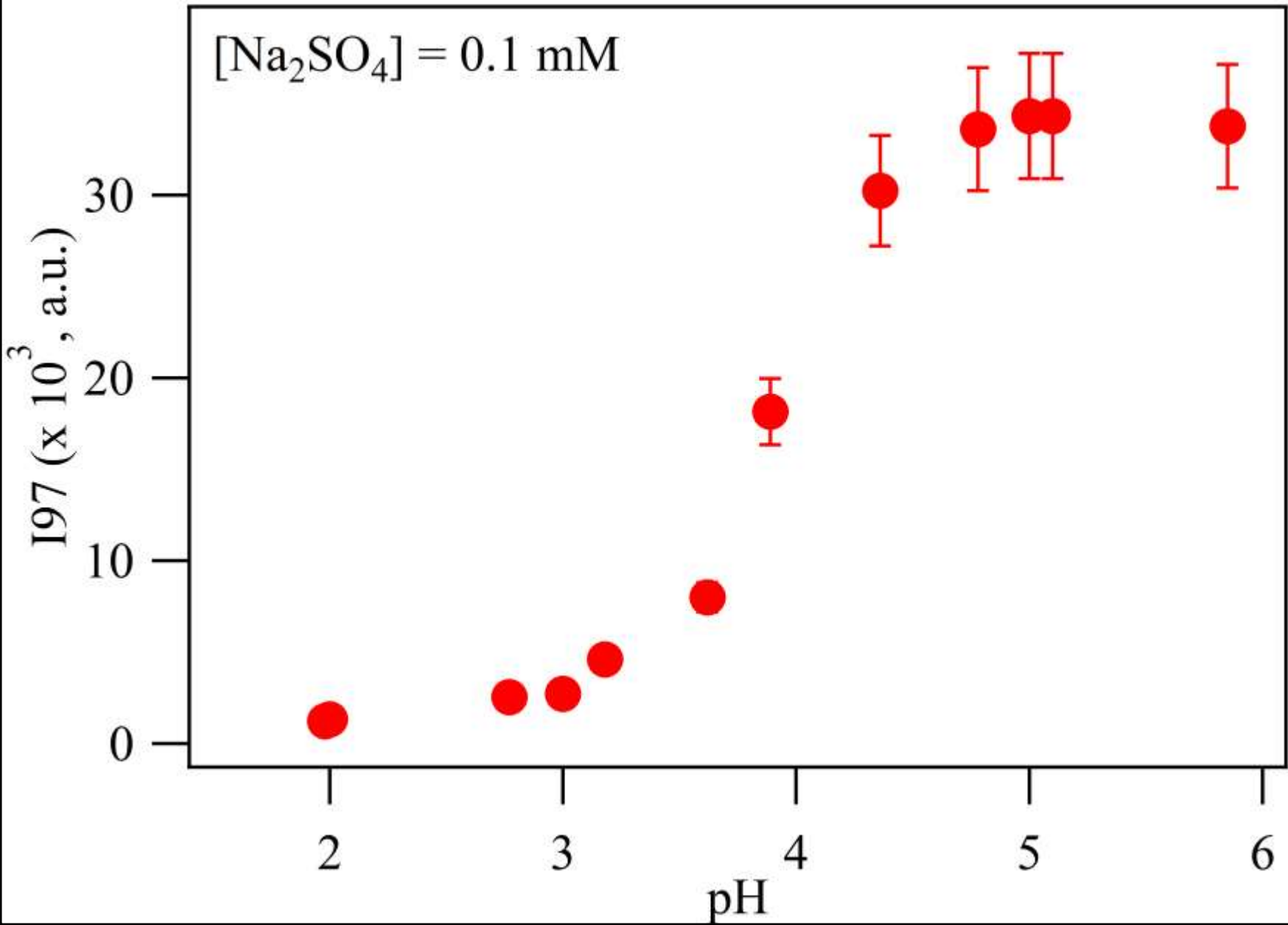


Quantification of the conversion efficiency

$\text{H}_2\text{O}_2 + \text{HCl}(\text{aq})$ exposed to $\text{SO}_2(\text{g})$

