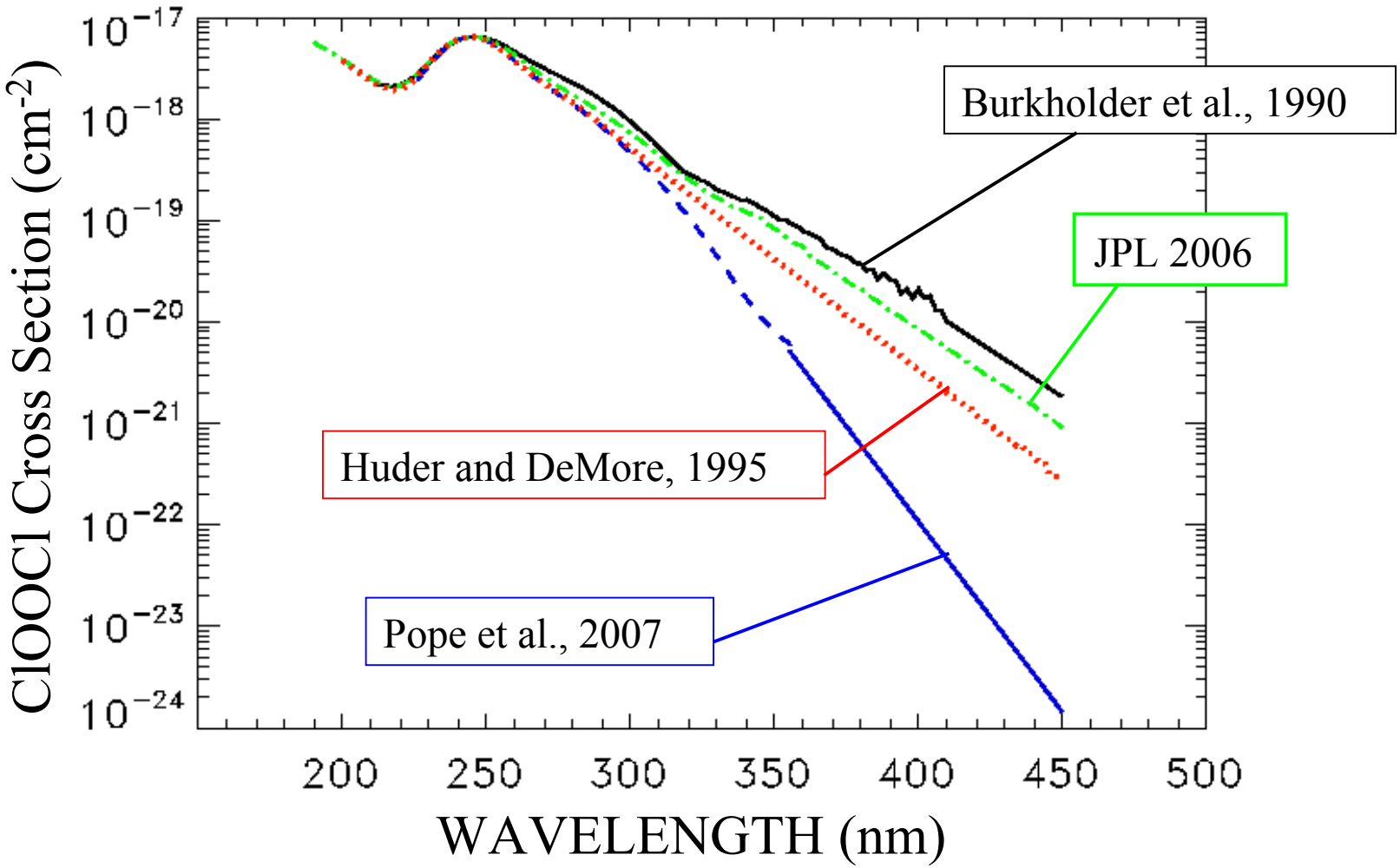
Impact of Recent Laboratory Measurements of the ClOOCl Absorption Cross Section On Our Understanding of Polar Ozone Chemistry

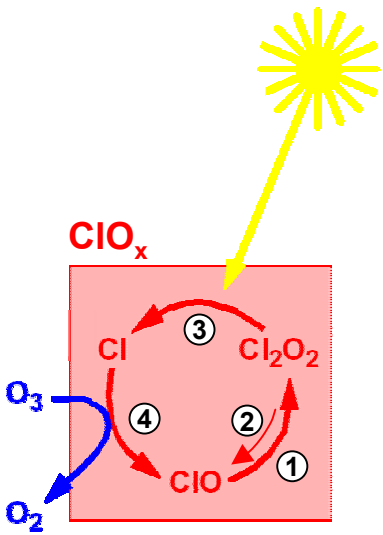
T. Canty[1], M. Rex[2], M. von Hobe[3], R. Salawitch[1], K. Frieler[2], R. Schofield[2],R. Stimpfle[4], D. Wilmouth[4]

[1]University of Maryland, College Park, MD
[2]Alfred Wegener Institute for Polar and Marine Research, Pottsdam, Germany
[3]Institute for Chemistry and Dynamics of the Geosphere, Julich, Germany
[4]Harvard University, Cambridge, MA

A recent study by Pope *et al.*, *JPC*, 2007 reports new measurements of the ClOOCl cross-section that challenge our understanding of polar chlorine chemistry.



Balance of ClO / ClO_x and ozone loss rate are governed by:



Step (1): Forward Reaction

$ClO + ClO + M \rightarrow ClOOCl + M$

Step (2): Thermal decomposition

$ClOOCl + heat \rightarrow ClO + ClO$

Null Cycle

Step (3): Photolysis

$ClOOCl + h\nu \rightarrow Cl + ClOO \rightarrow Cl + Cl + O_2$

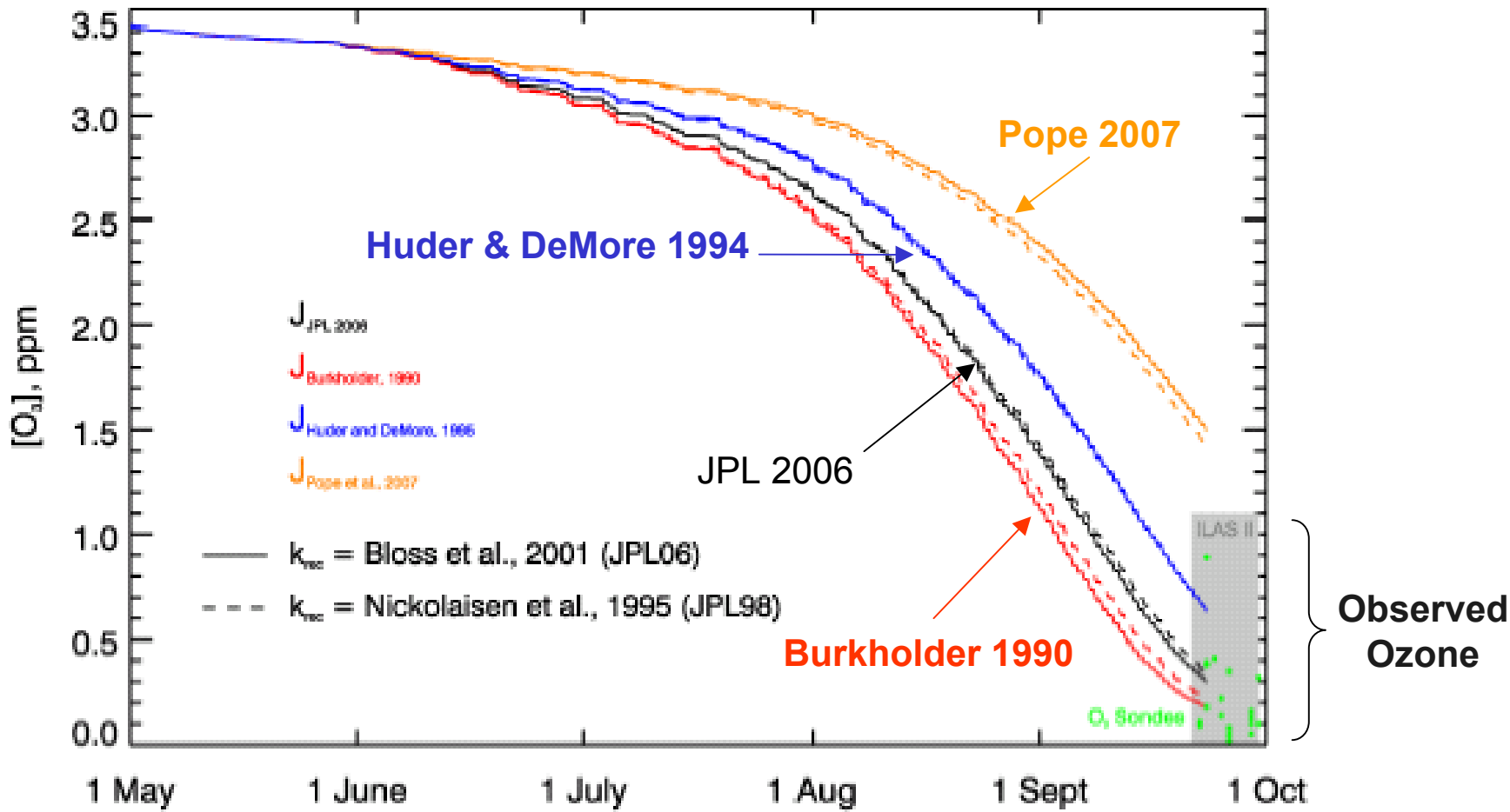
Rate = **J ClOOCl** x [ClOOCl]

O – O bond reformed here $\Rightarrow$ **rate limiting step for ozone loss**

Step (4): $Cl + O_3 \rightarrow ClO + O_2$:

Regeneration of ClO

Sensitivity of Antarctic ozone loss to the ClOOCl cross section:

