Multiplying Factors for Bromine Destruction of (Tropospheric) Ozone

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Bromine and Chlorine in the Troposphere

- Sea salt particles:

  -Cl^-/Br^- ~ 650

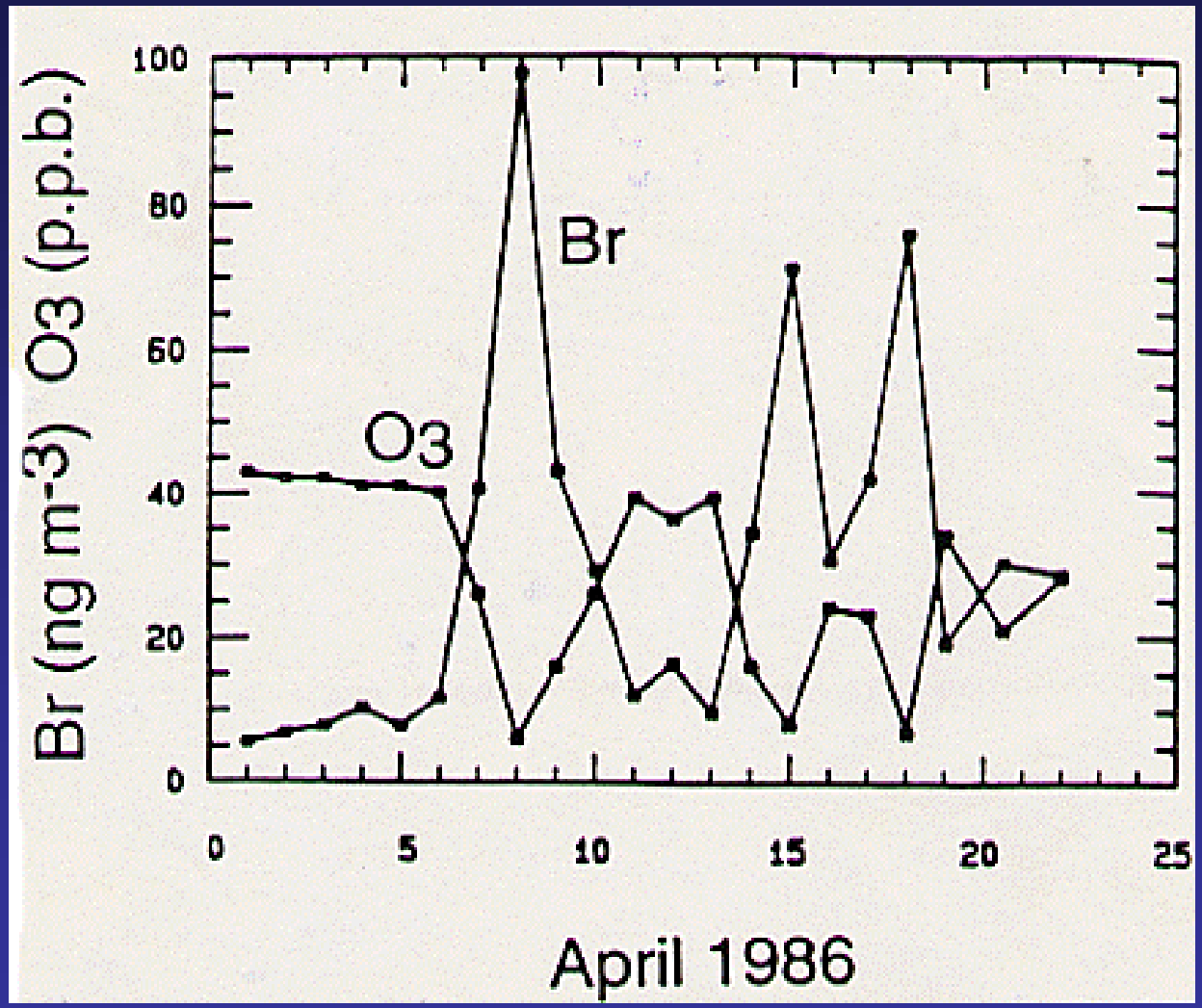
- Alkaline dry salt lakes:

  - Dead Sea
  - Great Salt Lake

- Plumes from burning oil wells:

