



EARTH SYSTEM RESEARCH LABORATORY

Serving Society through Science

Ozone Destruction and Recovery

The Role of Laboratory Studies

- A) A General Perspective
- B) The Cl_2O_2 Controversy and Recent CSD Lab Studies

James Burkholder

Chemical Sciences Division



ESRL Theme Presentation: Ozone Recovery
Dec. 4, 2008

What do we mean by “Laboratory Studies” ?

The study of elementary chemical processes relevant to Earth’s atmosphere under well-controlled conditions

Objective: Quantify a species

- (1) Reactivity (OH, Cl, O₃, HO₂, NO₃,...)
- (2) Atmospheric lifetime
- (3) Radiative properties
- (4) Environmental Impact

Products

Rates and Mechanisms
seconds - 1000s years
Radiative Efficiency
Air Quality
Climate-chemistry coupling
Ozone Depletion Potential (ODP)
Global Warming Potential (GWP)

Reaction Kinetics



Infrared Spectroscopy



Laboratory Studies

Photochemistry



UV Spectroscopy



Theoretical Calculations



Labs: 1A202,
1A204 Area

Classes of Compounds Studied and Their Impact on Ozone Recovery and Climate

Examples:

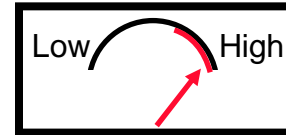
CFCs

Chlorofluorocarbons

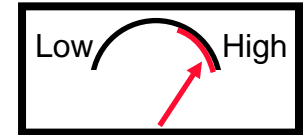
CCl_3F (Freon 11)

CCl_2F_2 (Freon 12)

Ozone Depletion Potential



Global Warming Potential

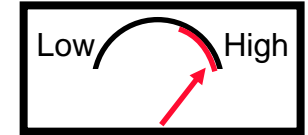
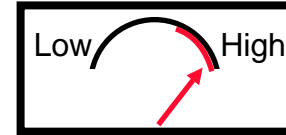


Halons

Bromocarbons

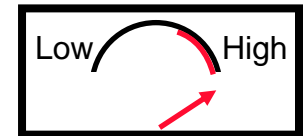
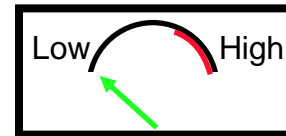
CF_3Br

CF_2ClBr



Perfluoro-compounds

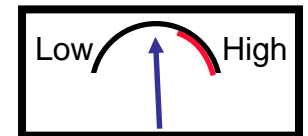
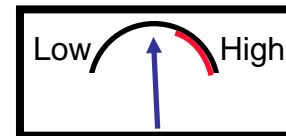
CF_4
 SF_6



HCFCs

Hydrochlorofluorocarbons

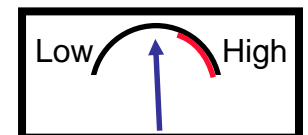
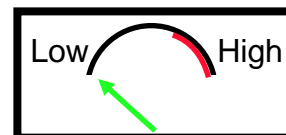
$\text{CH}_3\text{CCl}_2\text{F}$ (141b)



HFCs

Hydrofluorocarbons

CH_2FCF_3 (HFC-134a)