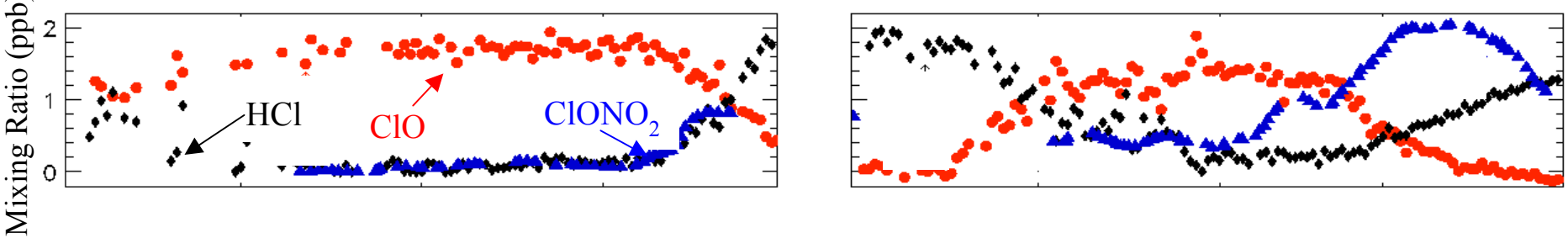


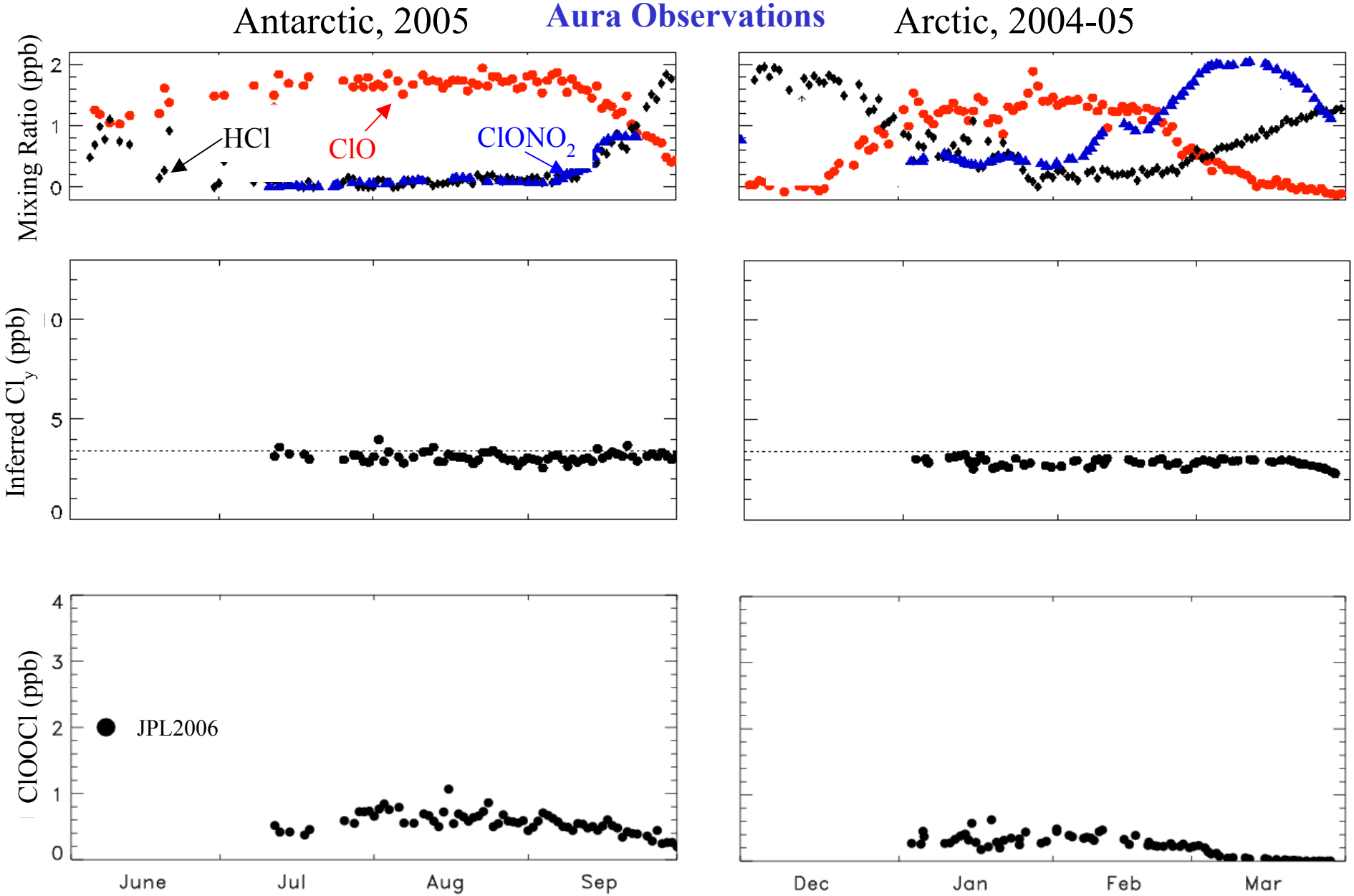
von Hobe et al., ACP, Phys., 7, 3055–3069, 2007