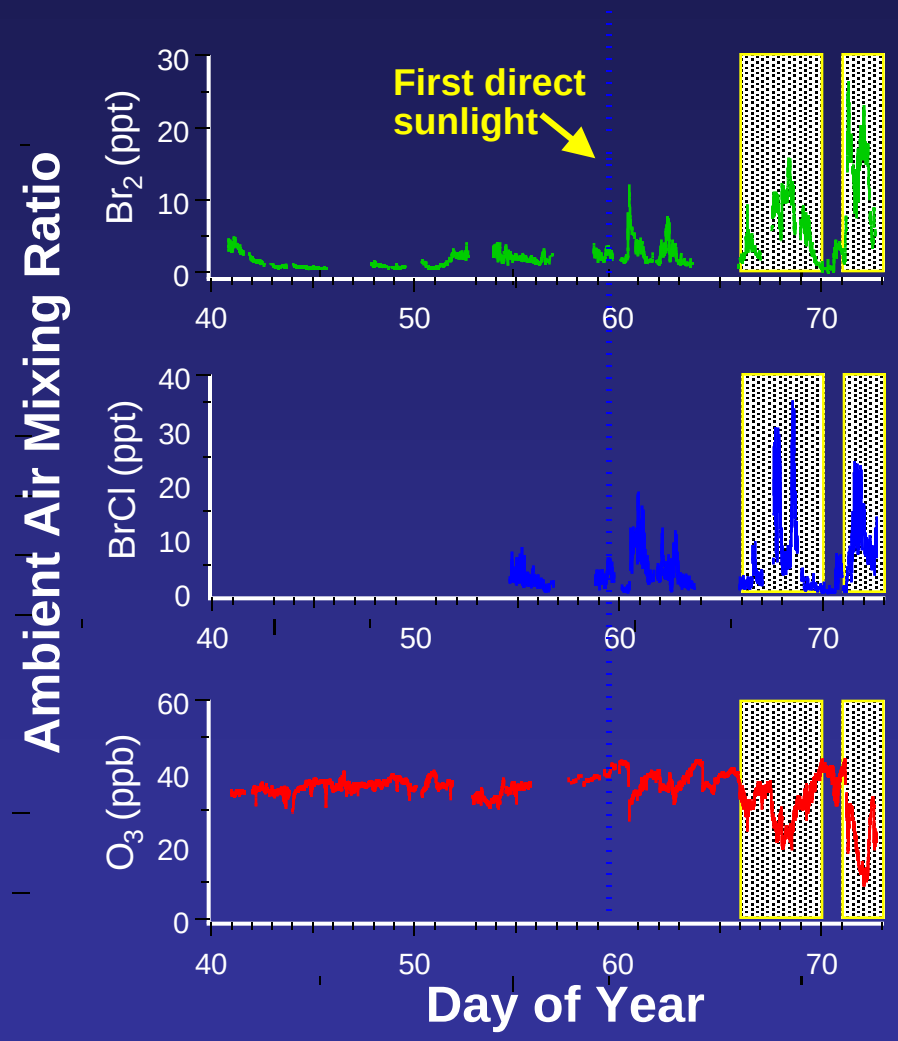
  - Kuwait

Loss of Ozone at Ground Level at Polar Sunrise at Alert, Canada



Barrie et al., ***Nature*** 334 138 (1988)

Specific Identification of Br_2 and BrCl at Alert



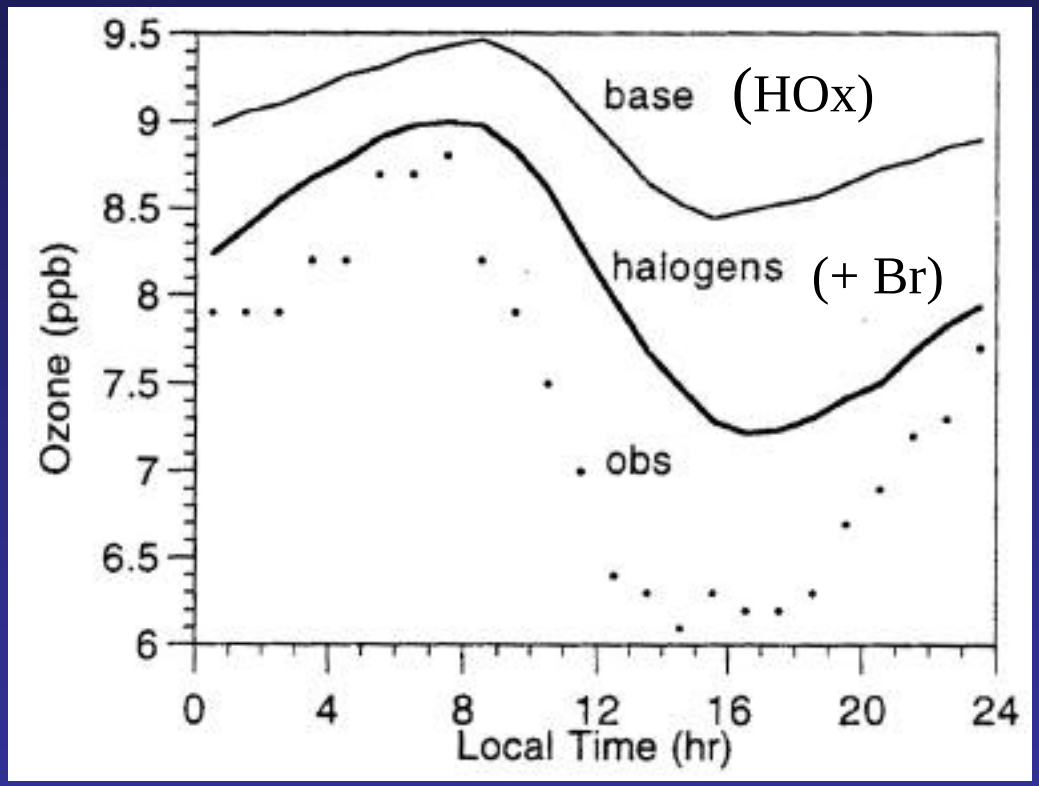
Br_2

BrCl

O_3

Foster et al., *Science* 291 471 (2001)

Bromine in Mid-Latitudes



- ~ 32% diurnal variation in O_3 over tropical Indian Ocean

- Br chemistry explains much of discrepancy between HO_x only model and observations

Dickerson et al., *JGR* 104 21385 (1999)

Bromine in Mid-Latitudes

- Nagao et al. (1999) report "sunrise ozone destruction" (SOD) in north Pacific Ocean MBL that is correlated to 0.3 - 5 μm particle volume (sea salt)

- Gabally et al. (2000) report SOD at Cape Grim, Tasmania

  - O_3 destruction rate in MBL underestimated by about a factor of two!

Tropospheric Ozone

- Greenhouse gas
- UV absorption
- Oxidant and oxidant precursor
- Toxic air pollutant

Goals

- To elucidate the chemistry that converts Br^- in sea salt particles and seawater ice into Br_2 and BrCl, and the associated effects on tropospheric ozone
  - To elucidate the "multiplying"factors that lead to enhancement of bromine compared to chlorine

Chlorine and Bromine Chemistry

Kinetics:

$$O_3 + Cl^- \rightarrow ClO^- + O_2 \qquad k = 2 \times 10^{-3}\ M^{-1}\ s^{-1}$$

$$\downarrow \times 10^5$$

$$O_3 + Br^- \rightarrow BrO^- + O_2 \qquad k = 3 \times 10^{2}\ M^{-1}\ s^{-1}$$