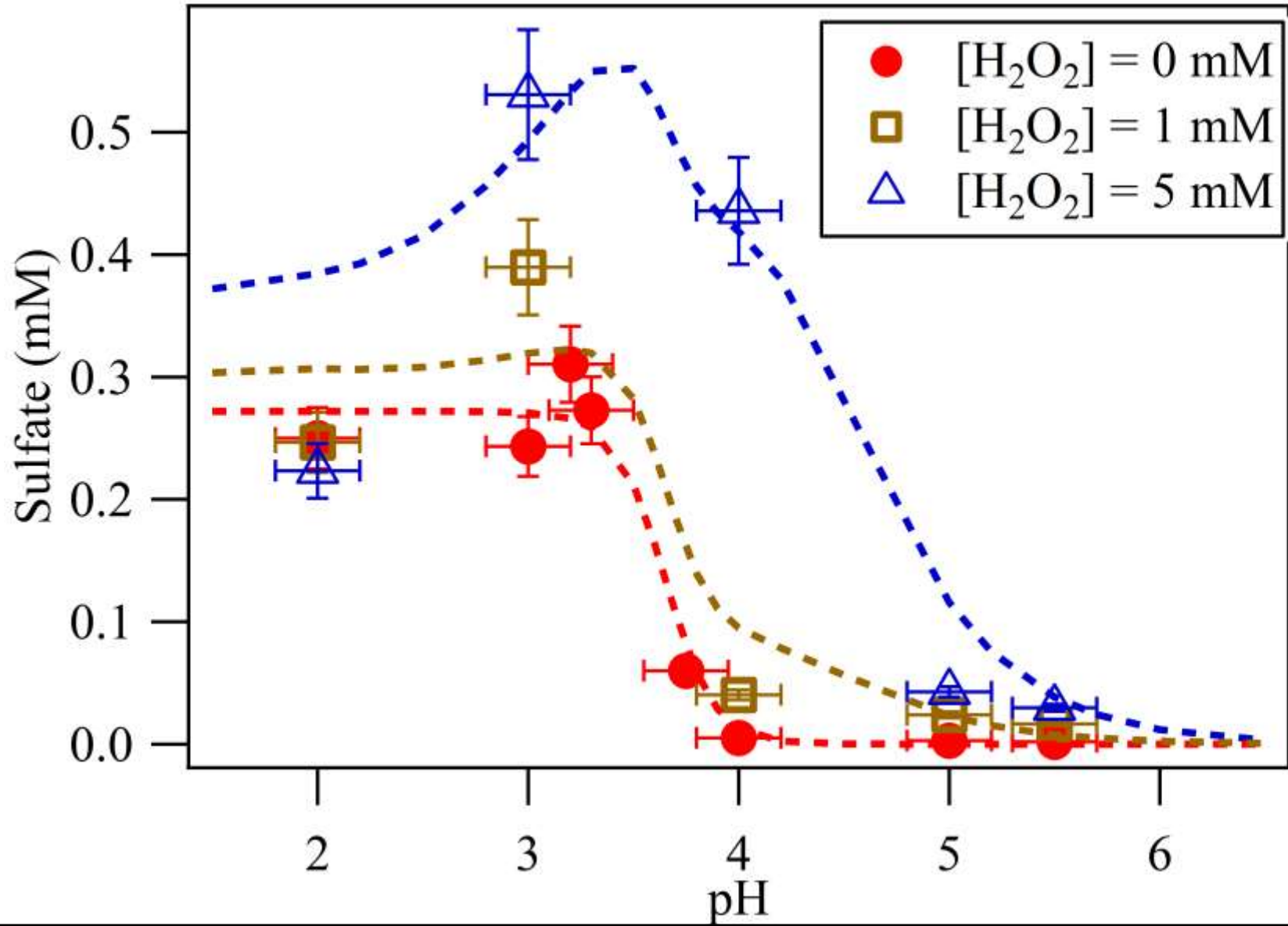
1. Sulfate concentration calibration using Na_2SO_4 .
2. Adapting the reaction rate via $\text{H}_2\text{O}_2(\text{aq})$, $R_{\text{H}_2\text{O}_2} = 7.45 \times 10^7 [\text{HSO}_3^-][\text{H}_2\text{O}_2(\text{aq})][\text{H}^+]/(1 + 13 \times [\text{H}^+])$ M/s
3. Assuming the reaction rate via the oxidation on the acidic surface is $R_i = \frac{1}{4} v n A q$ (molecules s^{-1})
where $v = (8RT/\pi M_w)^{1/2}$ the mean speed of molecule, M_w is the molecular weight of gas molecule, n is the molecule number density, A is the surface area of droplets and q is the reaction efficiency.

