Laboratory Studies of Heterogeneous Reactions of Sea Salt Particles

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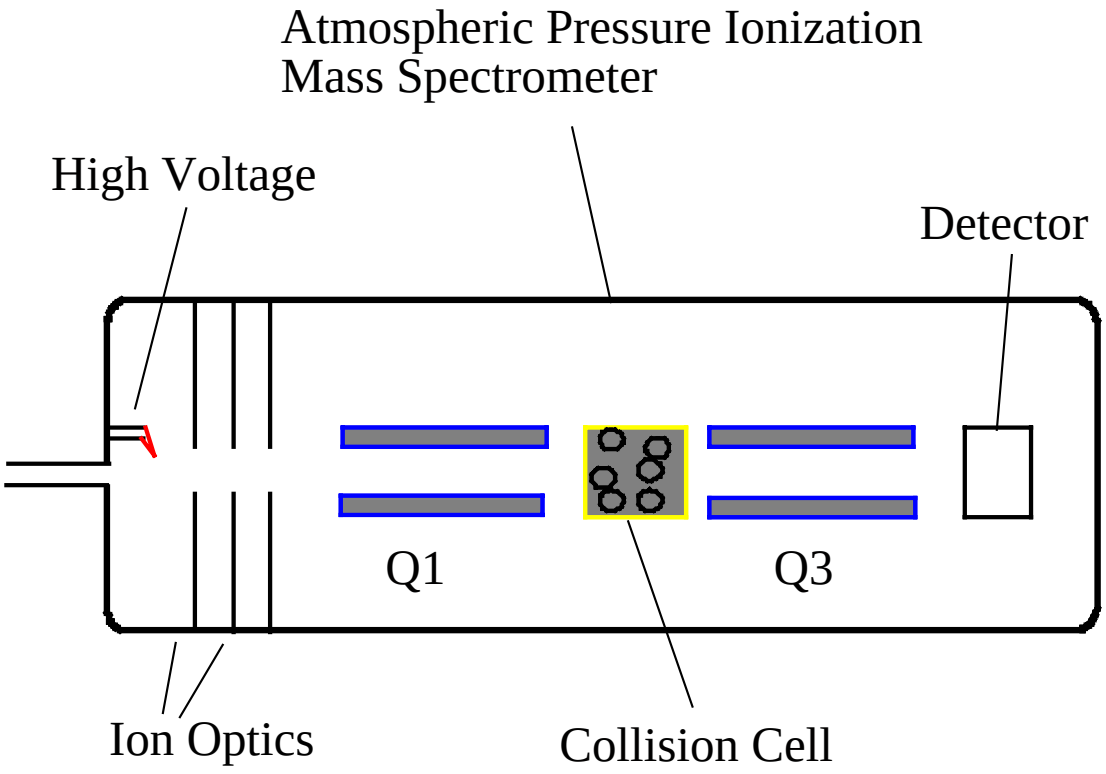
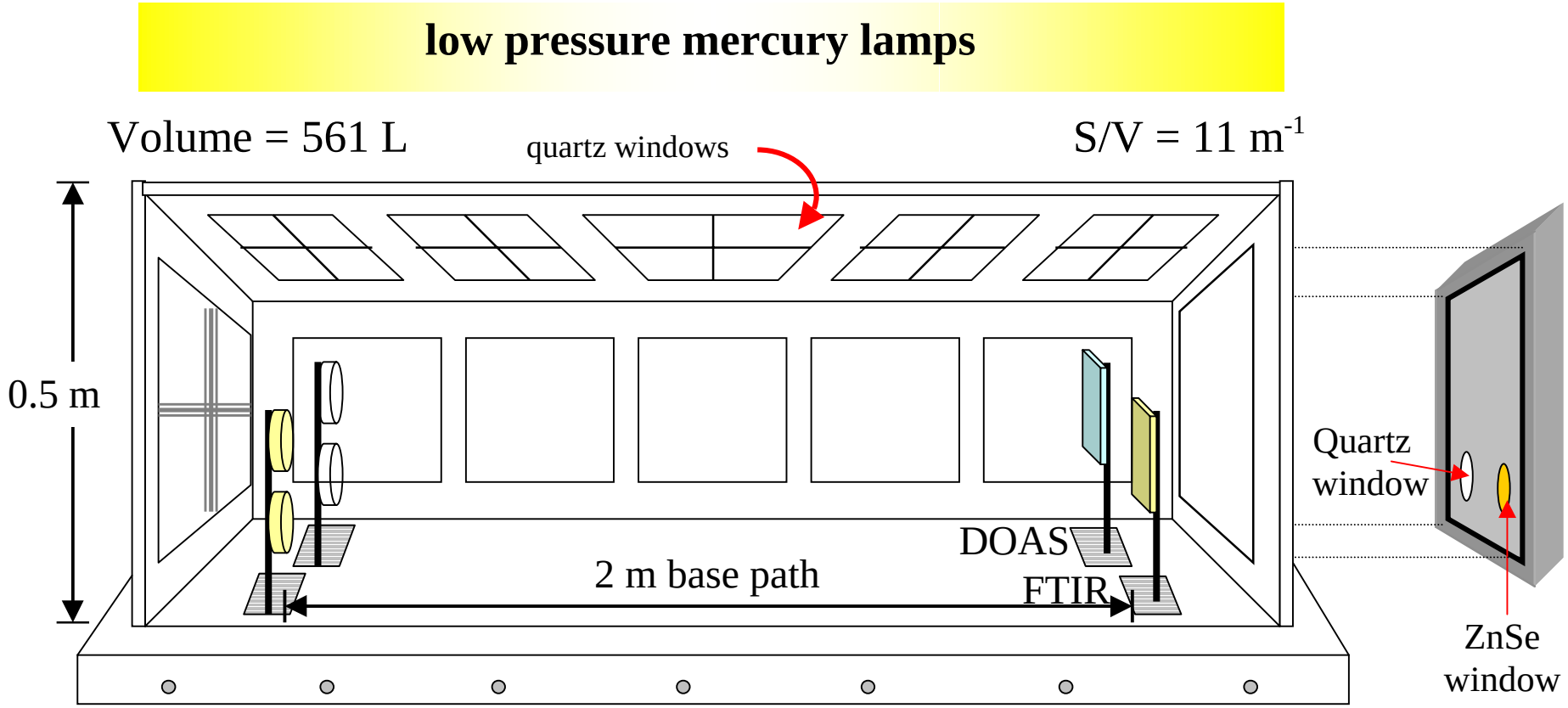
Tropospheric Halogen Chemistry