- **Bromine oxidation by O_3 much faster**

Chlorine and Bromine Chemistry

$$OH + Cl^- \leftrightarrow HOCl^-$$

$$K_{eq} = \frac{4.3 \times 10^9}{6.1 \times 10^9} = 0.70$$

$$\xrightarrow{H^+}$$

$$Cl_2 \leftarrow \leftarrow Cl$$

$\times$ 550

$$OH + Br^- \leftrightarrow HOBr^-$$

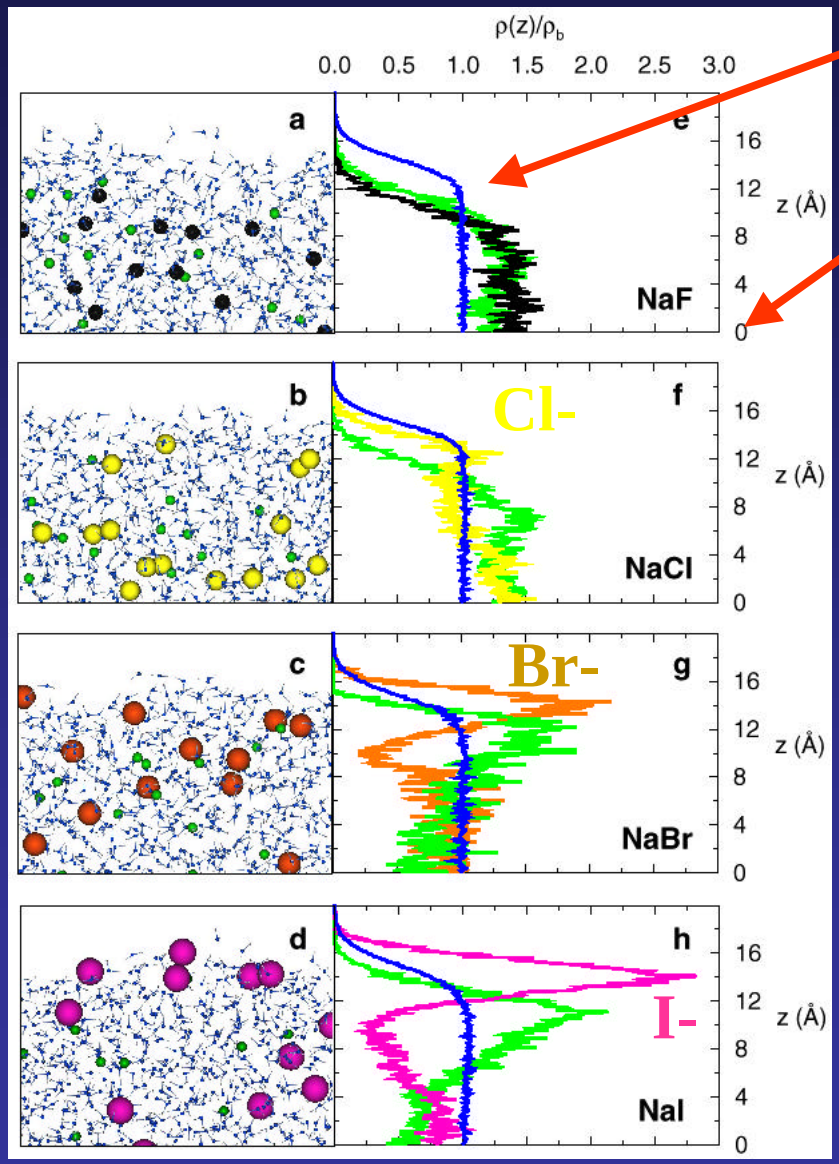
$$K_{eq} = \frac{1.3 \times 10^{10}}{3.3 \times 10^7} = 390$$

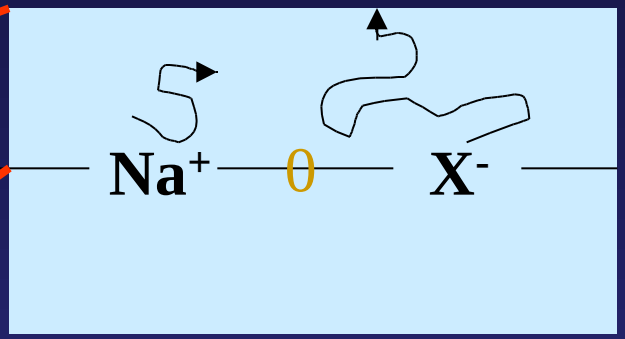
$$\xrightarrow{H^+}$$

$$Br_2 \leftarrow \leftarrow Br$$

- Bromine oxidation favored

MD Simulations of Salt Solutions (1.2 M)