Classes of Compounds Studied and Their Impact on Ozone Recovery and Climate

Potential Substitutes



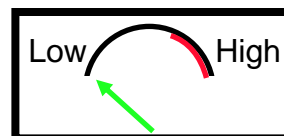
*Mobile Air Conditioning
(Cars)*



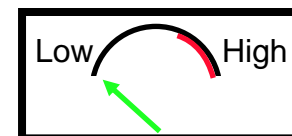
Fumigant

Ozone Depletion Potential

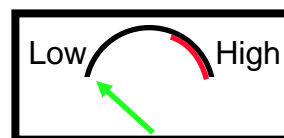
Global Warming Potential



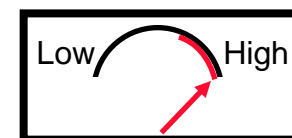
Win



Win



Win



Lose

Continuing Area of Research within CSD

Lab Results



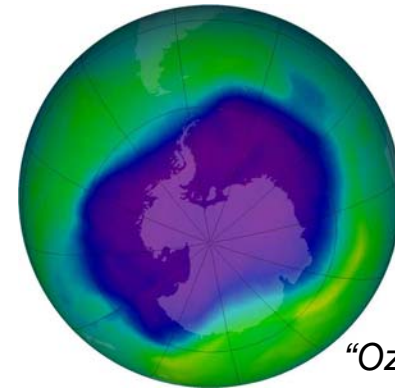
Informed Decisions



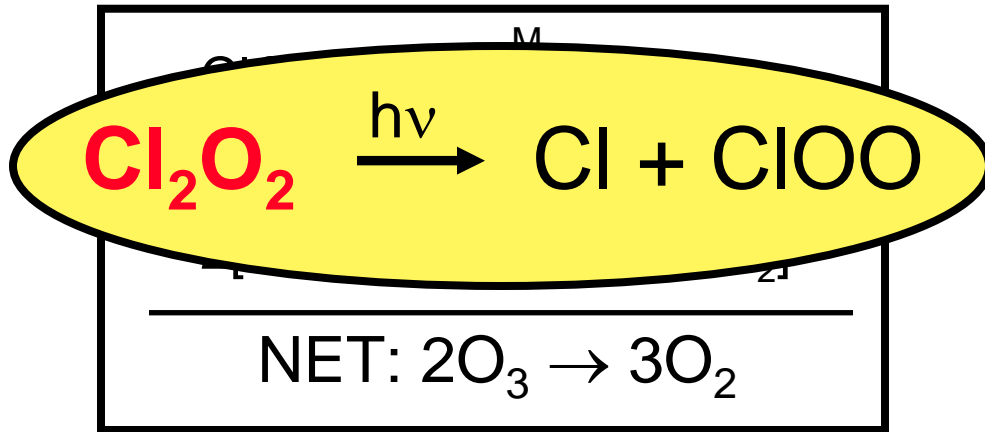
Commercial Sector
Policy (Protocols)

The Cl₂O₂ Controversy and Recent CSD Lab Studies

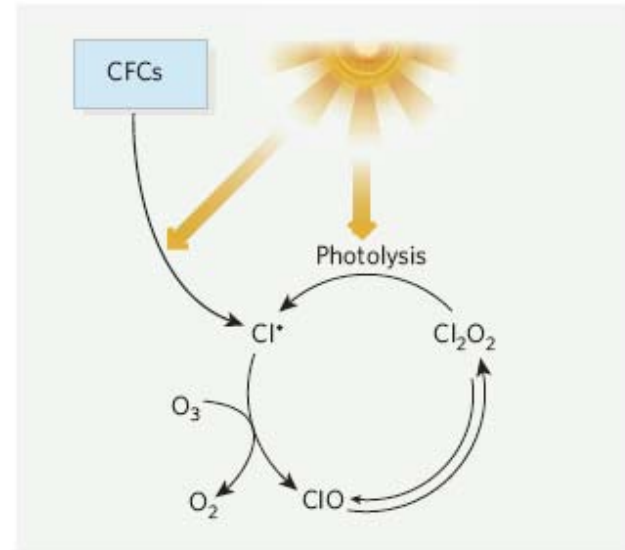
Chlorine chemistry plays a critical role in Polar Ozone Destruction