Antarctic, 2005

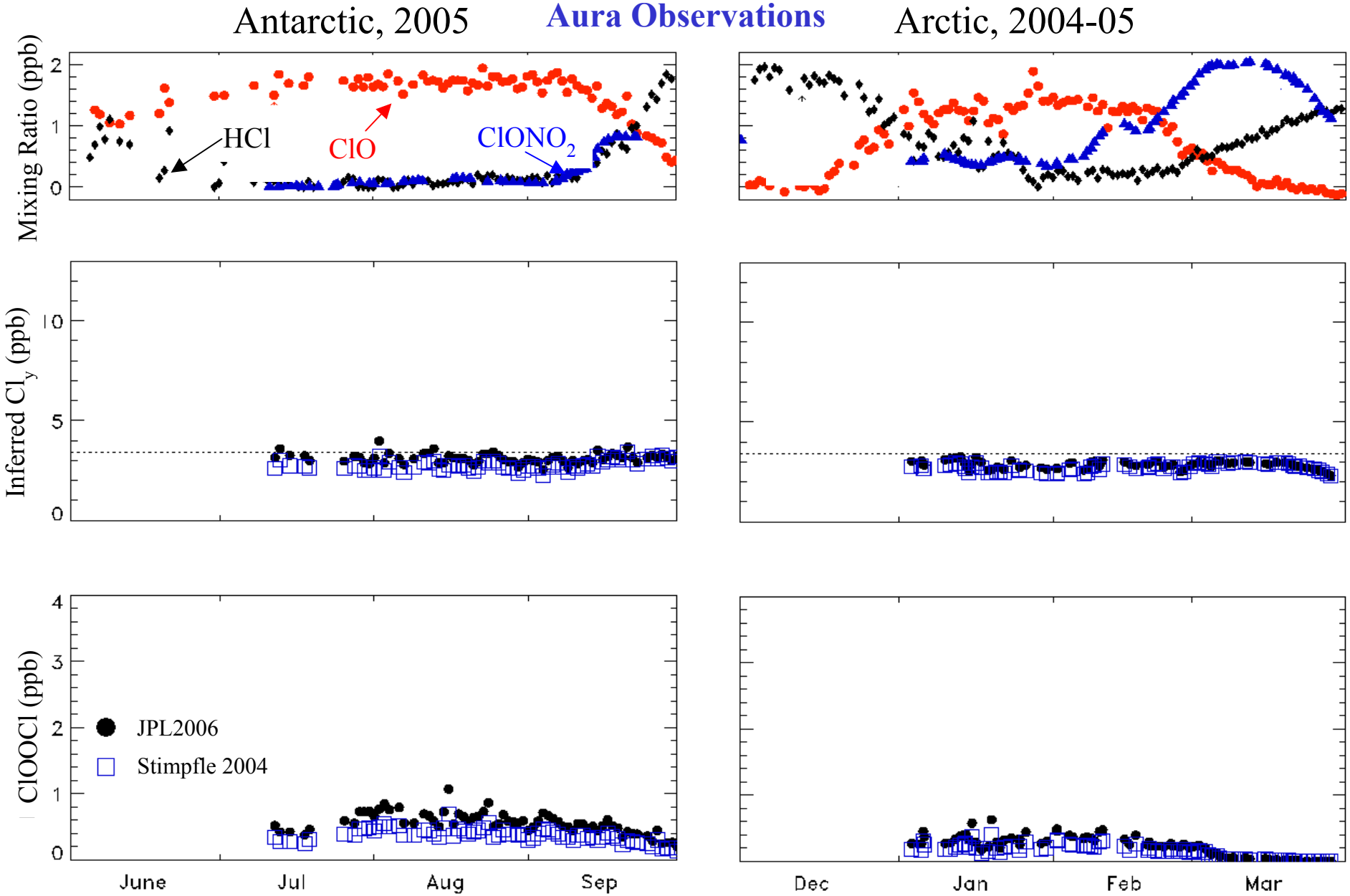
Aura Observations

Arctic, 2004-05



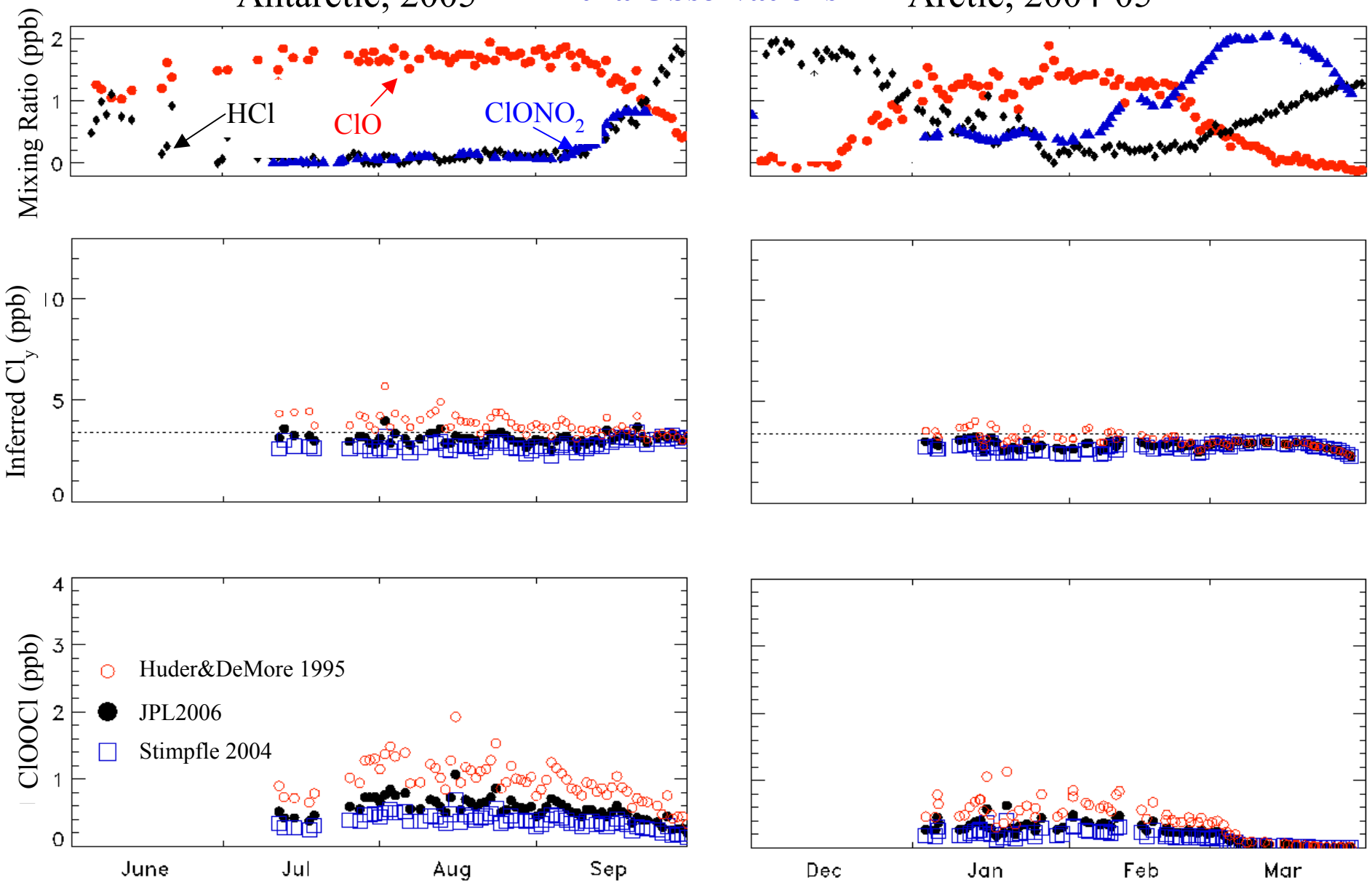


JPL2006 → JPL 2006 kinetics



JPL2006 → JPL 2006 kinetics

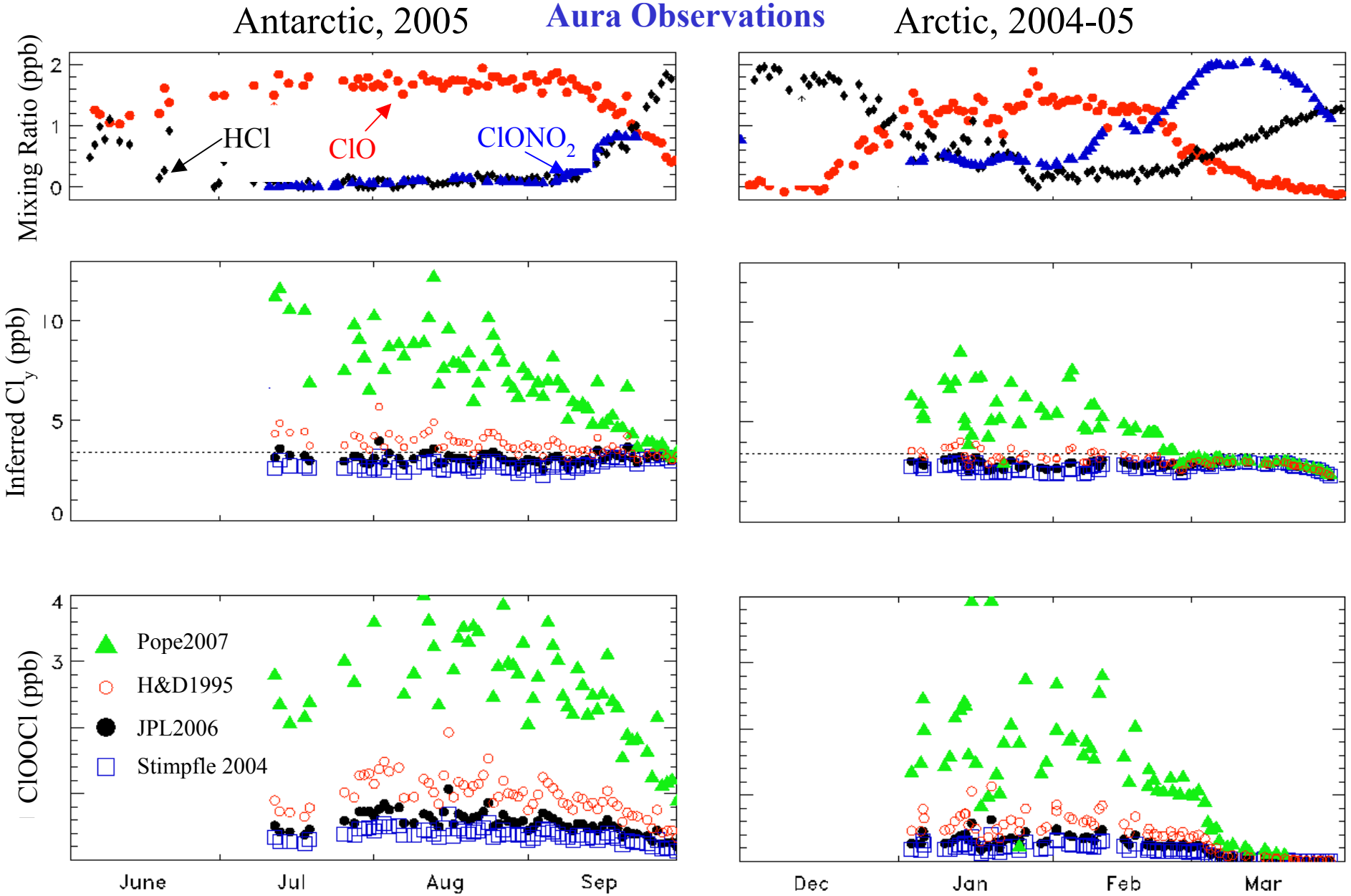
Stimpfle 2004 → J_{ClOOCl} Burkholder et al. 1990, K_{eq}=Cox&Hayman, 1988, K_f=Bloss *et al.*, 2001



JPL2006 → JPL 2006 kinetics

Stimpfle 2004 → J_{ClOOCl} Burkholder et al. 1990, K_{eq}=Cox&Hayman, 1988, K_f=Bloss *et al.*, 2001

Huder & DeMore 1995 → J_{ClOOCl} Huder and DeMore, 1995



JPL 2006 → JPL 2006 kinetics

Stimpfle 2004 → J_{ClOOCl} Burkholder et al., 1990, K_{eq}=Cox&Hayman, 1988, K_f=Bloss *et al.*, 2001

Huder & DeMore 1995 → J_{ClOOCl} Huder and DeMore, 1995

Pope 2007 → J_{ClOOCl} Pope et al., 2007

What is going on ???

Potential mechanisms fall into three categories:

(1) Direct mechanism:

$ClOOCl + X \longrightarrow Cl + Cl + O_2$

Species X must be a "daytime species", varying in a UV dependent manner similar to J_{ClOOCl} Burkholder

(2) ClOOCl is weakly bonded and can absorb out to 1.3 to 1.6 μm

A photolytic process involving visible or near IR light could be the missing sink for ClOOCl

(3) Formation of an unknown nightime reservoir (Cl^{NIGHT})

$ClOOCl + Y \longrightarrow Cl^{NIGHT} + \ldots$

$Cl^{NIGHT} + h\nu \longrightarrow \ldots \longrightarrow Cl + Cl + O_2 + Z$

Solutions?

$ClO + ClOOCl \rightarrow ClOCl + ClOO$

$BrO + ClOOCl \rightarrow BrOCl + ClOO$

$OH + ClOOCl \rightarrow HOCl + ClOO$

$ClOOCl$ + ice $\rightarrow$ products

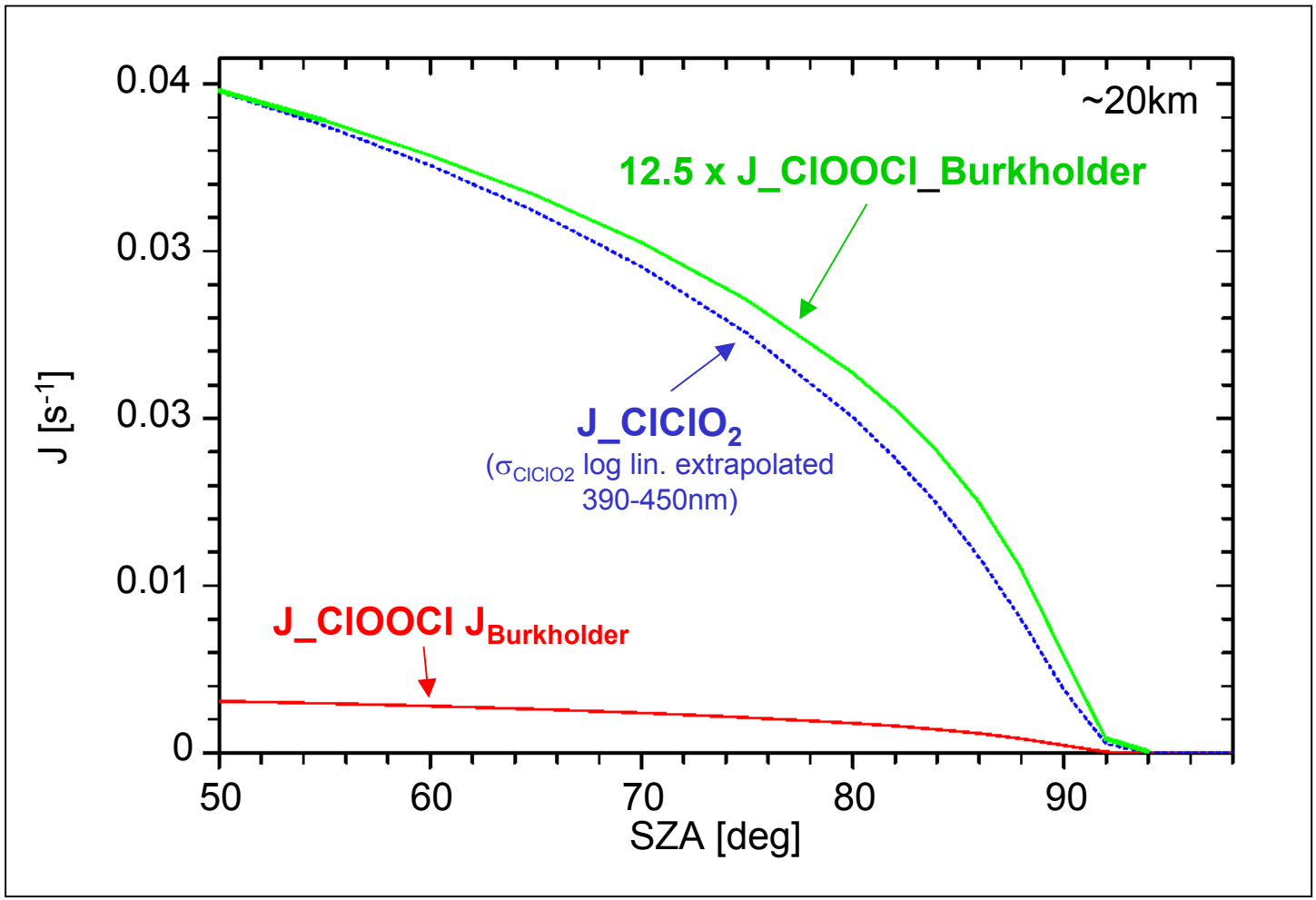
$ClOOCl$ + Vis or Near IR light

Solutions?

$ClO + ClOOCl \rightarrow ClOCl + ClOO$	If fast enough to affect ClOOCl, would have seen in lab (K. Bayes and S. Sander, priv. comm.)
$BrO + ClOOCl \rightarrow BrOCl + ClOO$	If fast enough, BrOCl becomes dominant daytime reservoir of BrOx. Inconsistent with atmospheric observation of BrO
$OH + ClOOCl \rightarrow HOCl + ClOO$	New rate constant much too slow (J. Hansen, priv. comm.)
ClOOCl + ice → products	Inconsistent with EUPLEX observations of very high ClO at ~205 K, after recent PSC processing
ClOOCl + Vis or Near IR light	Inconsistent with diurnal variation of ClO

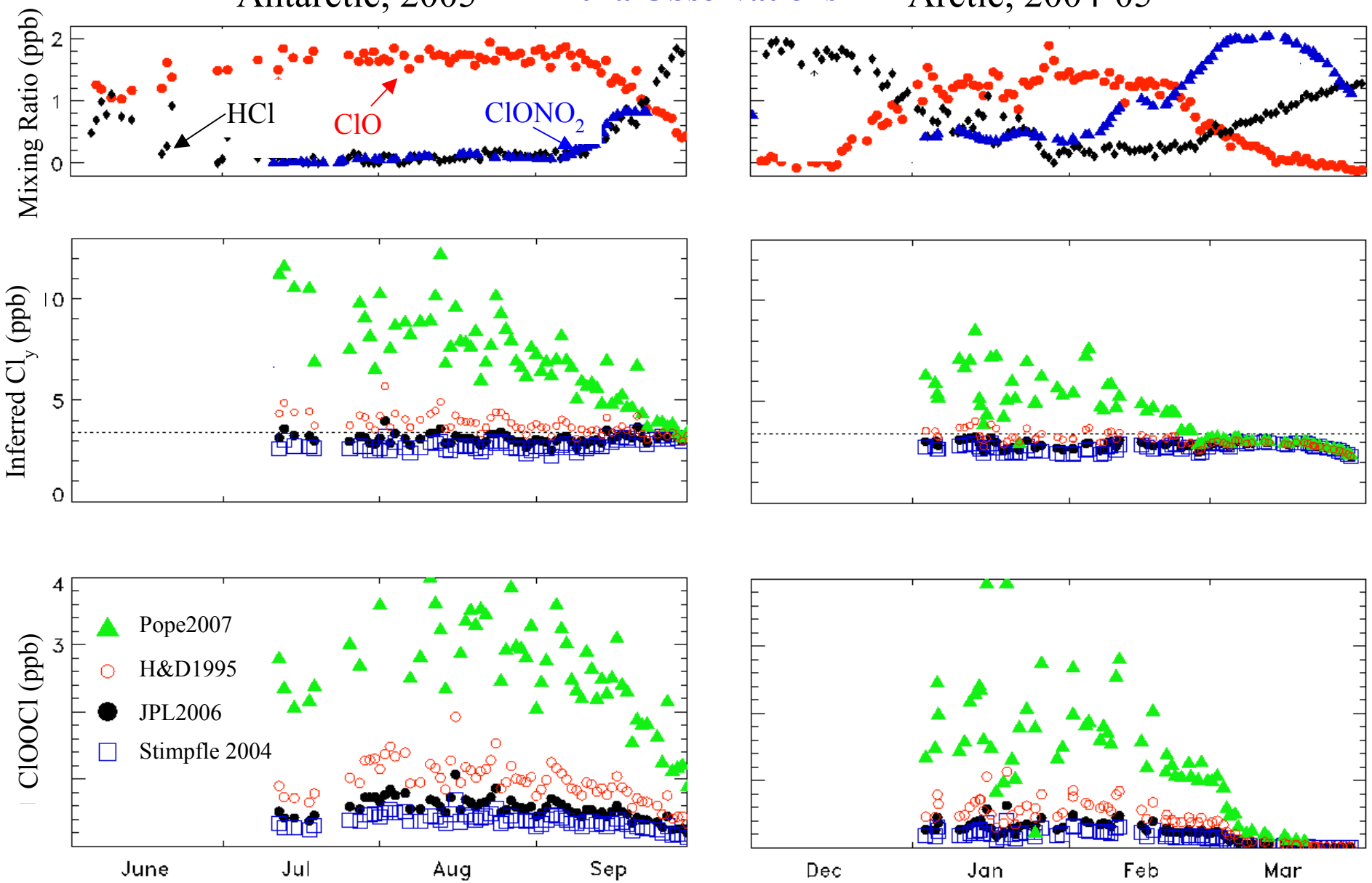
Rapid equilibrium between ClOOCl and $ClClO_2$ (Cl – Cl(=O)=O)?