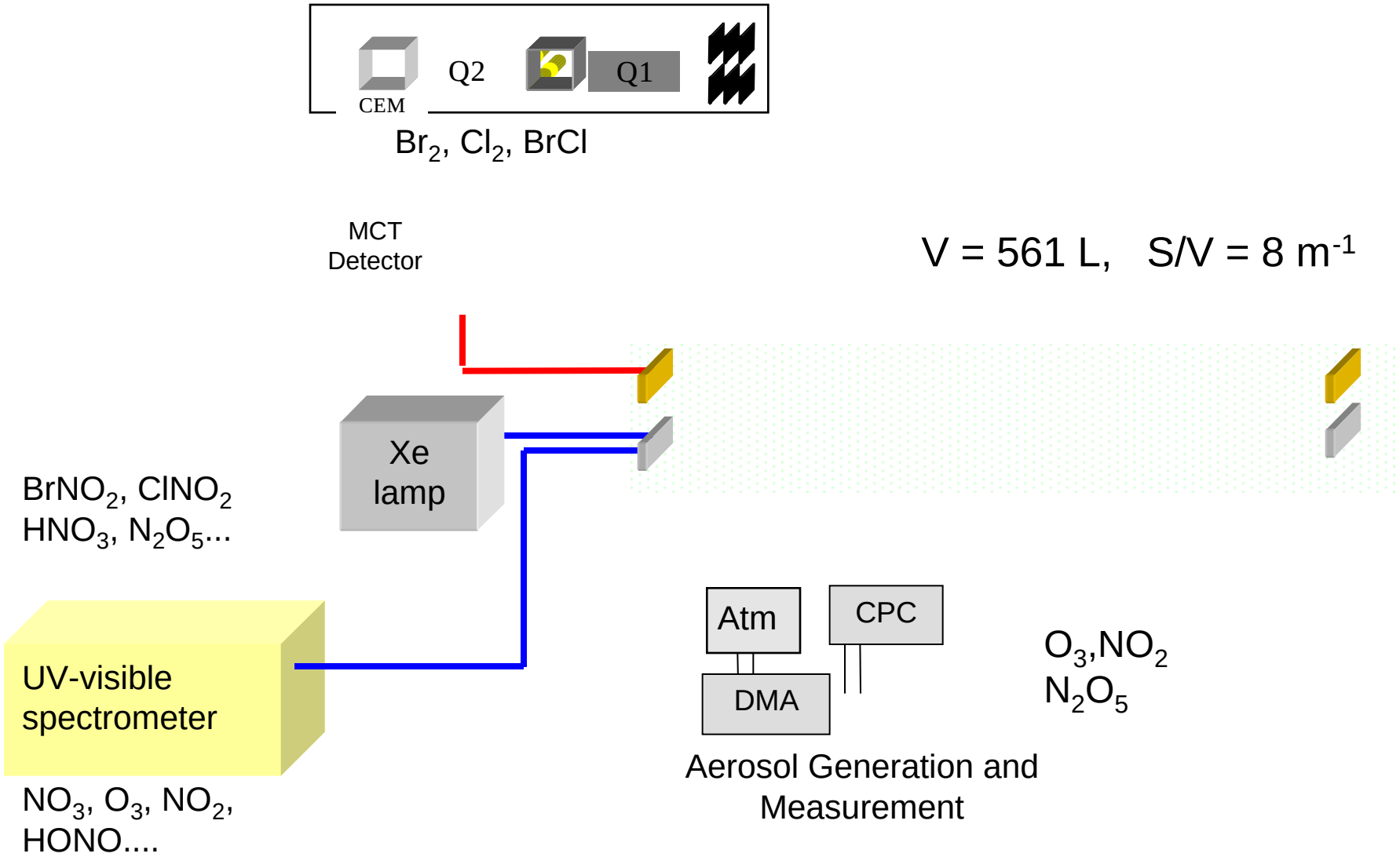




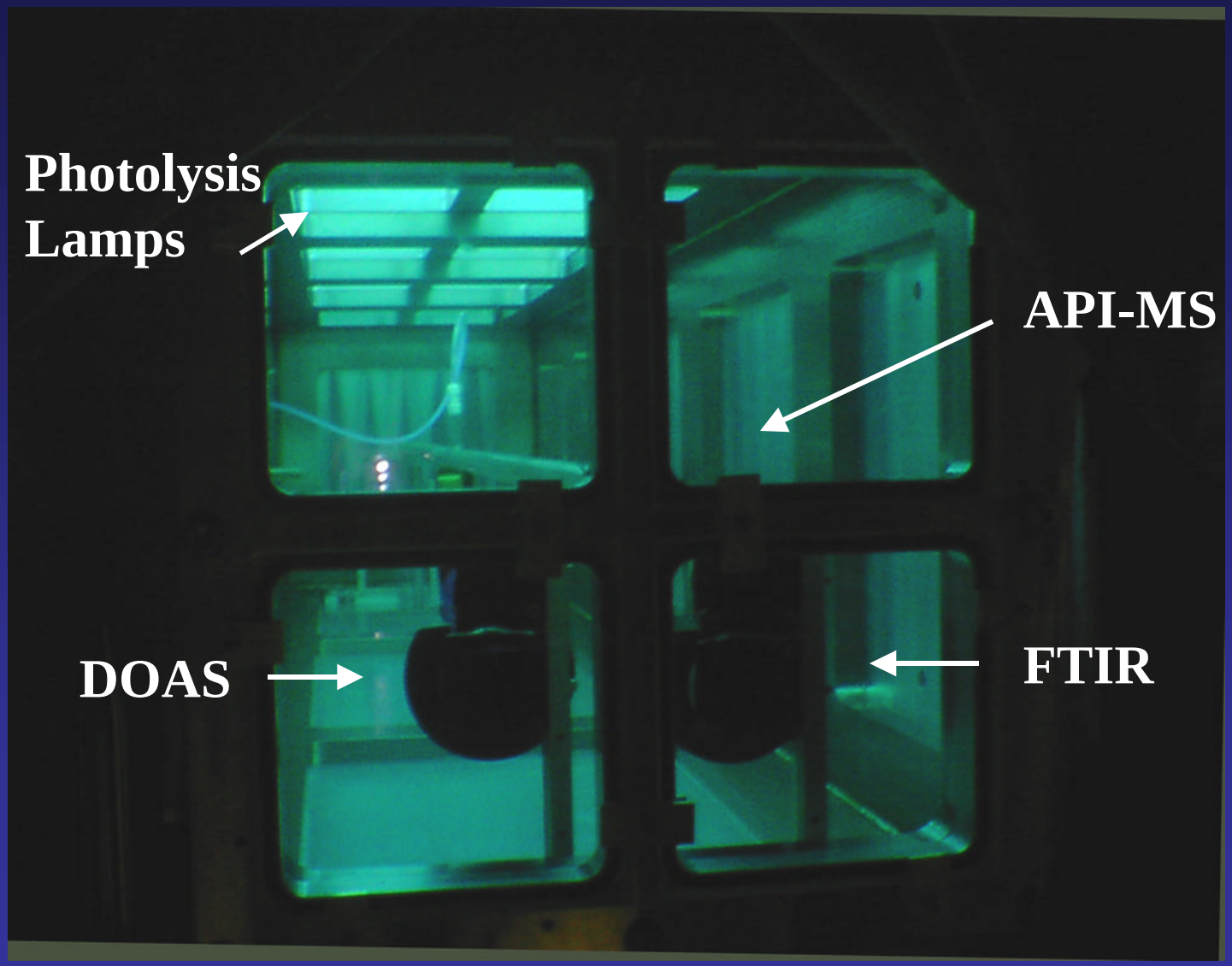
- Br^- prefers interface compared to Cl^-

Jungwirth & Tobias, *J. Phys. Chem B.* 105 10468 (2001)