"Dimer" Cycle

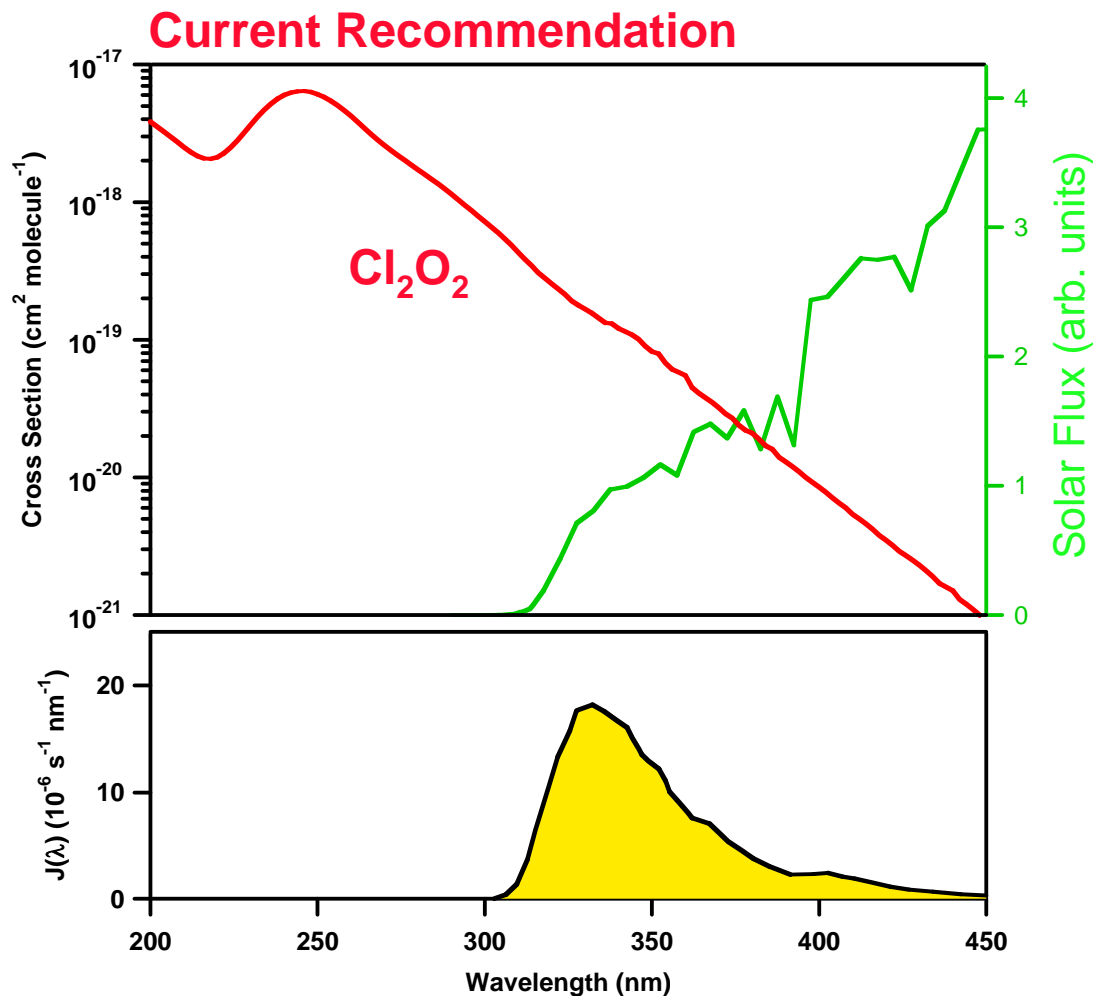


~60% of Total O₃ Loss



ClO + BrO Cycle: ~ 30%

The atmospheric photolysis of Cl₂O₂



Photolysis Rate

$$J = \int \underbrace{\sigma(\lambda)}_{\text{Cross Section}} \underbrace{\Psi(\lambda, z, \chi)}_{\text{Solar flux}} d\lambda$$