e.g. by: $ClOOCl + ClO \rightarrow ClClO_2 + ClO$
$ClClO_2 + ClO \rightarrow ClOOCl + ClO$



~10% of Cl_2O_2 in the form of $ClClO_2$ leads to "Burkholder like" photolysis of the mixture

Temperature dependent equilibrium could explain SOLVE / EUPLEX differences in ClO

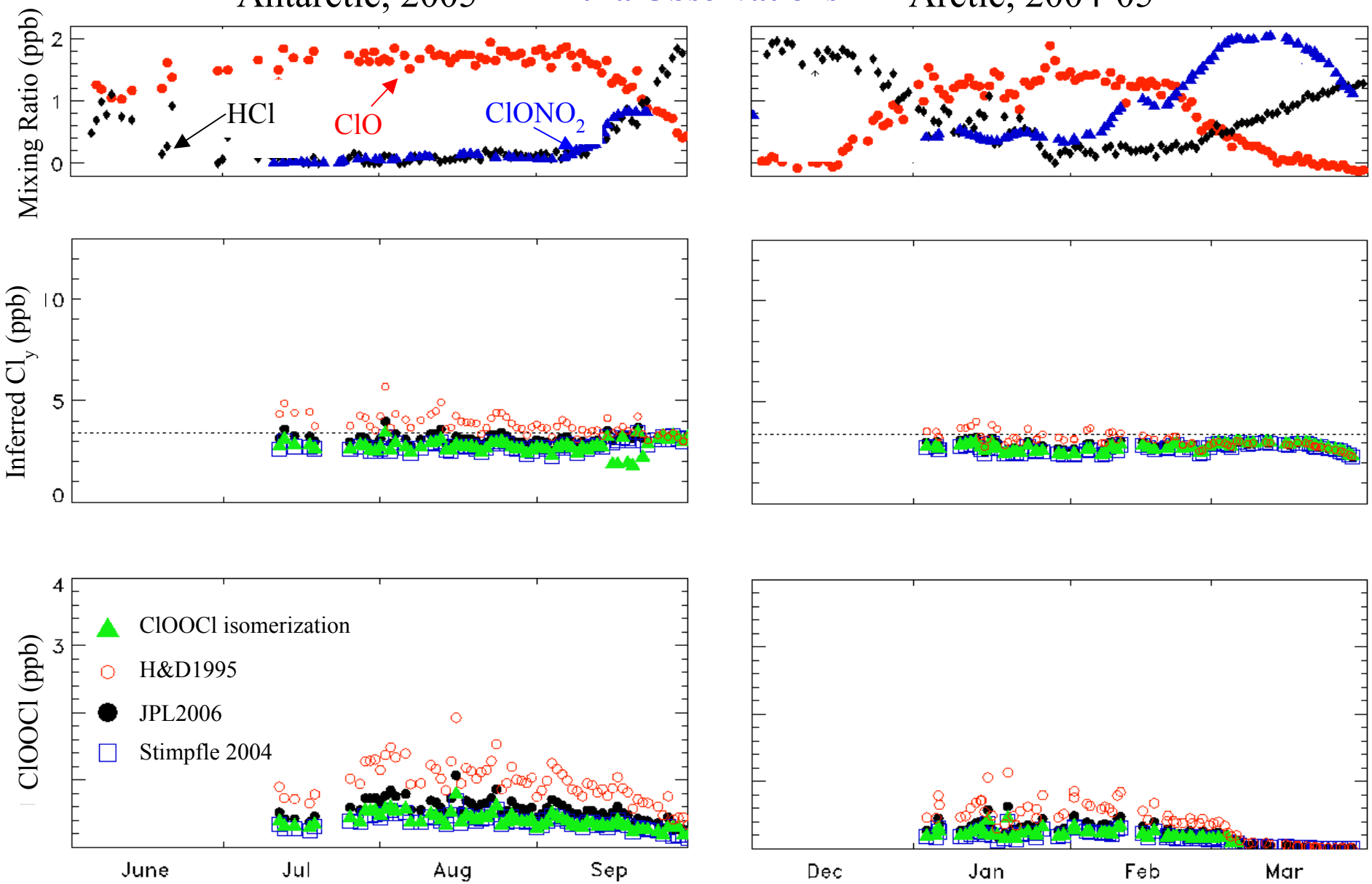


JPL 2006 → JPL 2006 kinetics

Stimpfle 2004 → J_{ClOOCl} Burkholder et al., 1990, K_{eq}=Cox&Hayman, 1988, K_f=Bloss *et al.*, 2001

Huder & DeMore 1995 → J_{ClOOCl} Huder and DeMore, 1995

Pope 2007 → J_{ClOOCl} Pope et al., 2007



JPL 2006 → JPL 2006 kinetics

Stimpfle 2004 → J_{ClOOCl} Burkholder et al., 1990, K_{eq}=Cox&Hayman, 1988, K_f=Bloss *et al.*, 2001

Huder & DeMore 1995 → J_{ClOOCl} Huder and DeMore, 1995

ClOOCl isomerization → J_{ClOOCl} Pope et al., 2007 + $ClClO_2$ chemistry

SOLVE

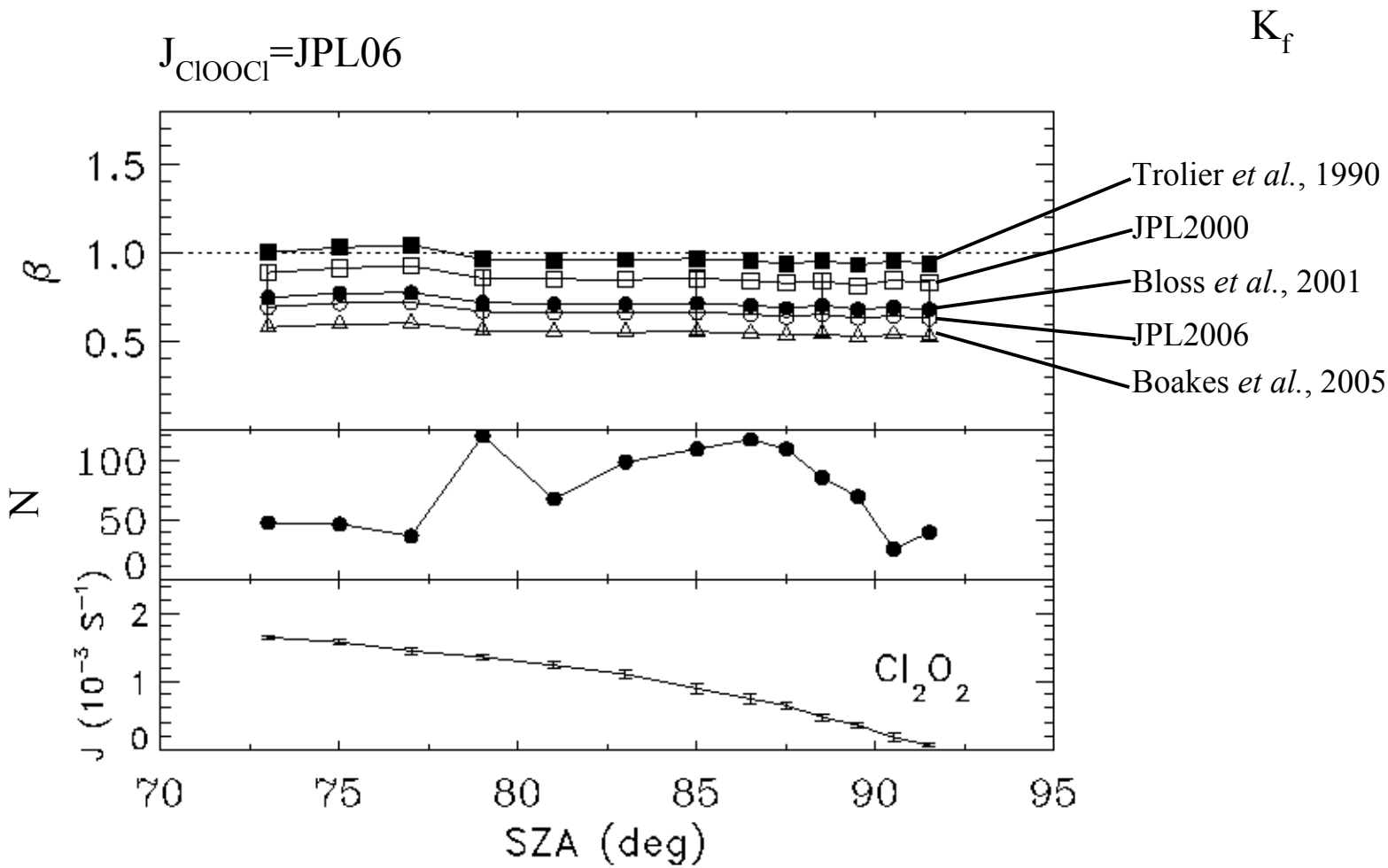
First measurements of ClOOCl from the ER-2 during SOLVE/THESEO-2000 (Stimpfle *et al., JGR*, 2004)

$$\beta \text{ Ratio} = \frac{[\text{ ClO } \textit{model} \times \text{ClO } \textit{model}\ ] / \text{ClOOCl } \textit{model}}{[\text{ ClO } \textit{meas} \times \text{ClO } \textit{meas}\ ] / \text{ClOOCl } \textit{meas}}$$