Atmospheric Pressure Ionization Mass Spectrometry (API-MS)



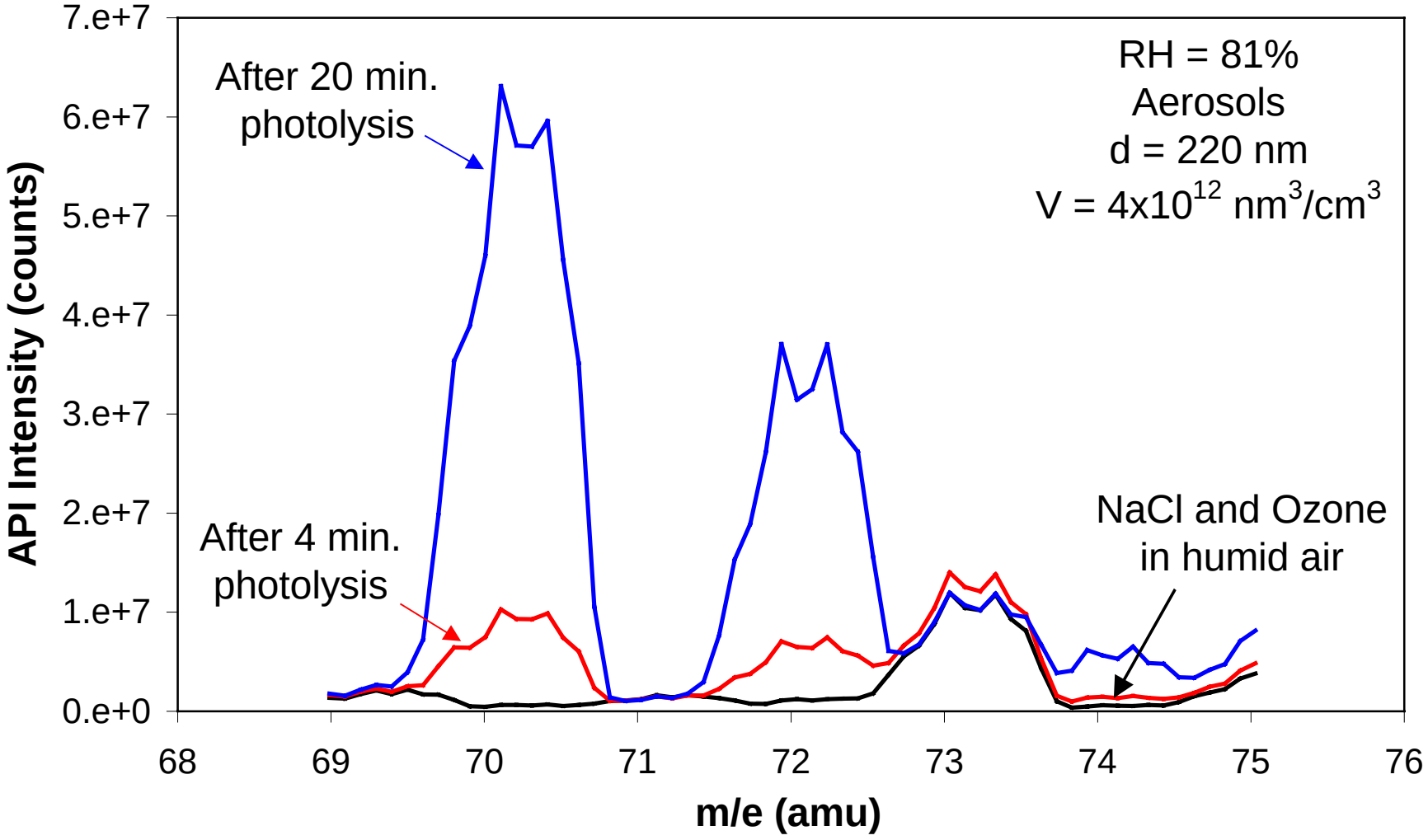
Chemical Ionization: O_2^- (O_2/H_2O) + $Cl_2 \rightarrow O_2 + Cl_2^-$