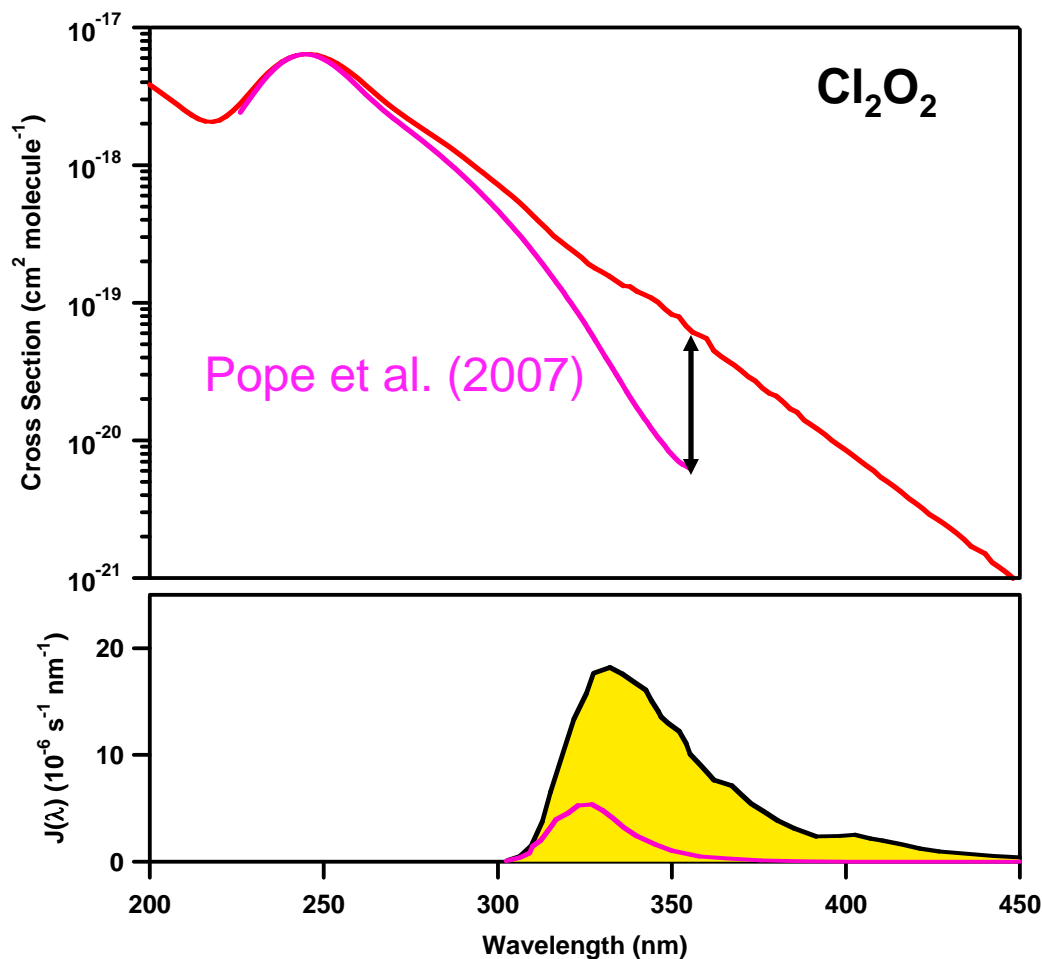
Cross Section

Solar flux

Important λ region: 310 - 400 nm

Input for Current Atmospheric Models

A Recently Reported Lab Study of Cl_2O_2 Creates Unrest !



Large Discrepancy with
Currently Recommended Values !

Is it important ?
YES !!

BIG IMPLICATIONS:

Much Slower Cl_2O_2 photolysis

Poor agreement between observations
and models

O_3 Loss and Rates
[ClO] and [Cl_2O_2]

High Profile Issue

Ripples through the
atmospheric science
community

nature

Vol 449/27 September 2007

NEWS

Chemists poke holes in ozone theory

ATMOSPHERIC SCIENCE

Revisiting Ozone Depletion

Marc von Hobe

21 DECEMBER 2007 VOL 318 SCIENCE www.sciencemag.org

Published by AAAS

New laboratory data imply unknown mechanisms in the formation of the ozone hole, but it is too soon to throw out the old paradigms.

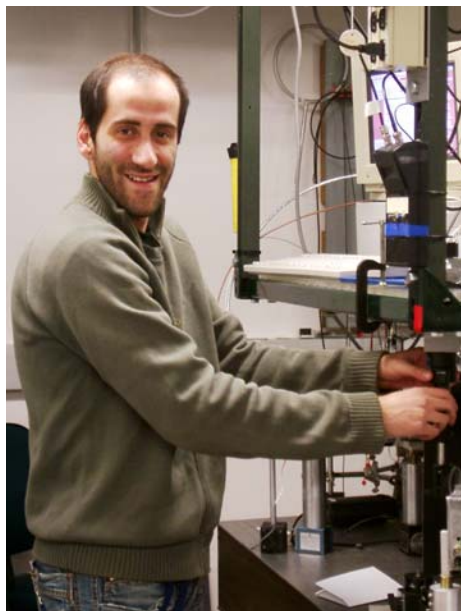
Public
Awareness

Why is it so hard to get the Cl_2O_2 spectrum Correct?