$$\approx \frac{(J / k_f)\ \textit{model}}{(J / k_f)\ \textit{actual}}$$

A value of $\beta=1$ indicates good agreement between observations and models

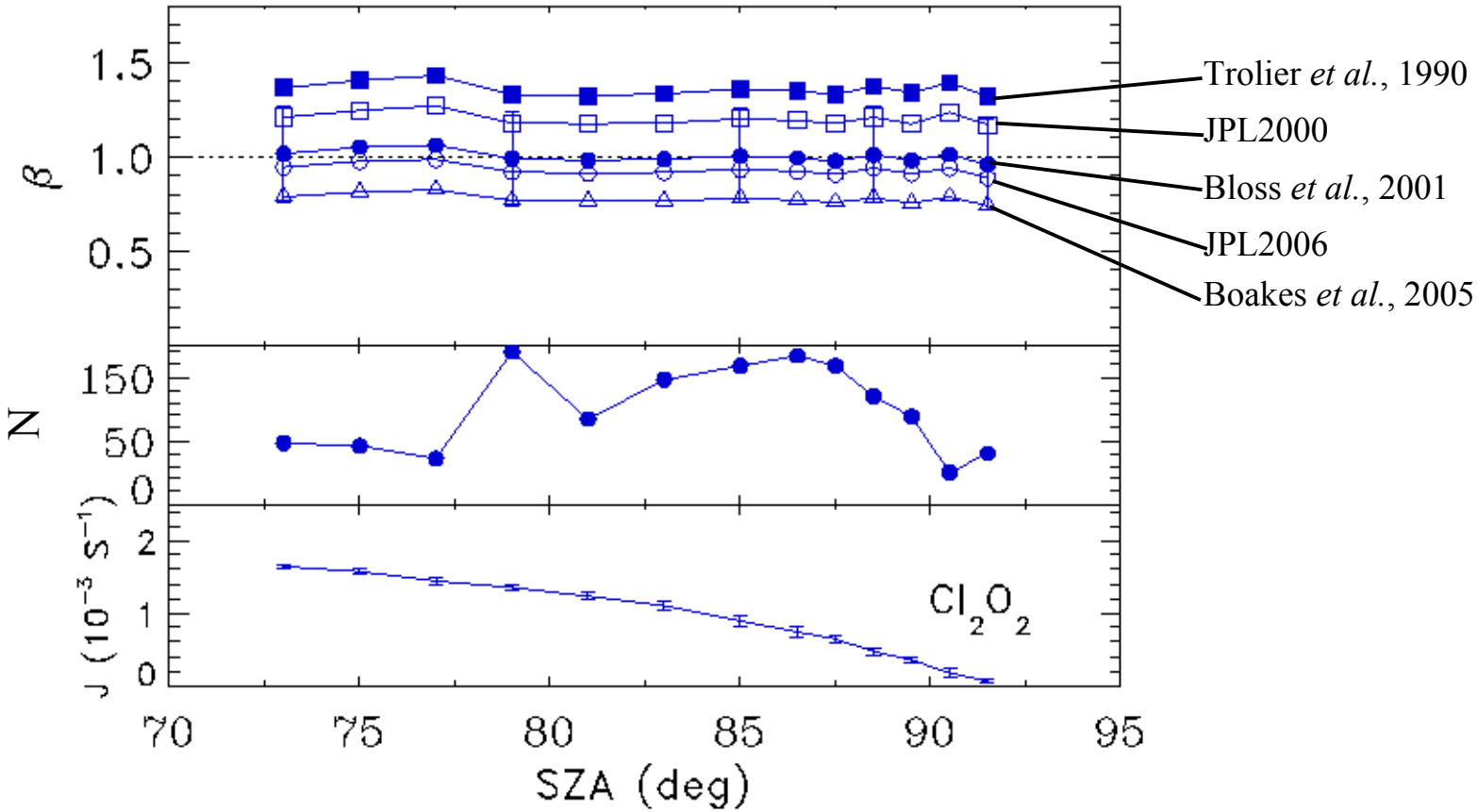
SOLVE


K_f
J_{ClOOCl}=JPL06
β
1.5
1.0
0.5
N
100
50
0
J (10^{-3} s^{-1})
2
1
0
Cl_2O_2
70
75
80
85
90
95
SZA (deg)
Trolier *et al.*, 1990
JPL2000
Bloss *et al.*, 2001
JPL2006
Boakes *et al.*, 2005