Aerosol Chamber Diagram



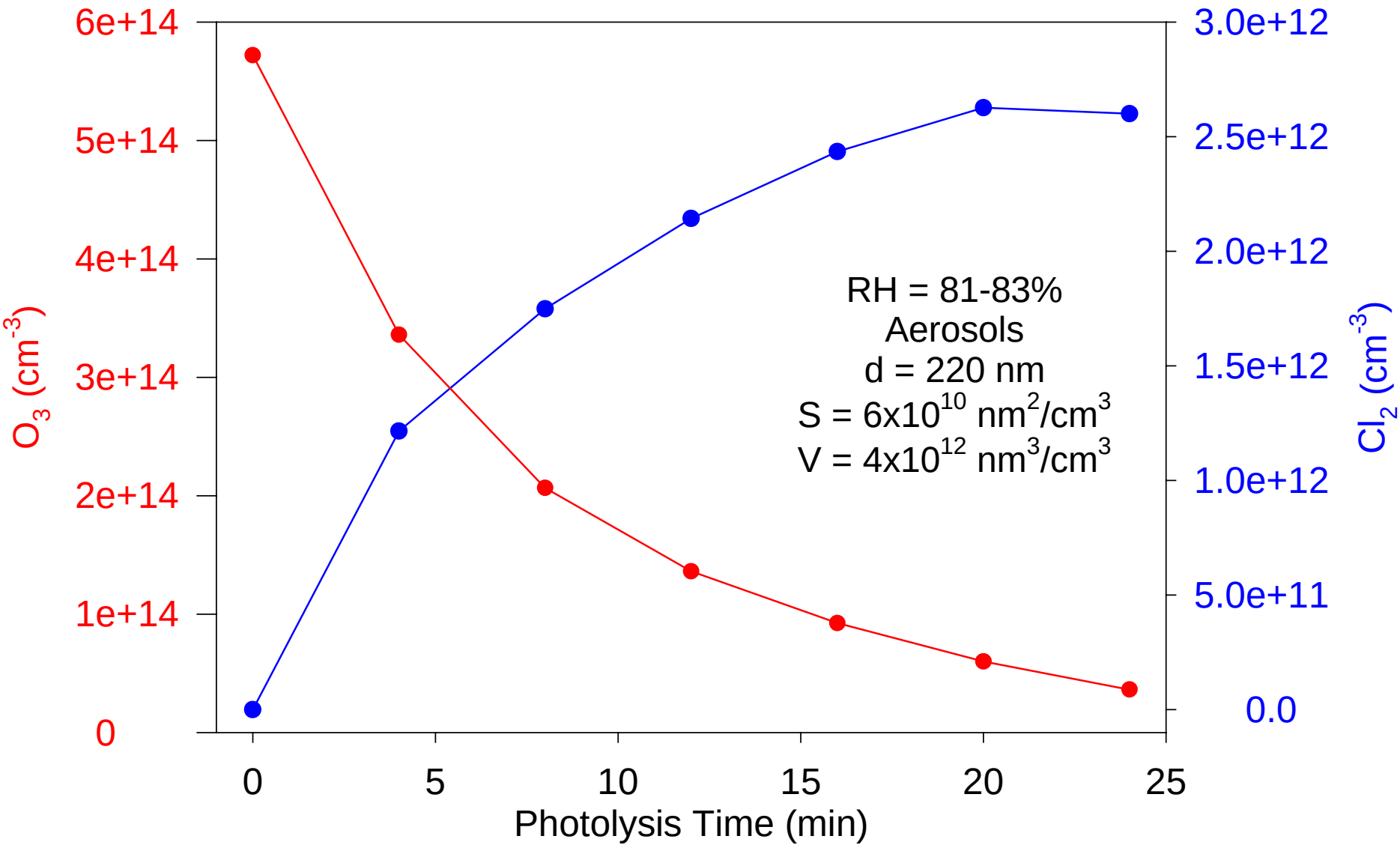
Analytical Techniques: Long-path FTIR, DOAS, and Atmospheric Pressure Ionization Mass Spectrometry

Cl_2 Production with Ozone and NaCl Aerosols



- In the ozone + NaCl aerosol experiments, peaks at 70, 72, and 74 were seen to increase only above 75 %RH and only with photolysis.

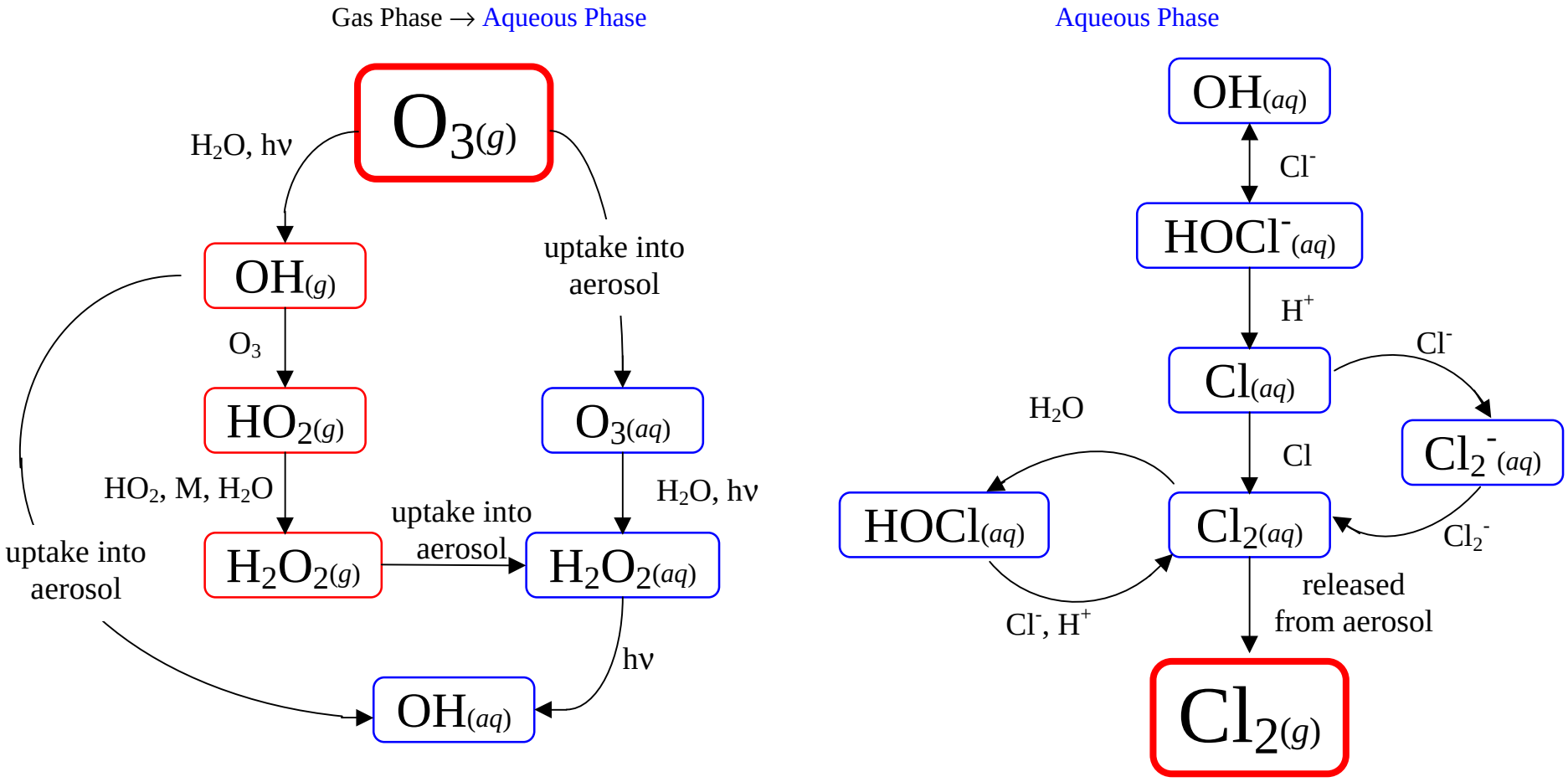
Typical Cl_2 Production: O_3 + NaCl(*aerosols*)