- * Difficult to prepare bulk samples of Cl_2O_2
- * Small cross sections in λ range of interest
- * **Impurities: Spectral Interferences (Cl_2)**

New CSD Lab Study: Pulsed UV Laser Photolysis of Cl_2O

Objective: Reduce uncertainties in $\sigma(\lambda)$ and spectrum shape

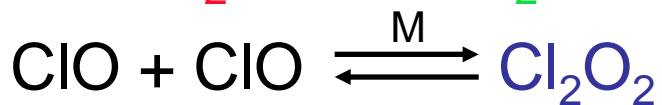
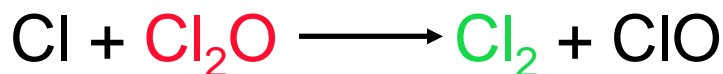
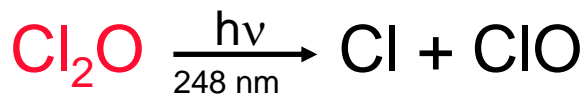


New Approach

- ✓ Minimizes uncertainties associated with Cl_2 spectral interference
A problem in most of the previous studies
- ✓ Direct measurements over the critically important wavelength range
Not achieved in many previous studies

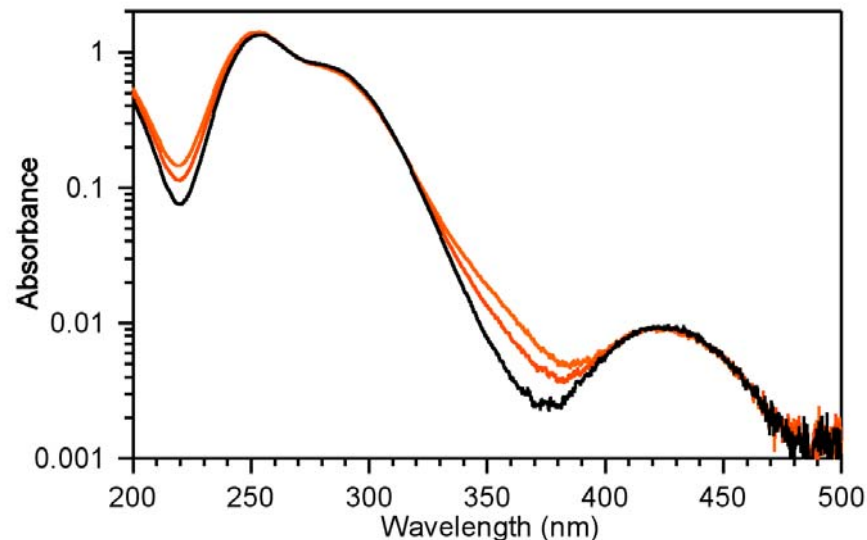
Pulsed UV Laser Photolysis of Cl₂O

Reaction Mechanism

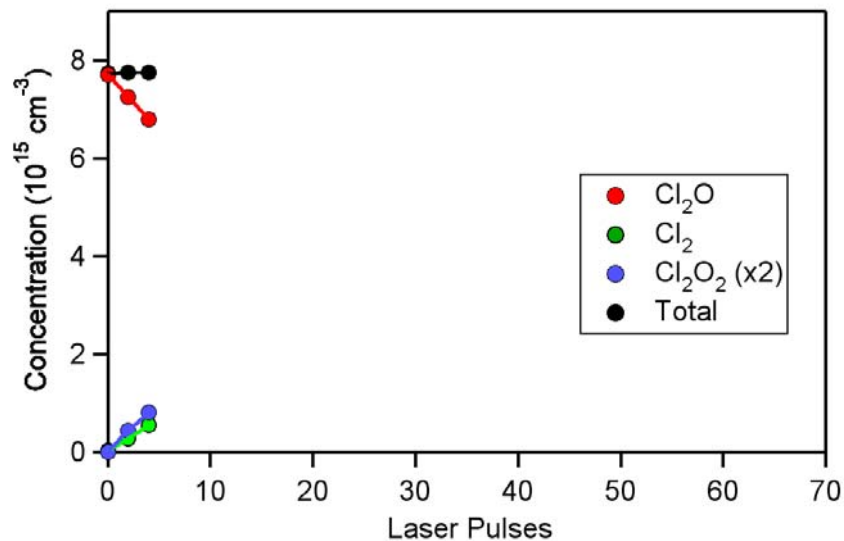
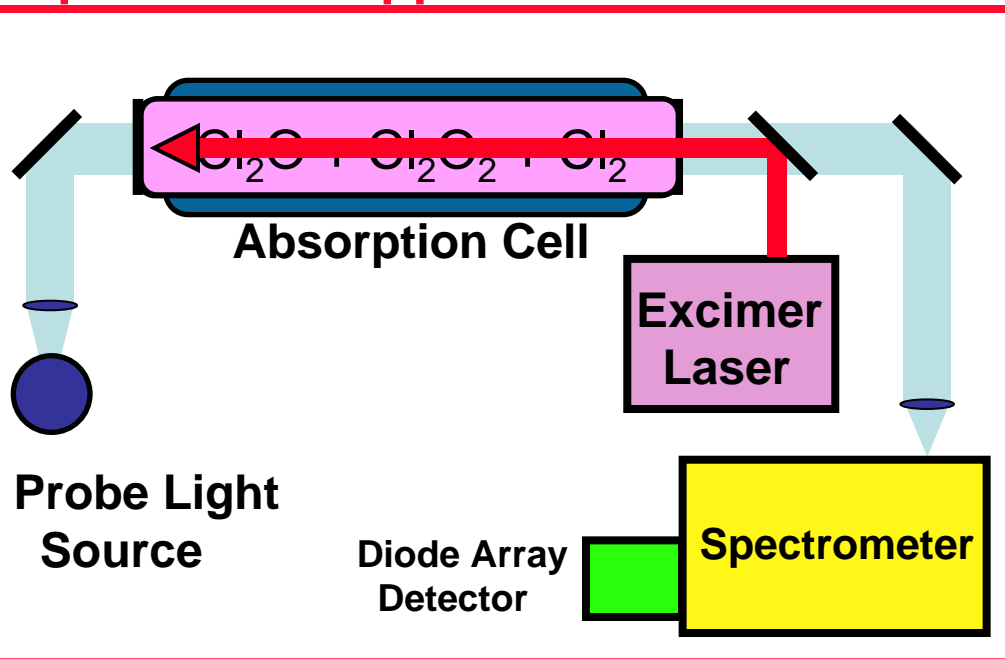


Simple Chemistry

Well-Known Stoichiometry

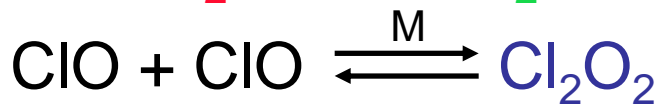
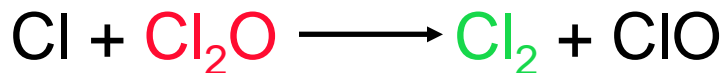
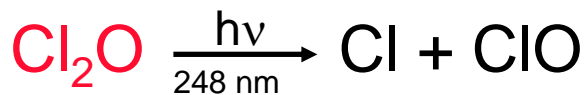