Aerosol Chamber



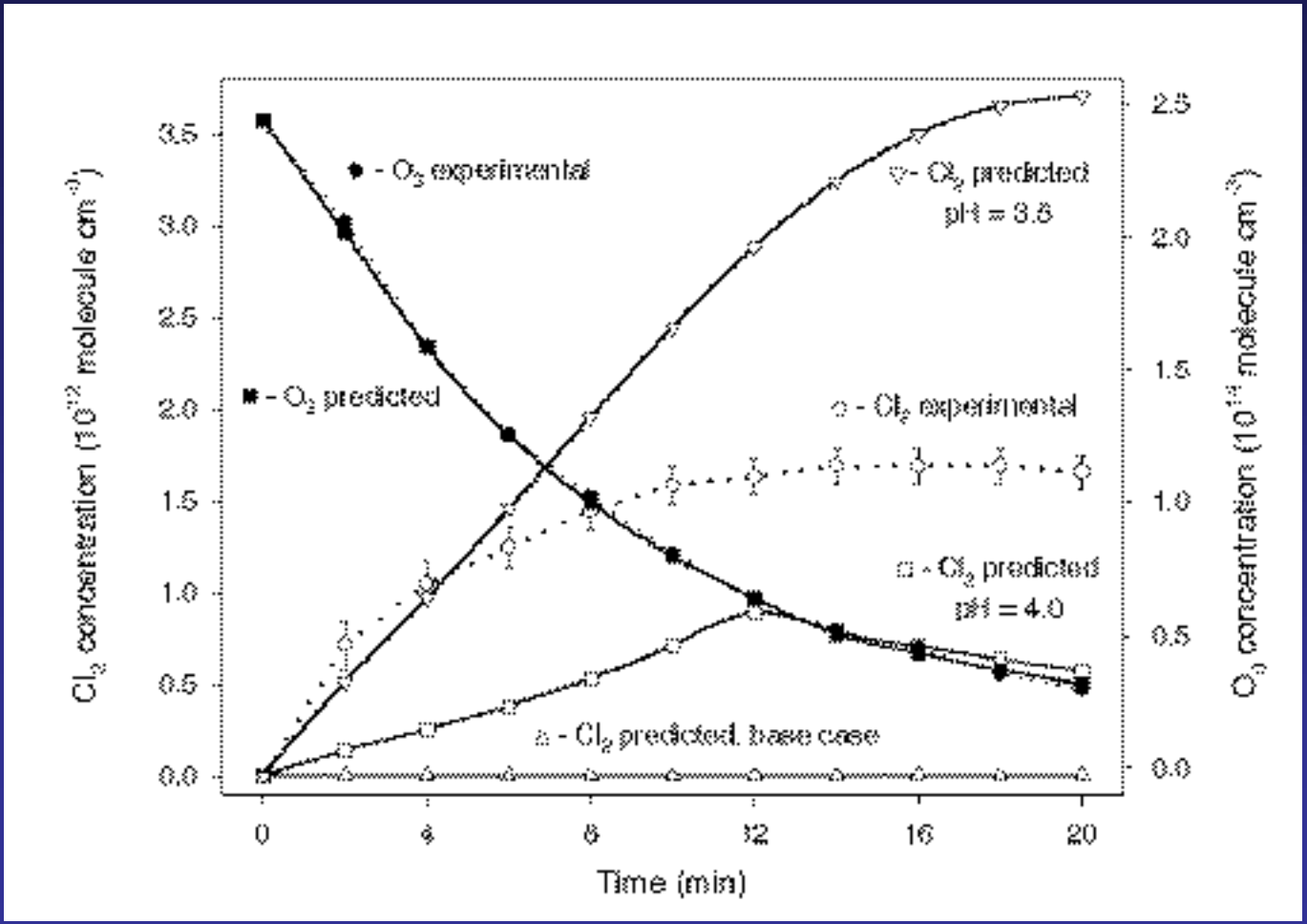
Aerosol Chamber



Experiment

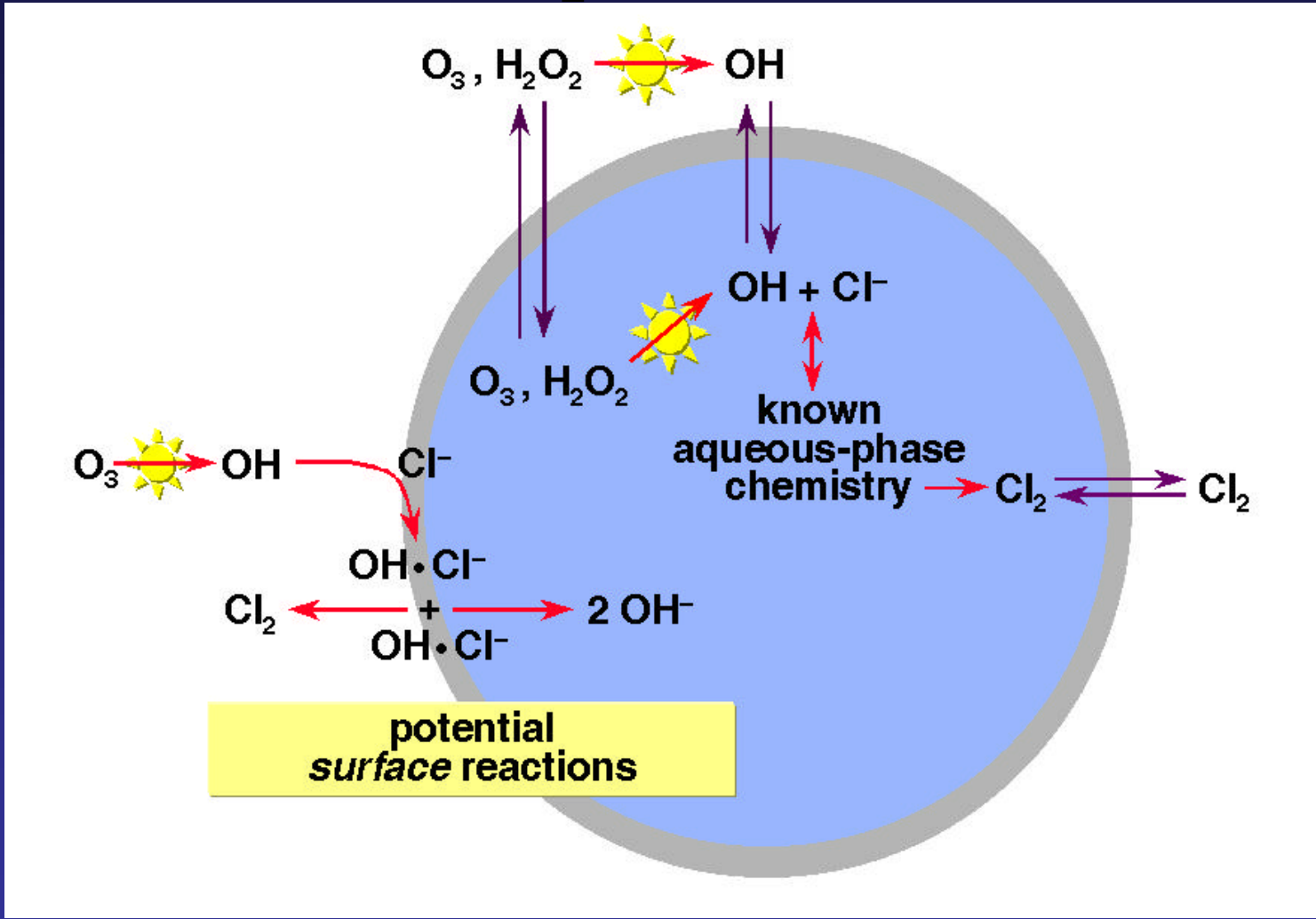
- Add NaCl or NaBr particles with measured size distribution to chamber in air at RH above the deliquescence point
- Add O_3
- Photolyze to generate OH
- Monitor loss of O_3 and formation of gas phase products by FTIR, DOAS and API-MS