SOLVE

K_f

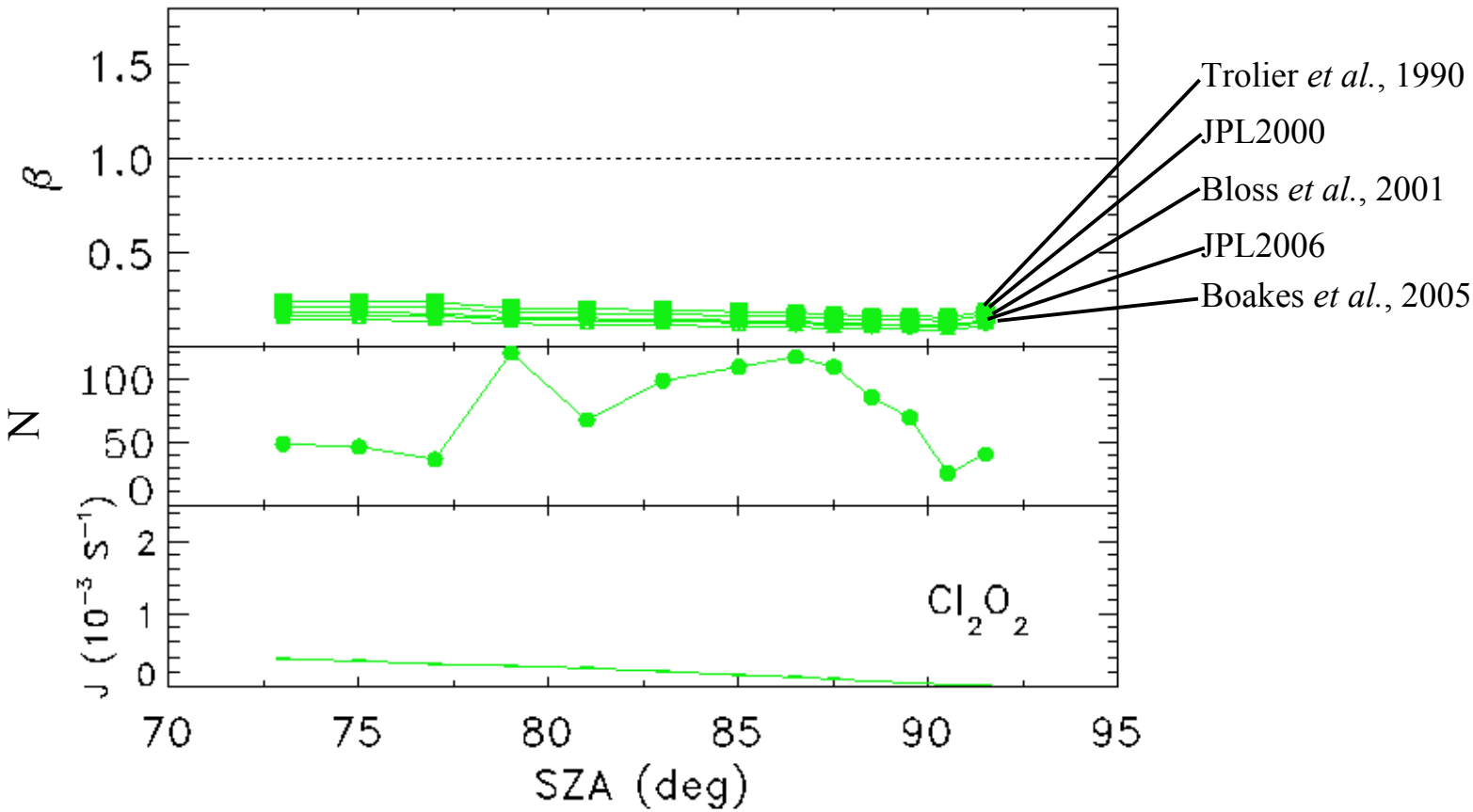
J_{ClOOCl}=Burkholder *et al.*, 1994



SOLVE

J_{ClOOCl}=Pope *et al.*, 2007

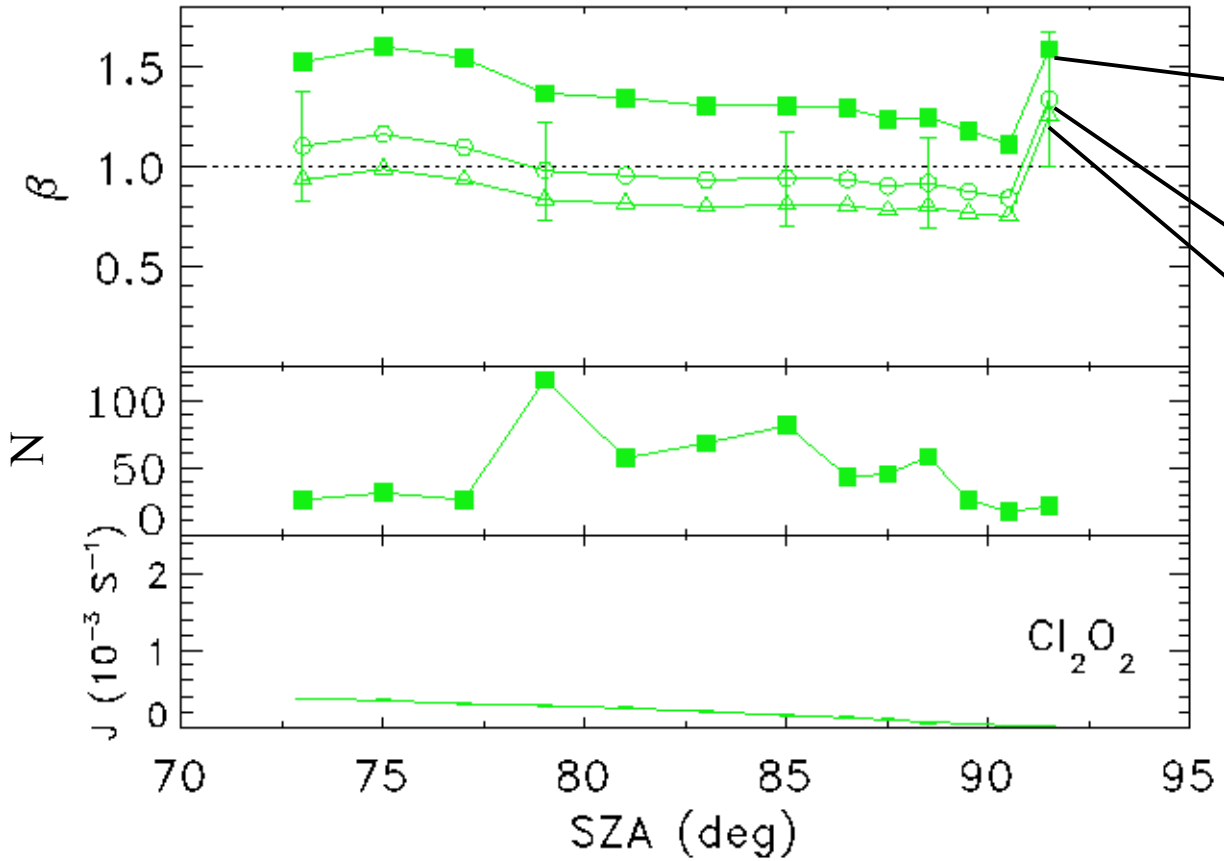
K_f



SOLVE

K_f

J_{ClOOCl}=Pope *et al.*, 2007, ClOOCl isomerization

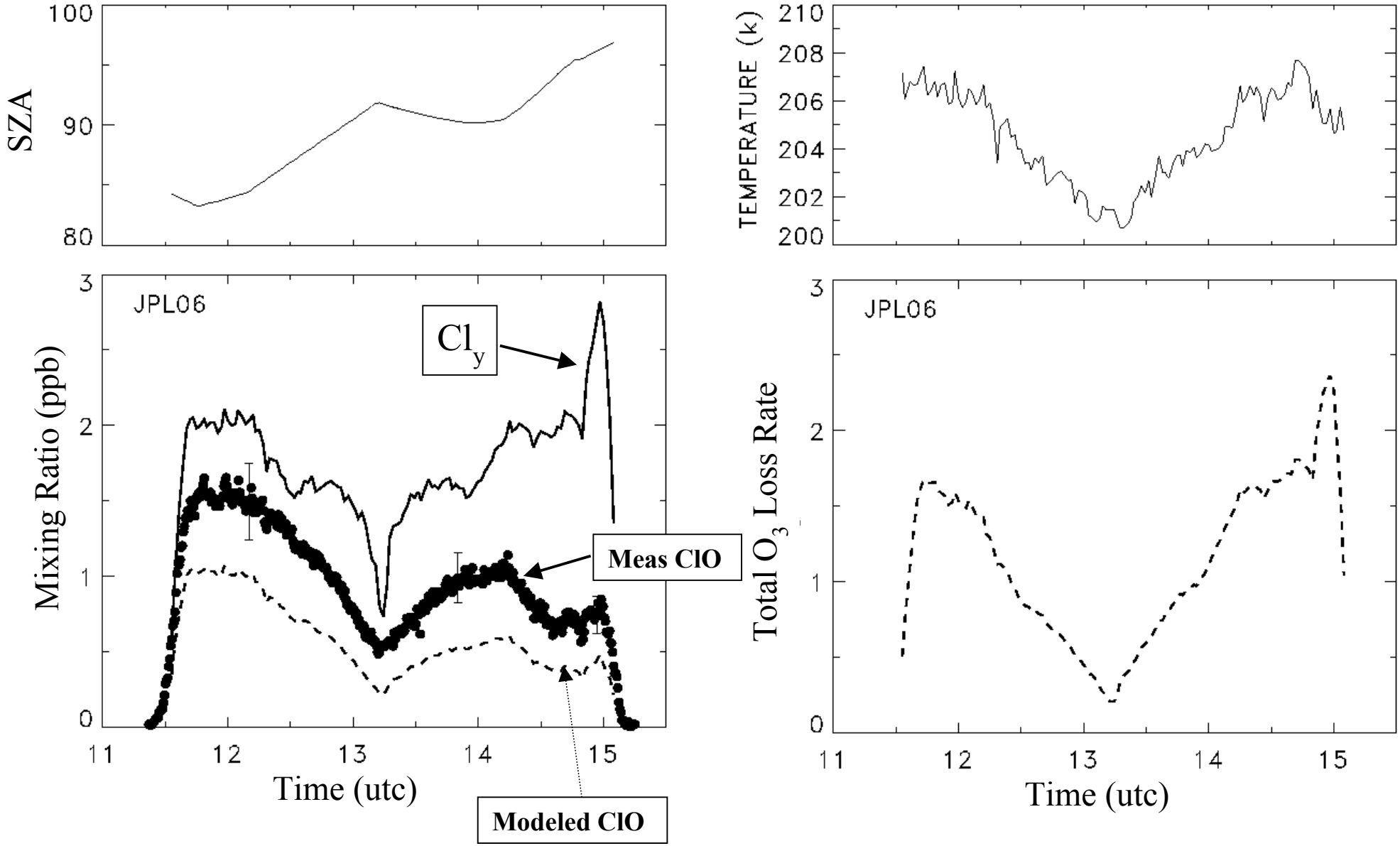


Trolier *et al.*, 1990

JPL2006

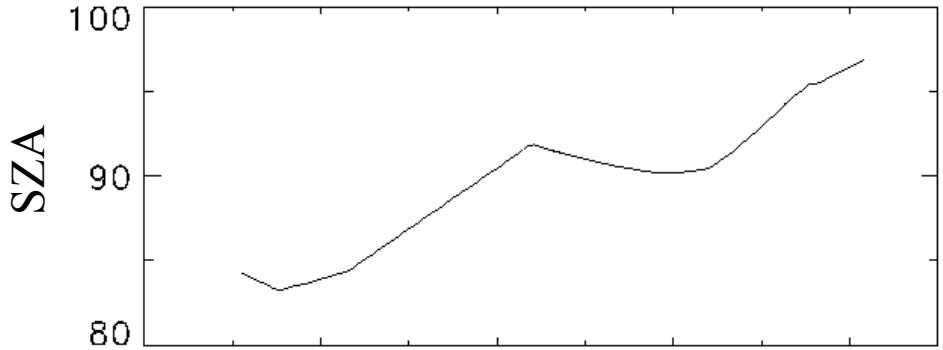
Boakes *et al.*, 2005

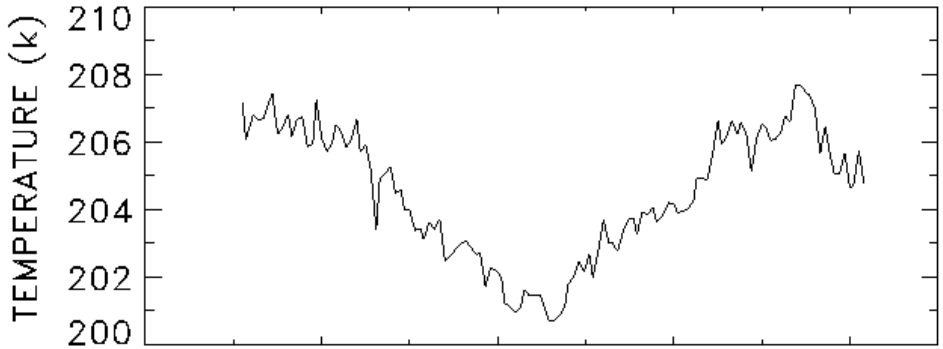
EUPLEX, 030130

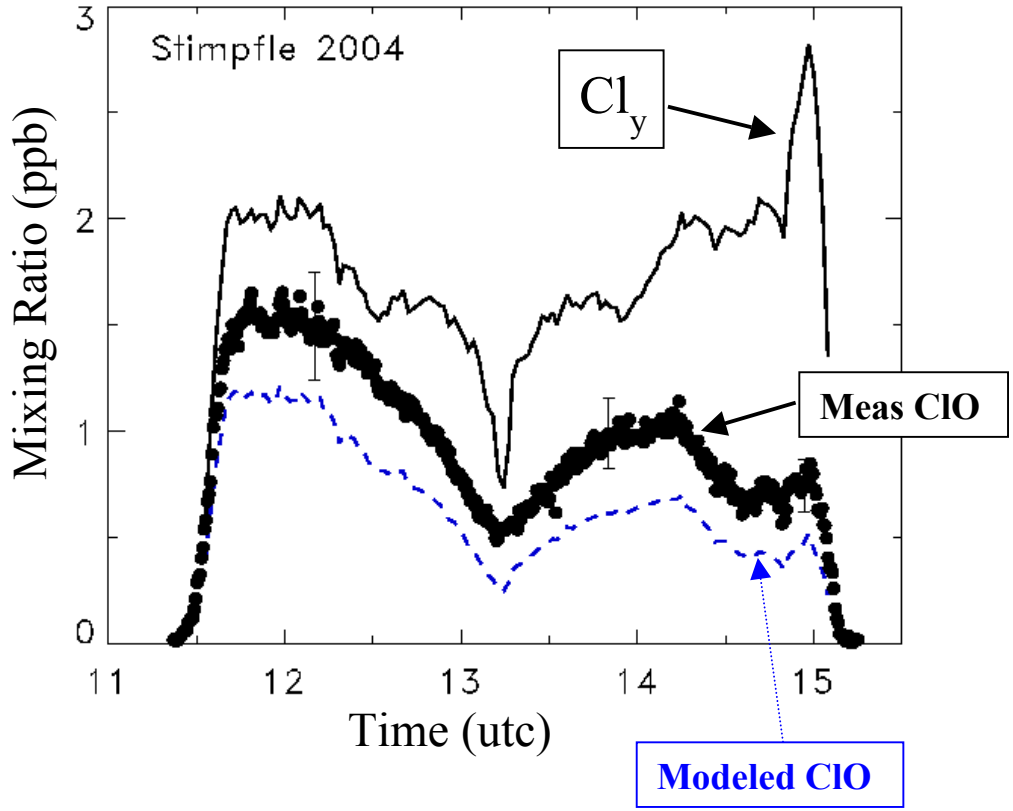


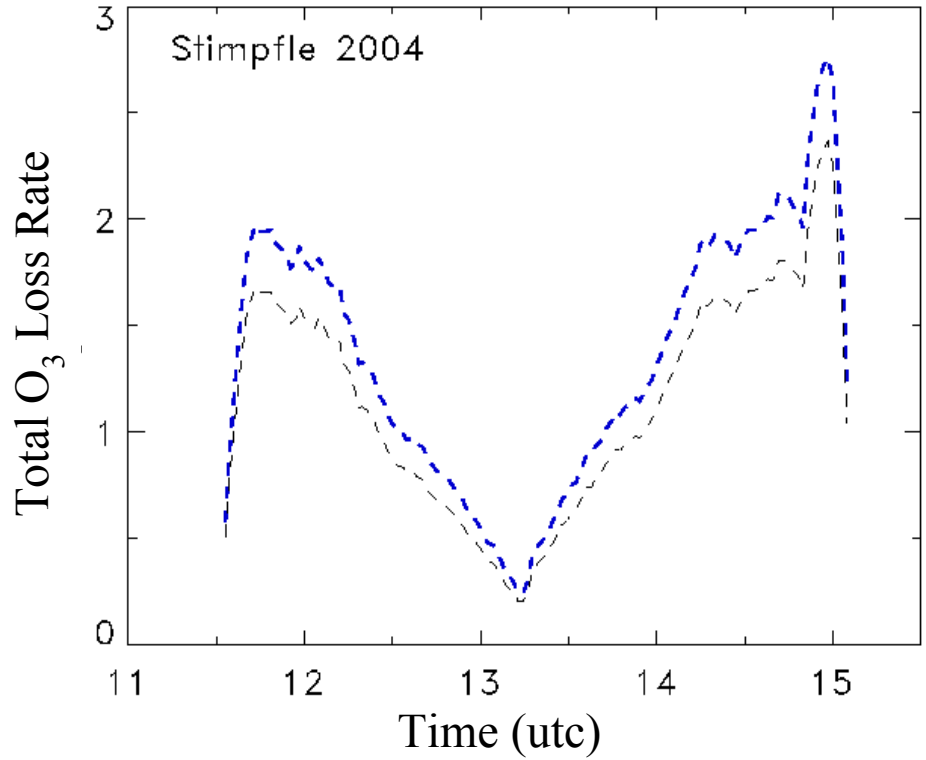
JPL 2006 → JPL 2006 kinetics

EUPLEX, 030130