- After 20 minutes photolysis, 23 ppm ozone produced 107 ppb Cl_2.

Potential Mechanism for Cl_2 Production

(based on known aqueous phase chemistry)



Eigen and Kustin, 1962; Jayson *et al*., 1973; Nagaran and Fessendon, 1985; Neta *et al*., 1988 and references therein

Cl Atom Kinetics and Mechanisms

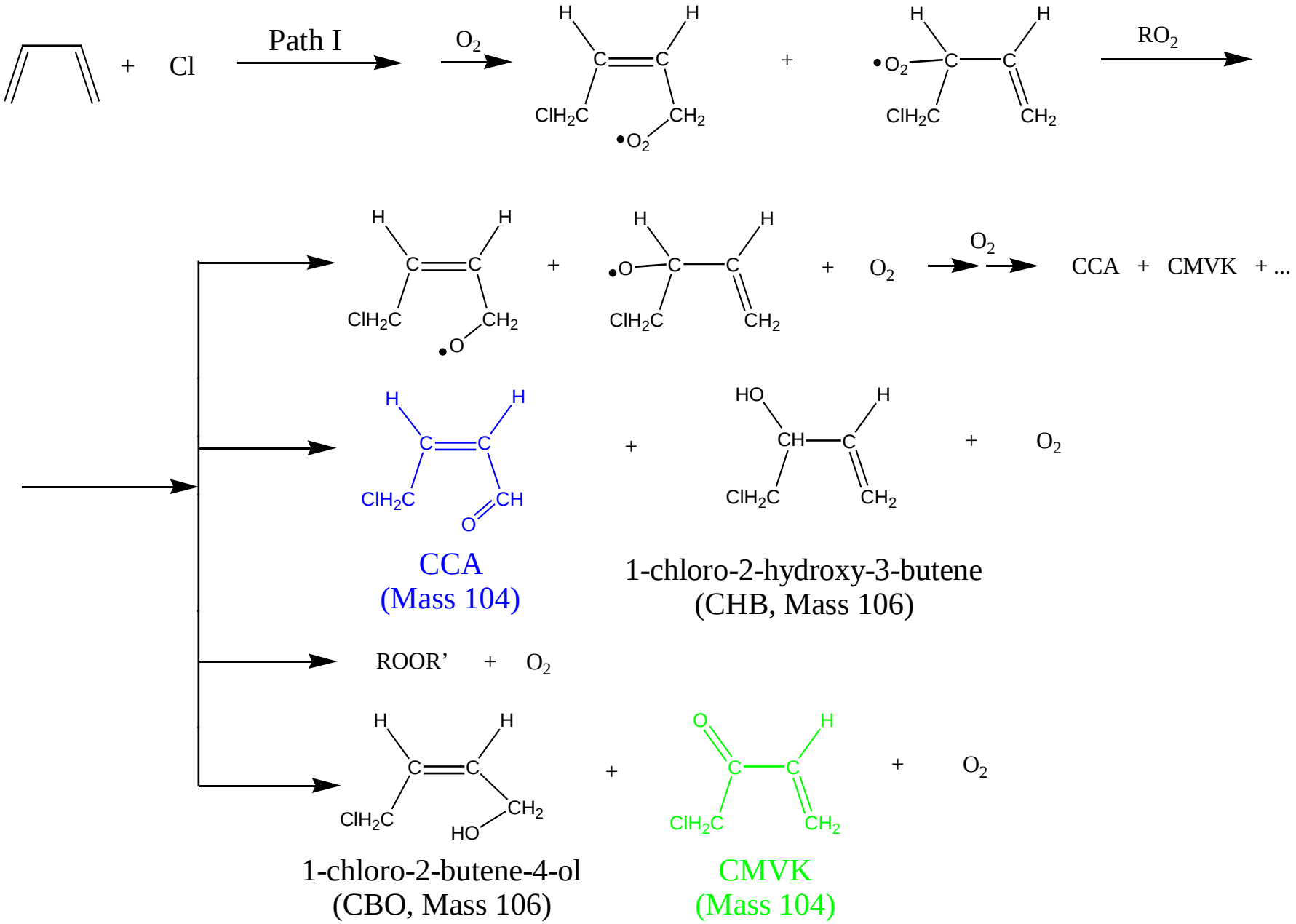
- 1,3-Butadiene is an airborne toxic substance. One of its major sources is automobile emissions.

- 1,3-Butadiene can react with OH radicals, O_3, NO_3 radicals and Cl atoms in air.