Model Results Using Known Gas and Aqueous Phase Chemistry: Disaster!



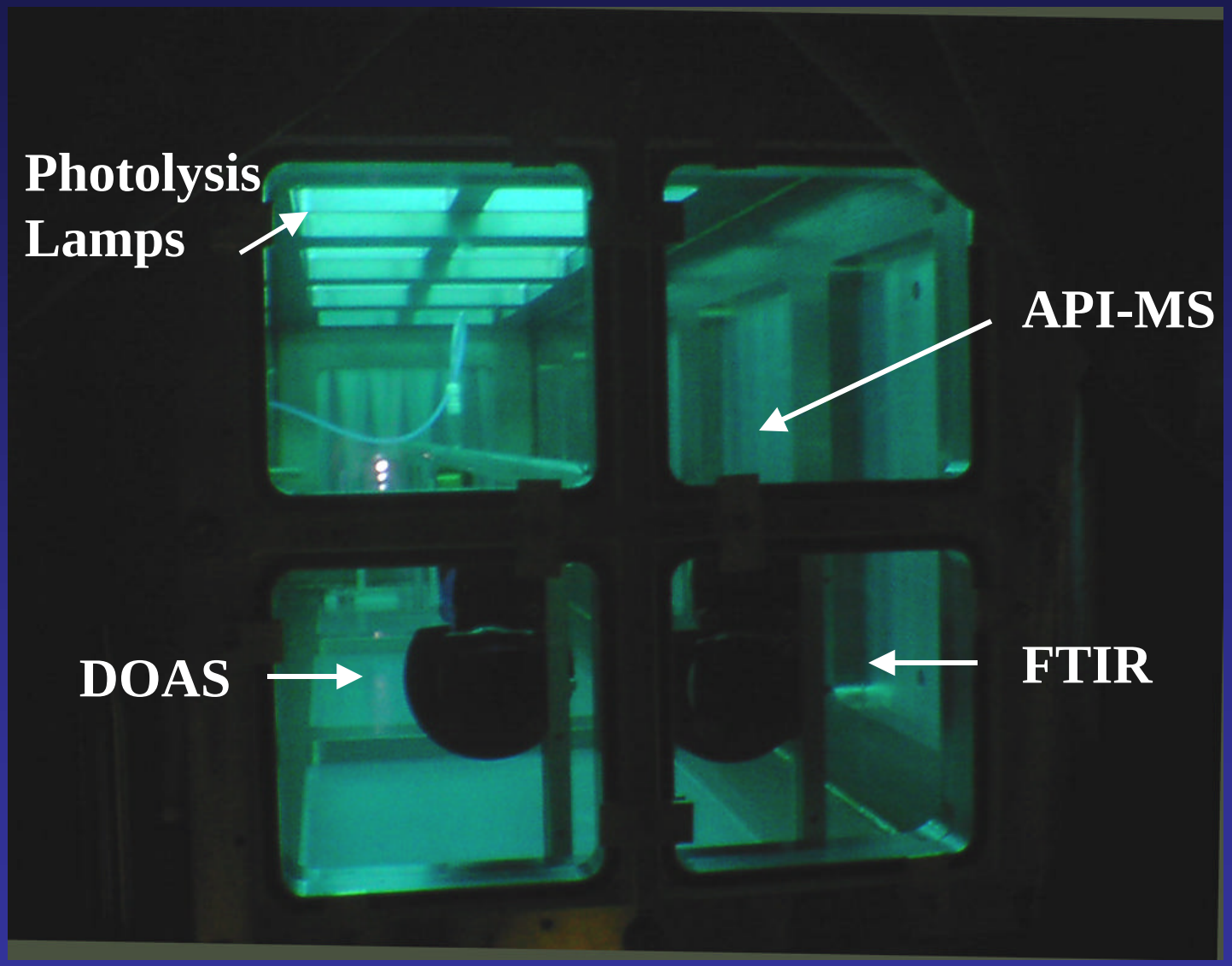
Knipping et al., *Science* 288 301 (2000)