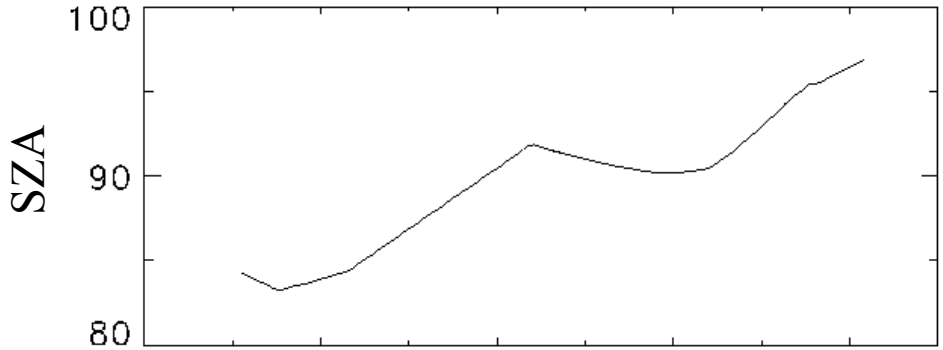


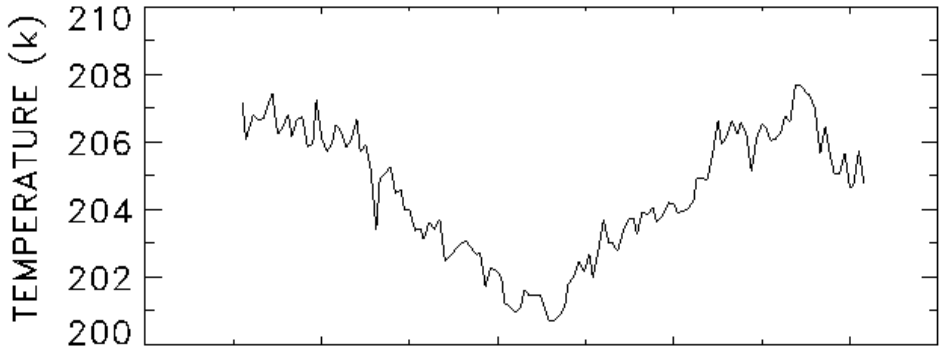


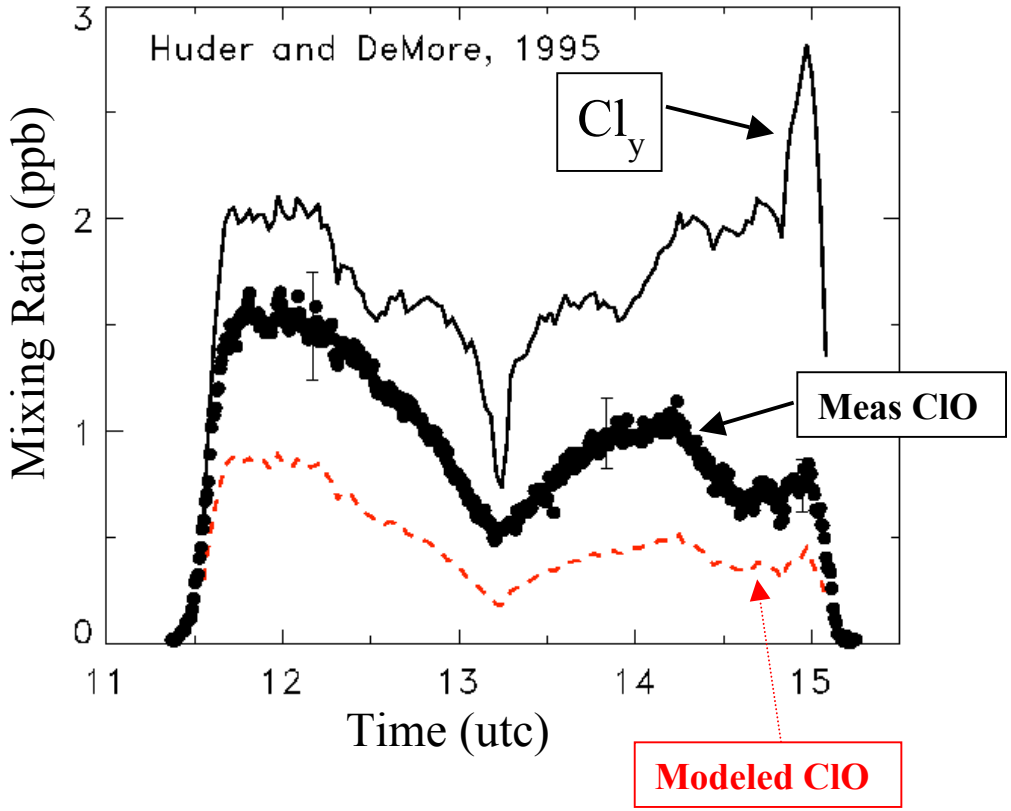
Black curve = JPL 2006

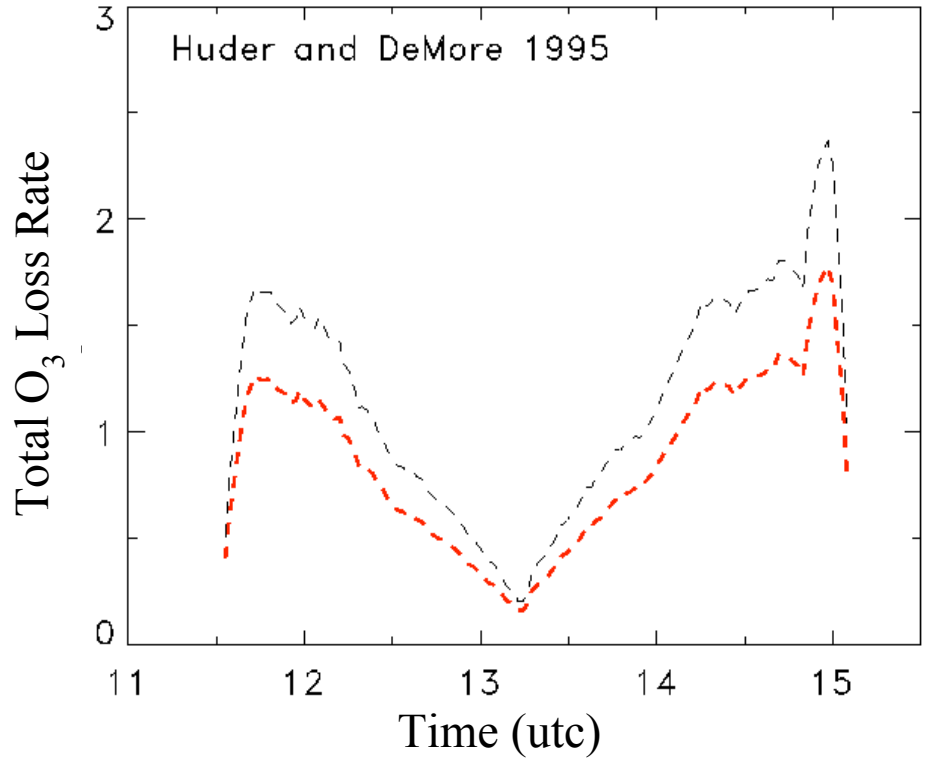
Stimpfle 2004 → J_{ClOOCl} Burkholder et al., 1990, K_{eq}=Cox&Hayman, 1988, K_f=Bloss *et al.*, 2001

EUPLEX, 030130





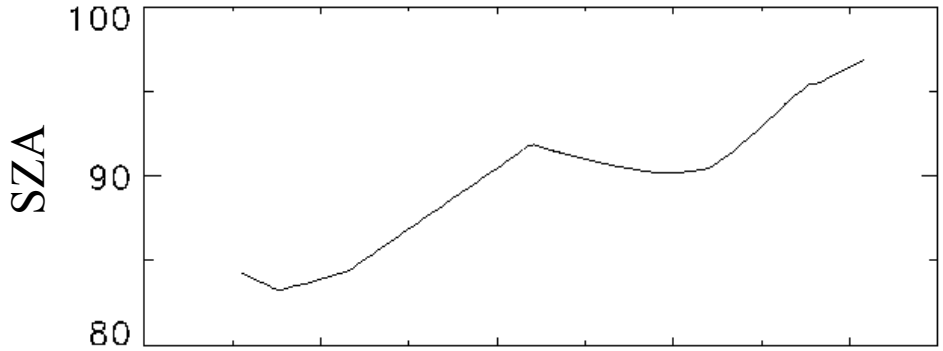


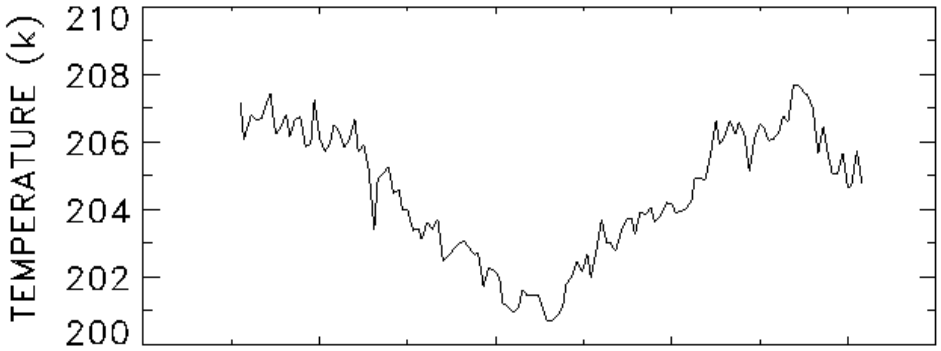


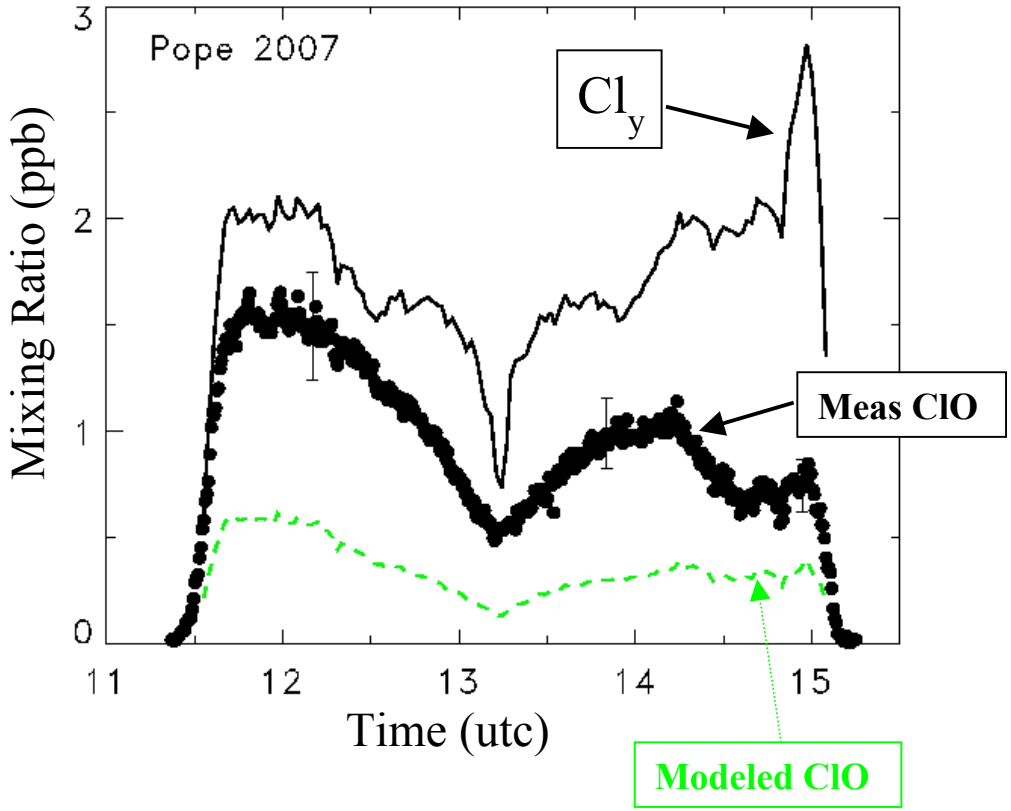
Black curve = JPL 2006

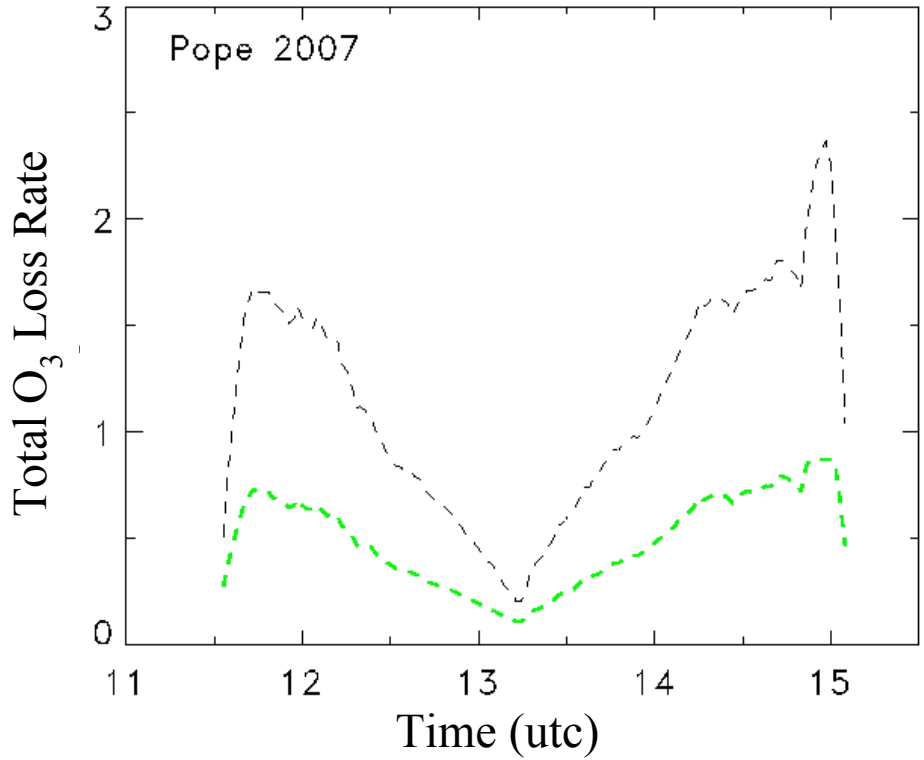
Huder & DeMore 1995 → J_{ClOOCl} Huder and DeMore, 1995