Sulfate Repose as a Function of pH

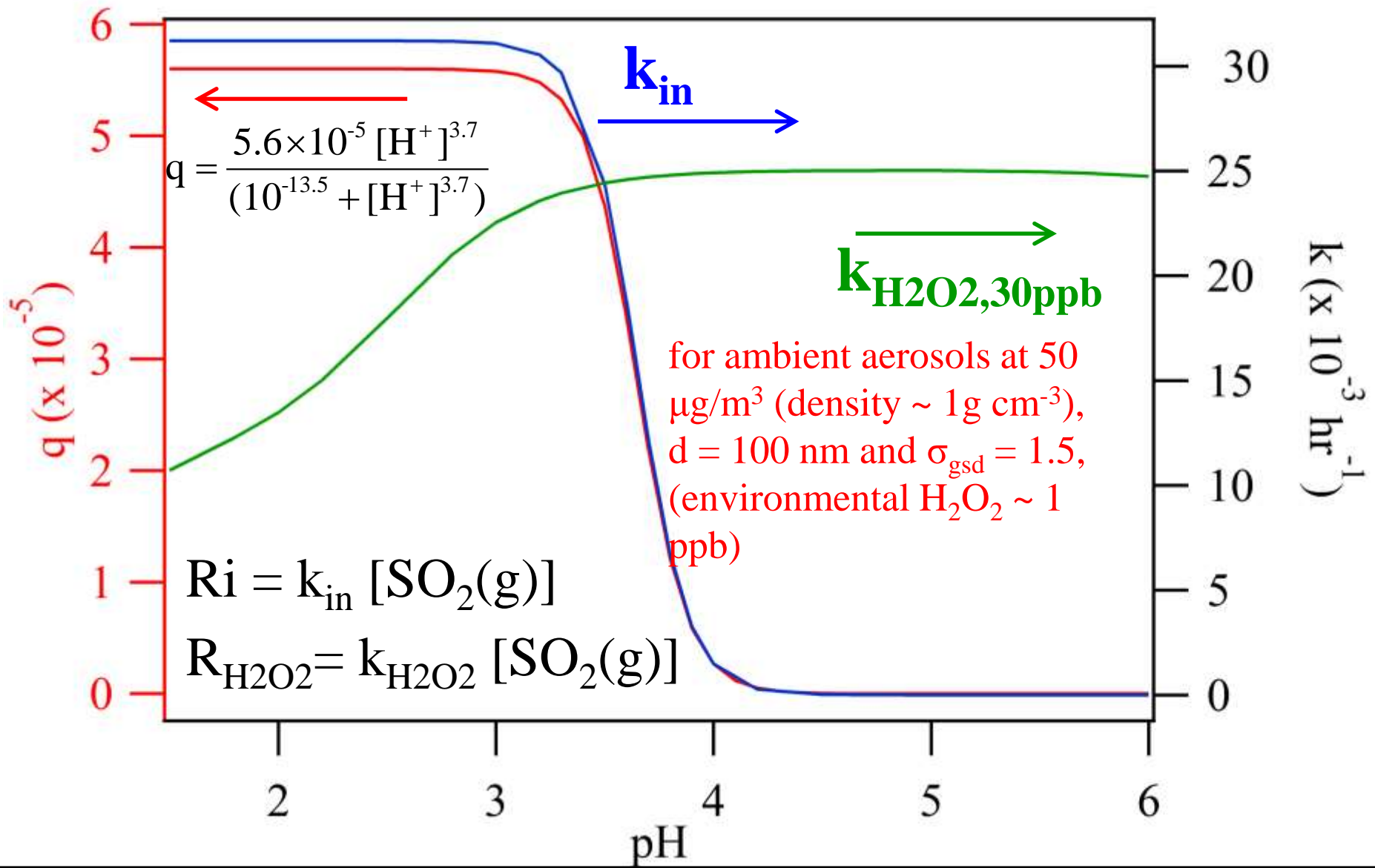


Quantification of the conversion efficiency

Results- $\text{H}_2\text{O}_2 + \text{HCl}(\text{aq})$ exposed to $\text{SO}_2(\text{g})$



Quantification of the conversion efficiency for SO₂(g) to Sulfate on Acidic Droplets



Conclusions

1. At $\text{pH} < 4$, the oxidation of SO_2 by O_2 on the interfacial air-water surface by dioxygen may start to proceed in the absence of catalysis due to the structural differences of water at the interface versus the characteristic water structure in bulk-phase water.
2. The observed interfacial reaction is efficient and can act as a major pathway for sulfate formation, especially at environments lack of cloud processing or with limited H_2O_2 .
3. In our field studies, sulfate is mainly distributed at sub-micronmeter sized particles which is likely to formed via the surface reactions.