Schematic of Proposed Surface Reactions

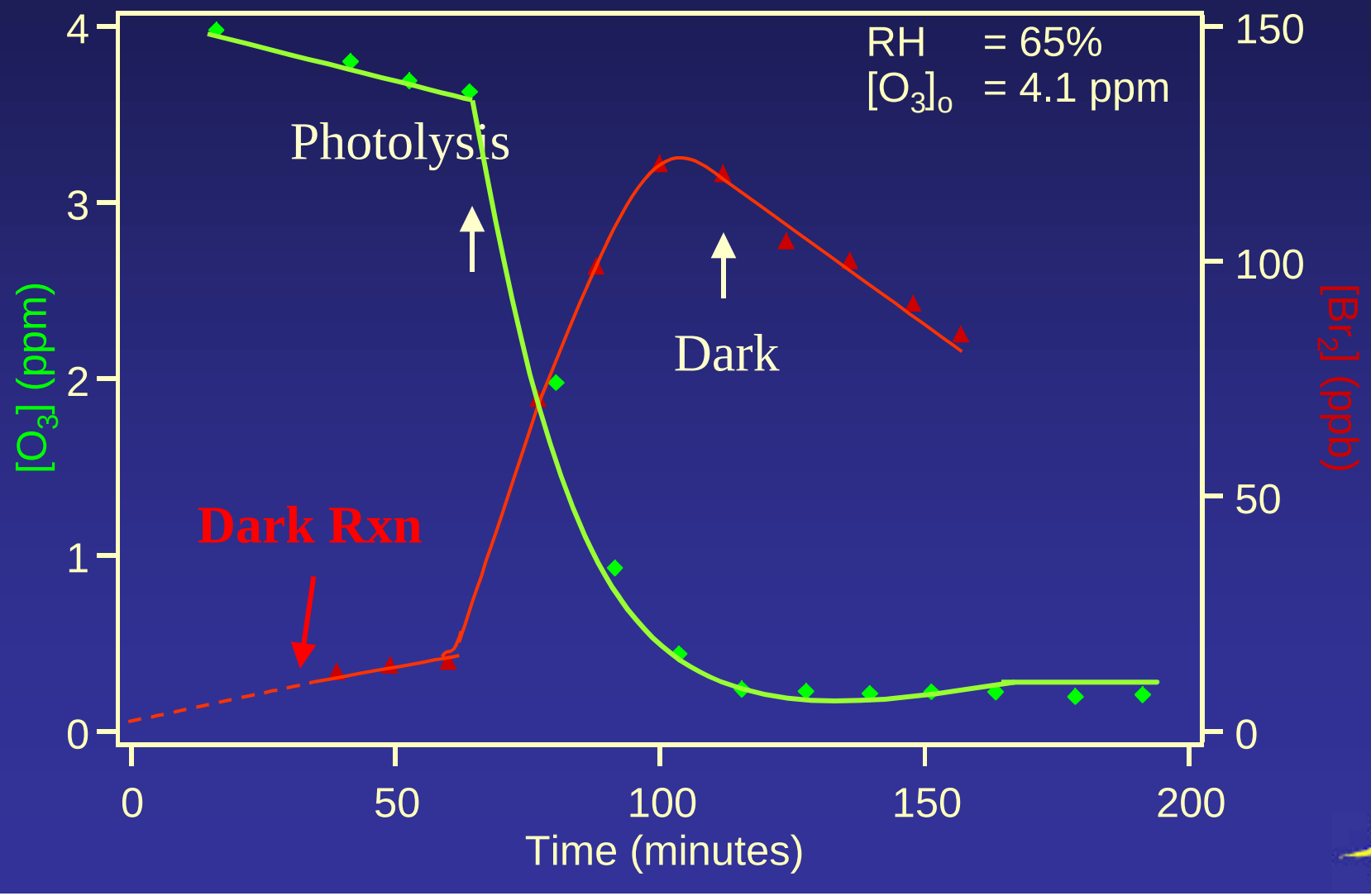


Does Br^- also undergo interface reactions, and if so, how important might they be?