EUPLEX, 030130





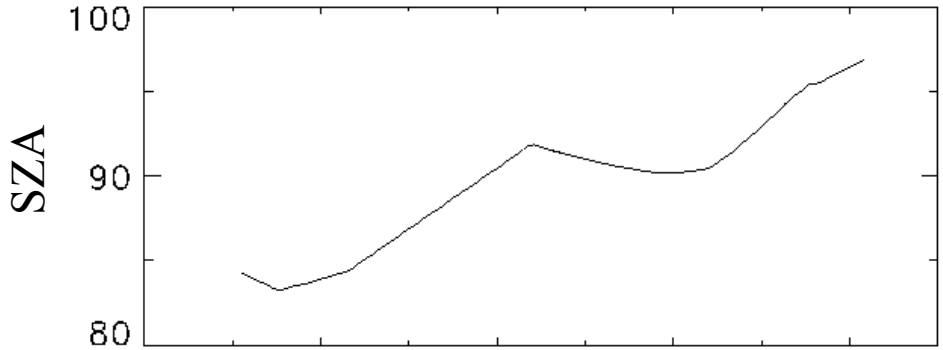


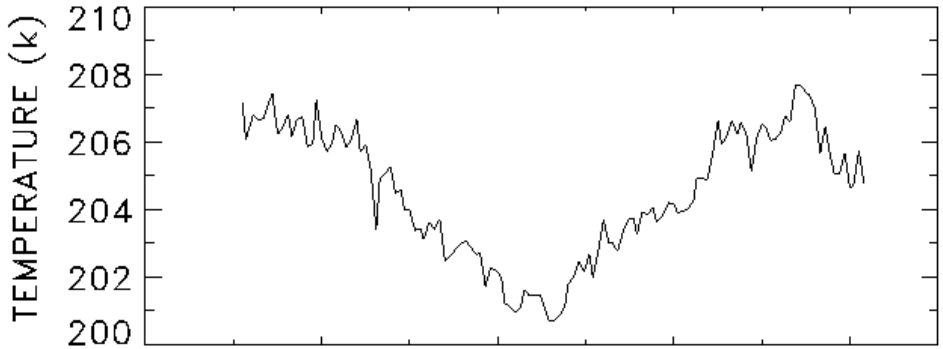


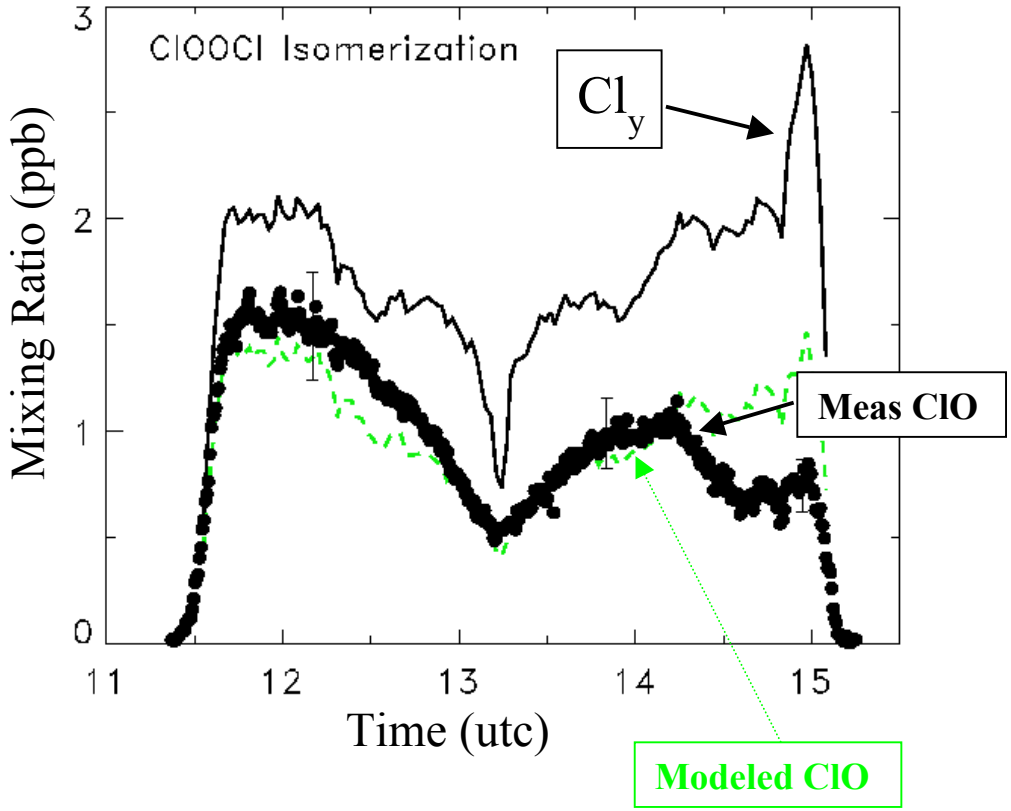
Black curve = JPL 2006

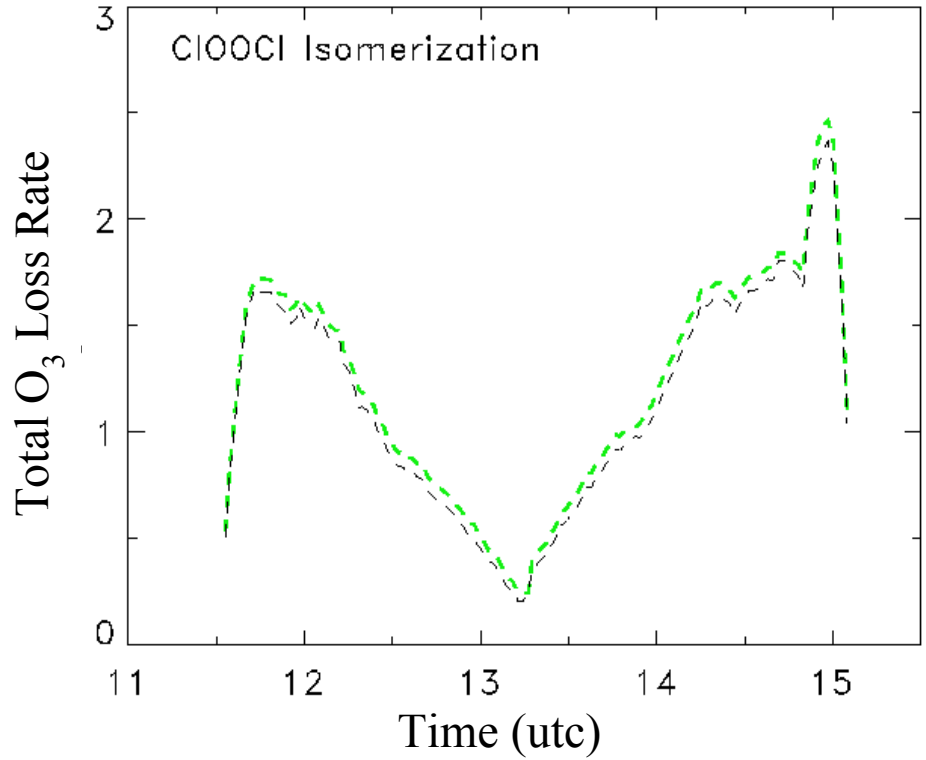
Pope 2007 → J_{ClOOCl} Pope et al., 2007

EUPLEX, 030130









Black curve = JPL 2006

ClOOCl isomerization → J_{ClOOCl} Pope et al., 2007 + $ClClO_2$ chemistry

Conclusions

1. New measurements of the ClOOCl cross section by Pope et al., 2007 reduce both modeled ClO and polar O_3 loss,leading to large discrepancies with observations.

2. A process that converts ClOOCl into a species that undergoes fast photolysis and re-creates the O_2 bond can potentially resolve both discrepancies.

3. A focused effort of laboratory experimentalists and theorists, field measurement investigators, and modelers is needed to reconcile theory and observation of polar ozone loss.

Acknowledgements

Derived Meteorological Products for MLS were calculated and provided by Gloria Manney and William Daffer, with support from the MLS team at NASA's Jet Propulsion Laboratory, California Institute of Technology.

We appreciate *very much* numerous, extremely helpful conversation with Kyle Bayes and Stan Sander.

SPARC Workshop / Study: *The Role of Halogens in Ozone Depletion*

Purpose: This new SPARC Initiative will have three principal objectives:

- Evaluate the consequence of new data on the photolysis rate of the ClO dimer on simulations of stratospheric ozone depletion, particular in winter polar regions.
- Evaluate old and new results from laboratory studies of the photolysis rate and the type of further studies that are necessary to resolve current differences.
- Assess qualitative / quantitative evidence from the laboratory, field observations, and models that links ozone depletion to stratospheric active chlorine / bromine amounts.

Deliverables: A white paper describing the first two objectives and a peer-reviewed manuscript addressing the third objective.

Timeline: Next 6-8 months for the workshop; 12-18 months for deliverables.
The completion date for objective #3, in particular, is critical to the 2010 UNEP/WMO Ozone Assessment (expected to begin in late 2008 / early 2009)

Participants: Laboratory Experimentalists and Theorists, Field Experimental Investigators (Ground, Balloon, Aircraft, Satellite), and Modelers.

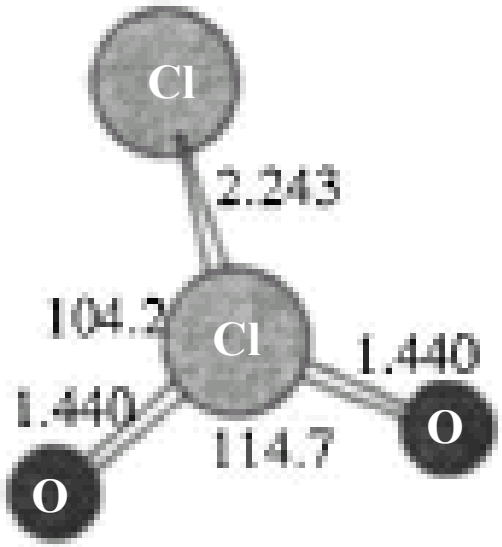
Venue: TBD (possibly multiple)

Organization: Co-Chaired by Michael Kurylo (NASA) & Björn-Martin Sinnhuber (U. Bremen); a Steering Committee is being assembled; announcement to be issued soon.

Please let us know of your interest in participating (you might be invited anyway)!

michael.j.kurylo@nasa.gov **bms@iup.physik.uni-bremen.de**

Backup Material



< ClClOO =113.2