Experimental Apparatus



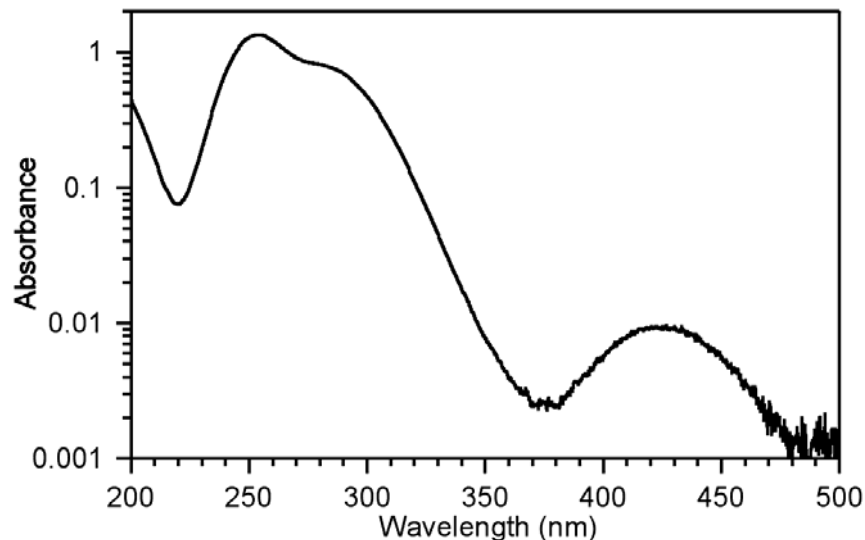
Pulsed UV Laser Photolysis of Cl₂O

Reaction Mechanism

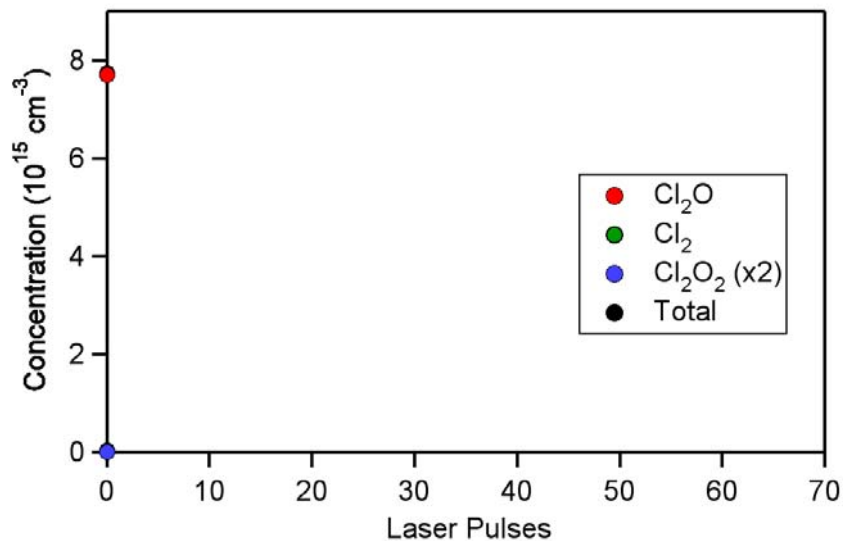
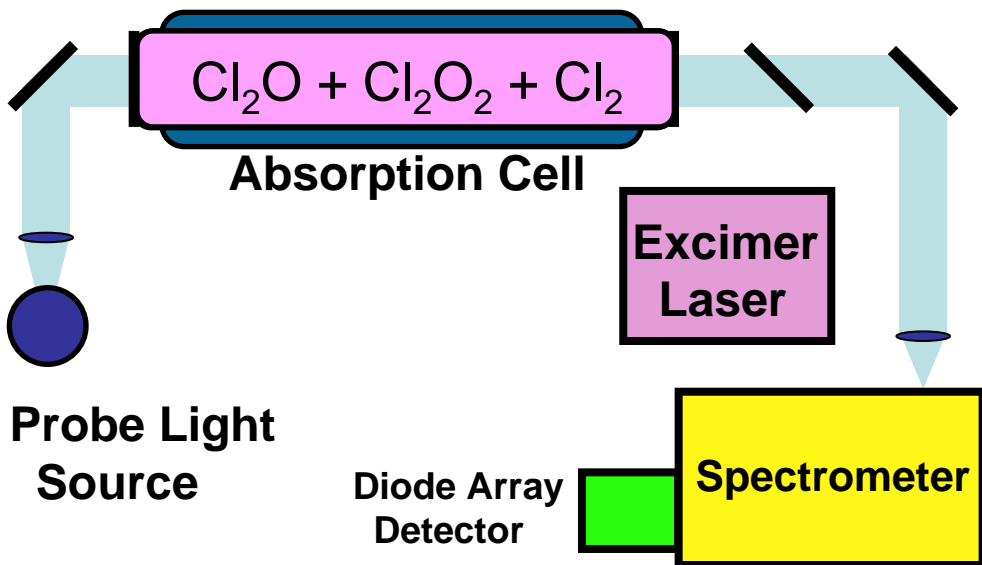