Aerosol Chamber



Generation of Br_2 in O_3/OH Reaction with Deliquesced NaBr Aerosols



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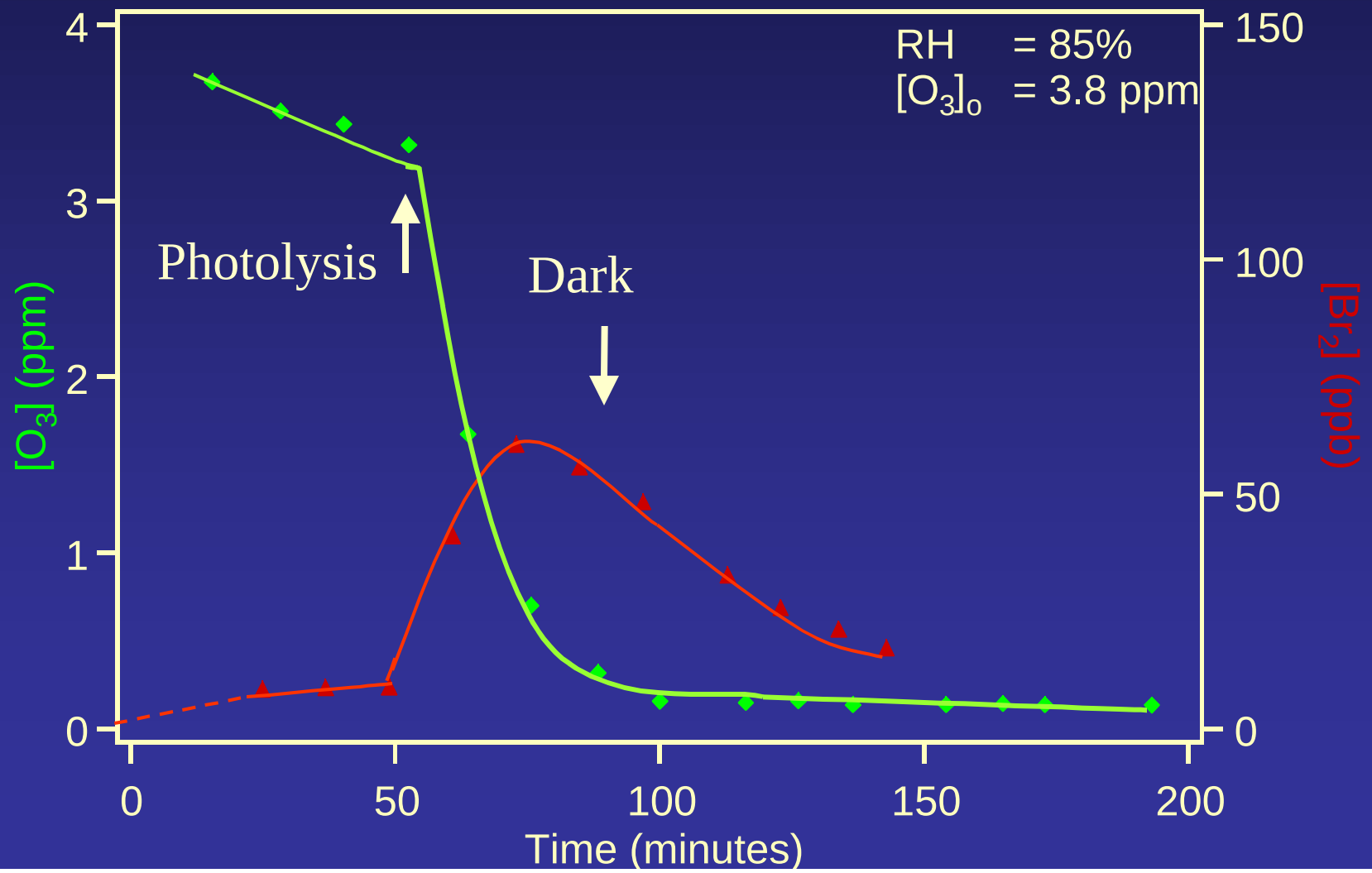
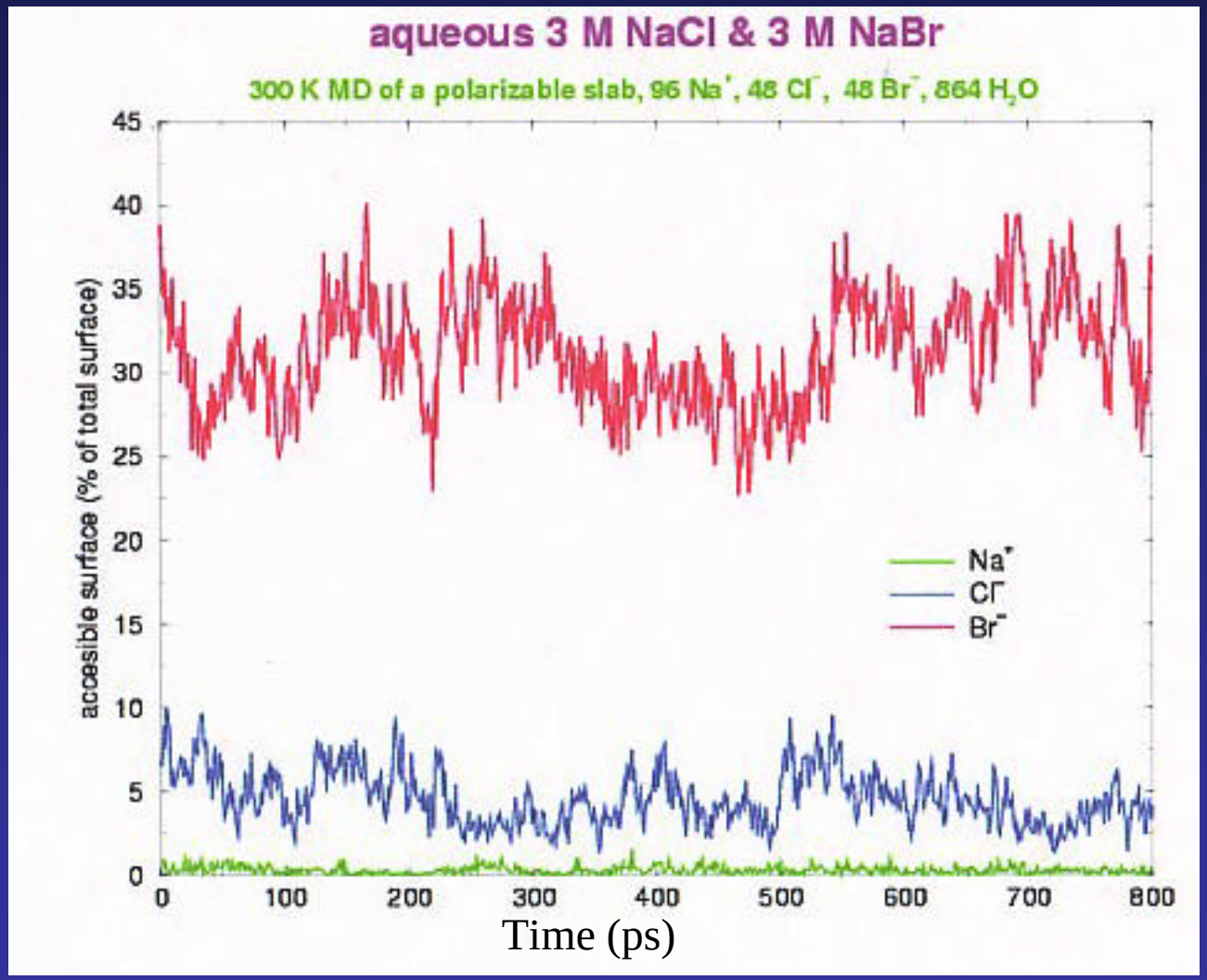


Current Work

- NaBr chemistry over wider range of conditions (O_3, RH, particle concentration and size distribution etc)
- Assess importance of interface vs bulk chemistry
- NaCl/NaBr mixtures

Br^- and Cl^- in Water "Slab"



Jungwirth and Tobias, *JPC*, in press

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