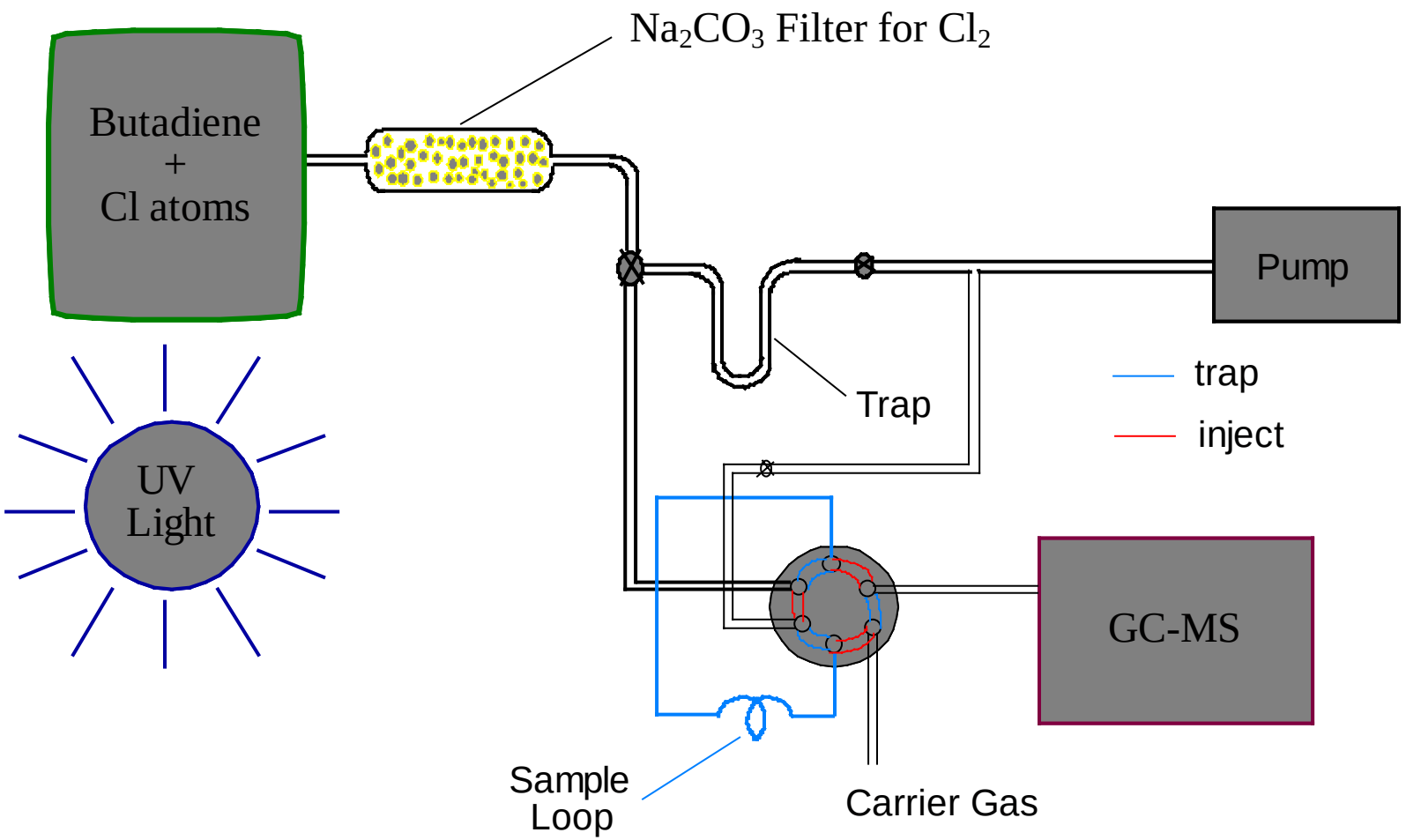
- Cl atoms may be generated by reactions of sea salt particles transported inland with air masses.

- A potential approach to investigate the importance of chlorine atom chemistry in the coastal areas is to identify the products and mechanisms of its reactions with organics, e.g. 1,3-butadiene, since both 1,3-butadiene and chlorine atoms can be abundant.

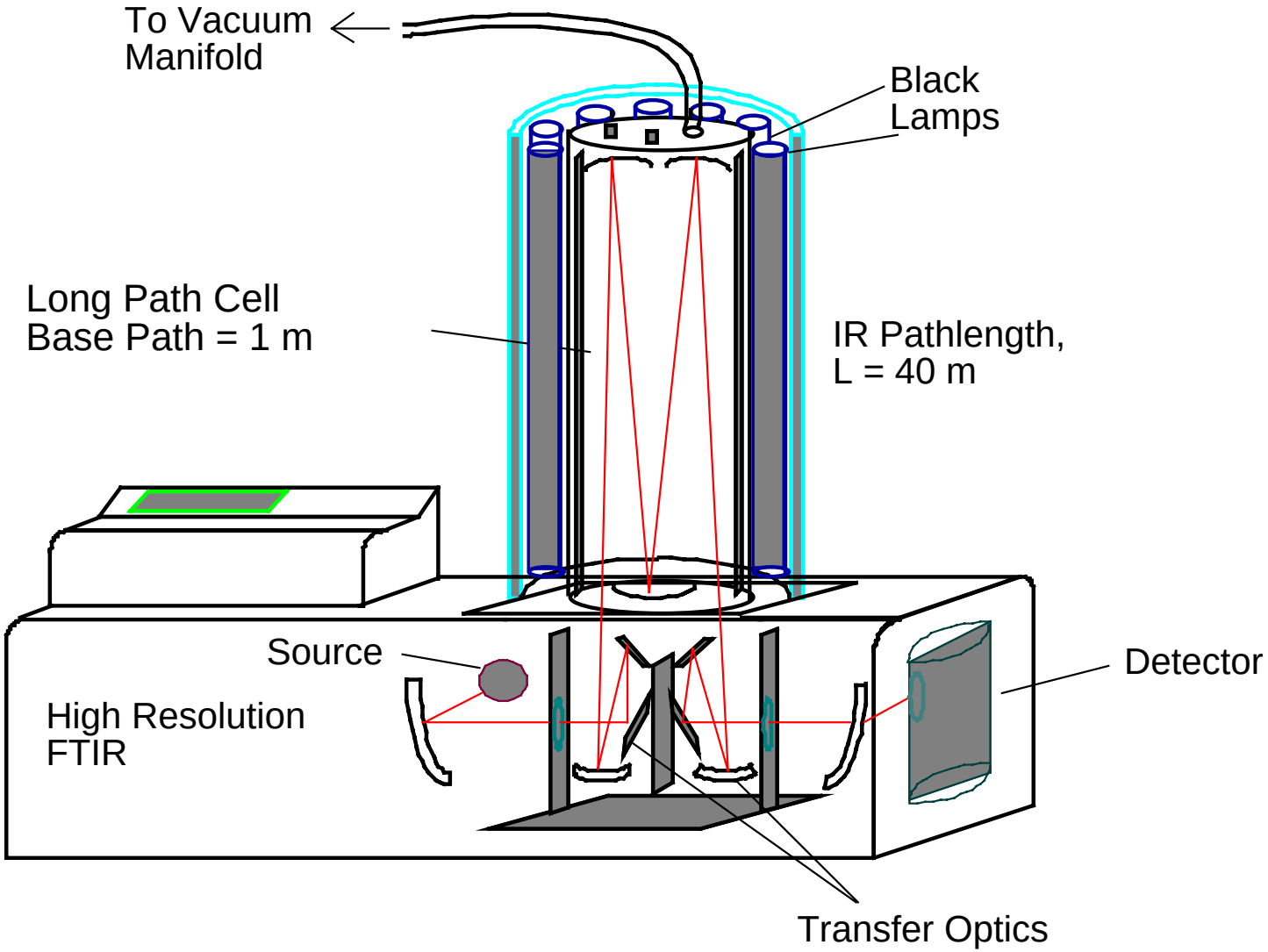
Reaction of 1,3-Butadiene With Cl Atoms in the Absence of NO