Simple Chemistry

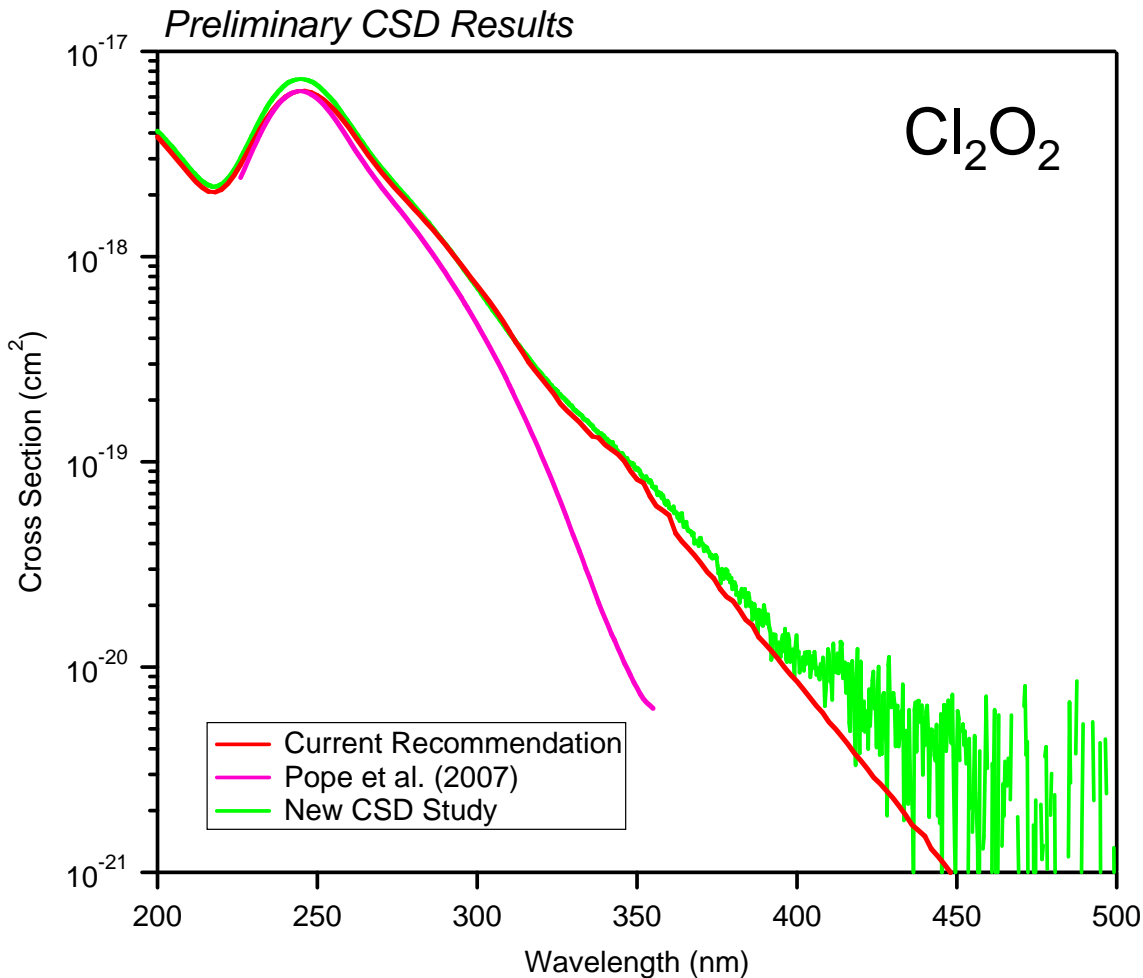
Well-Known Stoichiometry



Experimental Apparatus



WHAT is the BOTTOM LINE ?



**CSD Lab Study is
Consistent with Current
Recommendations**

**Studies of other
chemical processes
still needed and being
carried out in CSD**

- ✓ Laboratory studies play an important role in developing a more thorough understanding of atmospheric processes
- ✓ ESRL laboratories address key atmospheric issues