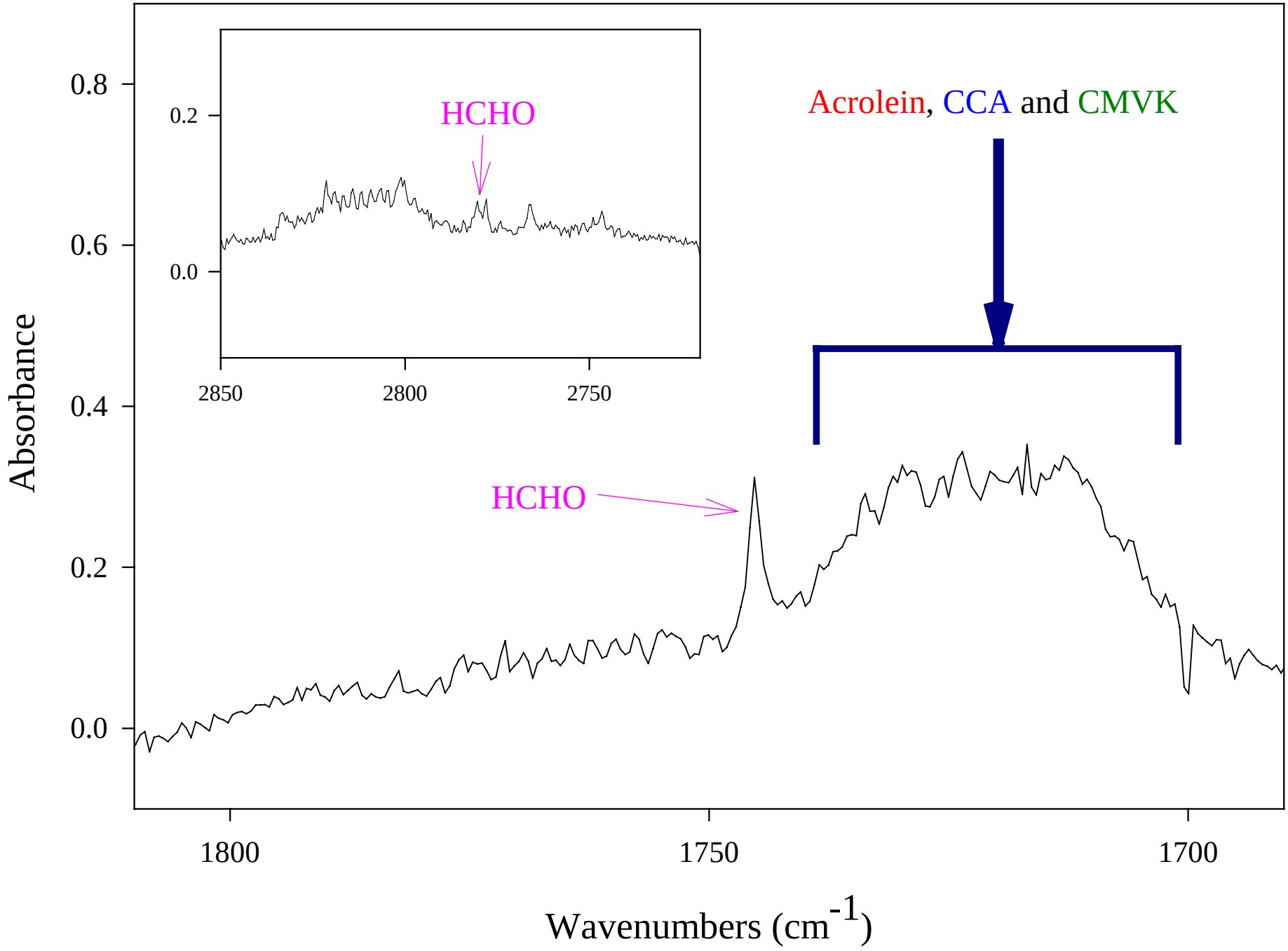
GC-MS Experimental Apparatus



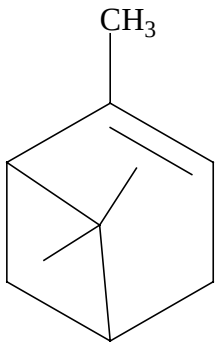
FTIR Experimental Apparatus



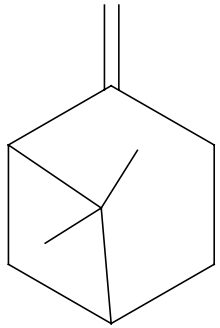
Carbonyl Products of 1,3-Butadiene + Cl + NO



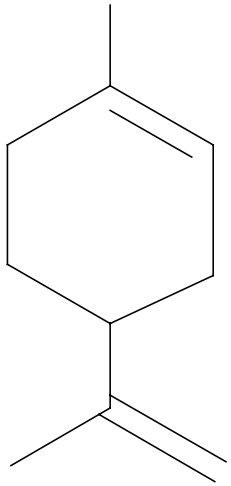
Biogenic Compounds Used in Relative Rate Study



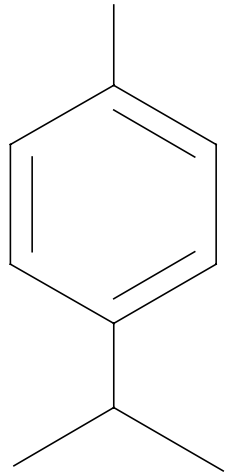
α-pinene



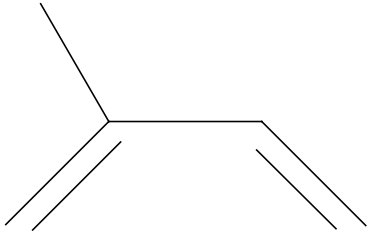
β-pinene



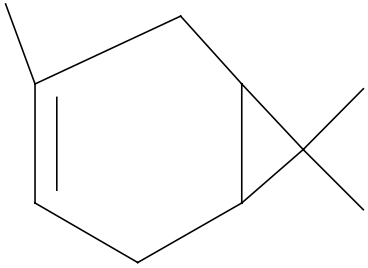
limonene



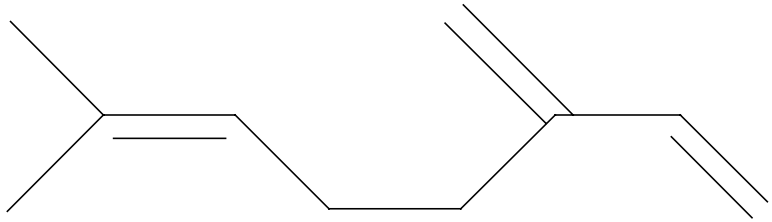
p-cymene



isoprene

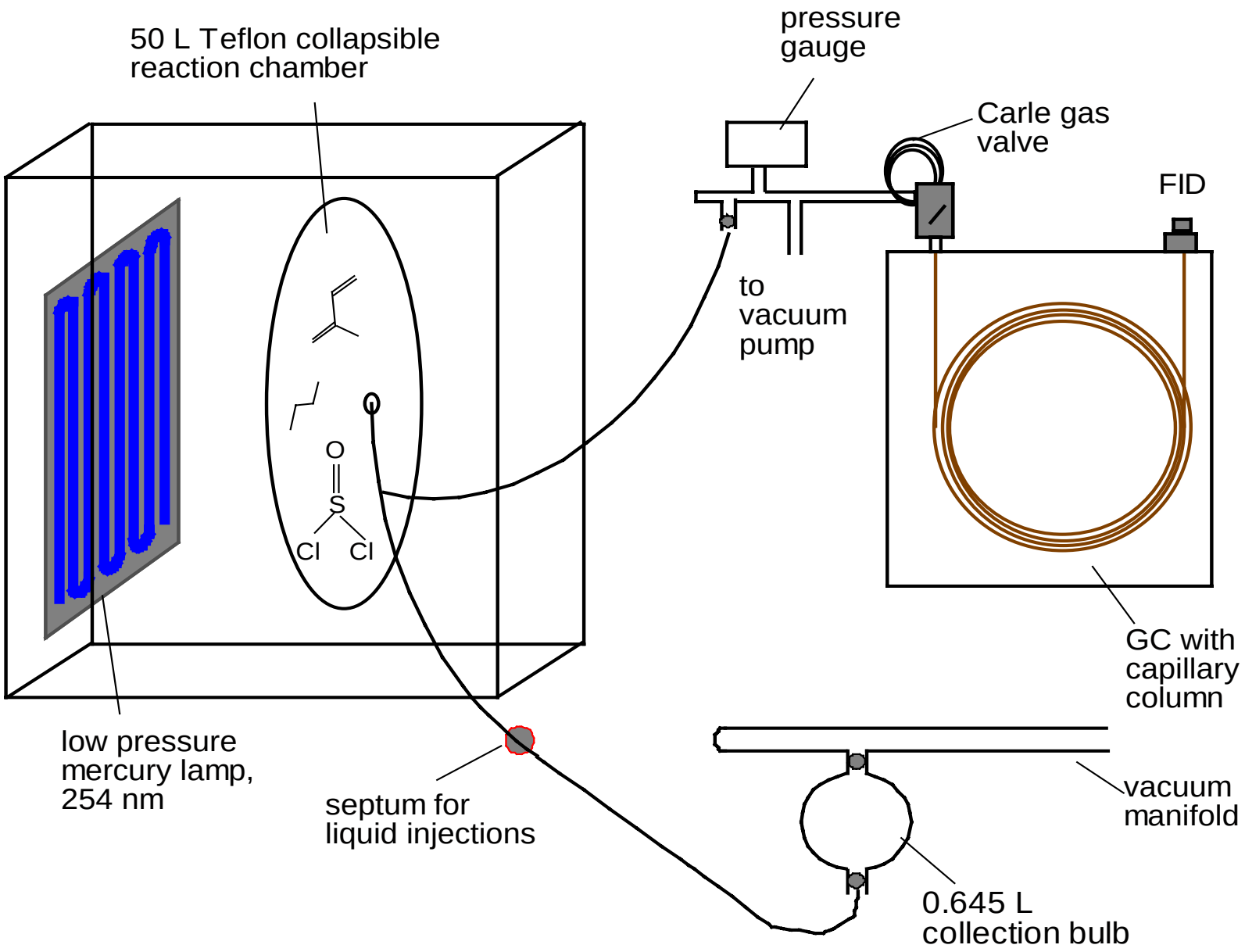


3-carene

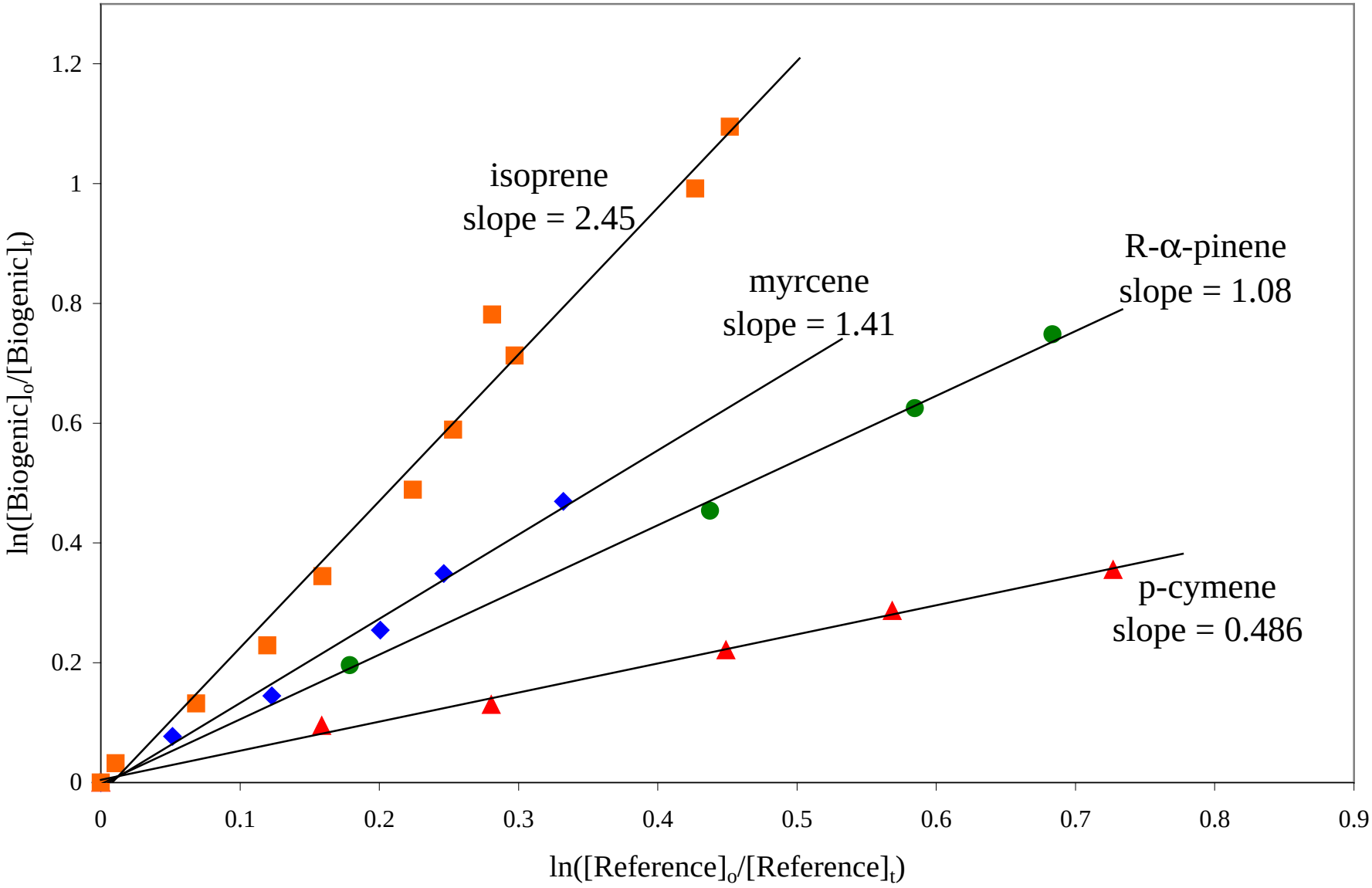


myrcene

Experimental Apparatus



Typical Relative Rate Plots for Some Biogenics



- Reactions of biogenics with chlorine atoms are fast, approximately collision-controlled.

Atmospheric Implications

- Chlorine atom reactions are fast.

Biogenic	**k_{Cl} (10^{-10} cm^3 $molecule^{-1}$ s^{-1})[a]**	**τ_{Cl}[b] (hrs)**	**k_{OH} (10^{-10} cm^3 $molecule^{-1}$ s^{-1})[c]**	**τ_{OH}[b] (hrs)**
isoprene	5.1	11	1.01	5.6
α-pinene	4.7	12	0.537	10
β-pinene	5.3	10	0.789	7.0
limonene	6.4	8.7	1.71	3.2
myrcene	6.6	8.4	2.15	2.6
3-carene	5.6	9.9	0.88	6.4
p-cymene	2.1	26	0.15[d]	38
methyl vinyl ketone	2.0	28	0.19[d]	30

[a]From this work and Ragains and Finlayson-Pitts, *J. Phys. Chem. A*, 101, 1509 (1997).
[b]Assuming [Cl]=5×10^4 atoms cm^{-3} and [OH]=5×10^5 radicals cm^{-3}.
[c]From Atkinson, *J. Phys. Chem. Ref. Data*, 26, 215 (1997).
[d]Atkinson, *J. Phys. Chem. Ref. Data, Monograph No. 2* (1994)

- Chlorine atom chemistry is likely to be important in the early morning when photolysis of ClX compounds occurs, while OH chemistry is important in midday.

- If chlorine forms unique products with biogenics, then these products might serve as accurate markers for the determination of chlorine atom reactions and chlorine atom concentration.

Acknowledgments

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- National Science Foundation