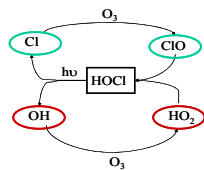


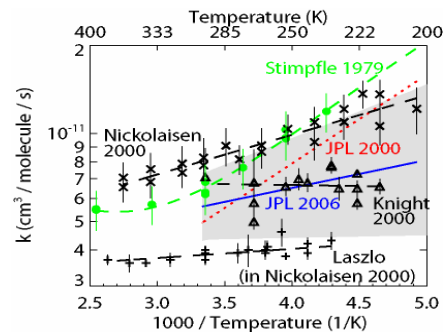
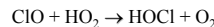
## Introduction

The HOCl (hypochlorous) cycle is among the primary halogen mechanisms for ozone loss in the mid-latitude lower stratosphere:



## Problem

There is a large discrepancy among laboratory measurements of the rate constant,  $k$ , for the rate limiting step,



## Our work

### Part I. Comparison of modeled and measured HOCl and its precursors ClO and HO<sub>2</sub>

- Field measurements of HOCl are obtained by two balloon-borne Fourier Transform spectrometers

MkIV	Measures solar absorption over the entire mid-IR (from 1.8 to 15.4 $\mu\text{m}$ ), thus probing vibrational transitions
FIRS-2 (Far-InfraRed Spectrometer 2)	Measures thermal emission in the far-IR (from 8 to 125 $\mu\text{m}$ ), thus probing rotational transitions

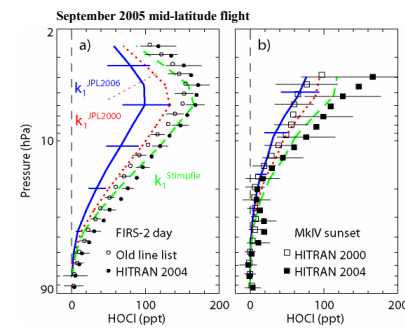
- Photochemical box model, constrained by measurements of T, p, O<sub>3</sub>, and, indirectly NO<sub>x</sub>, Cl<sub>x</sub>, is run for three values of  $k$ 
  - JPL 2006 (slowest)
  - JPL 2000 (fast)
  - Stimpfle et al. (fastest)
- Field measurements of precursors ClO and HO<sub>2</sub>
  - Balloon-borne instrument FIRS-2
  - Balloon-borne instrument SLS (Submillimeterwave Limb Sounder)
  - Aura satellite-borne instrument MLS (Microwave Limb Sounder)

### Part II. Satellite-borne MLS observations of HOCl

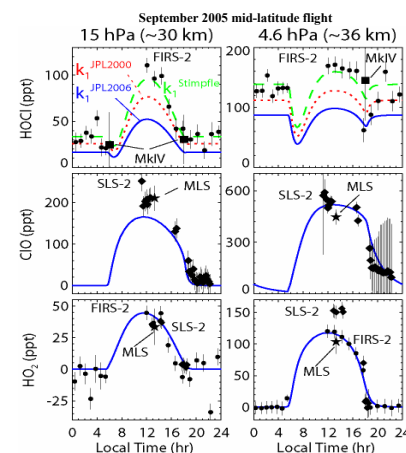
- Preliminary comparison of MLS and FIRS-2 HOCl

## Part I. Comparison of modeled and measured HOCl and its precursors ClO and HO<sub>2</sub>

- We've been working on this for years, for over a decade's worth of data from balloon flights, and had always found a discrepancy among the observations:
  - MkIV HOCl agreed best with slow rate constant (JPL 2006)
  - FIRS-2 HOCl agreed best with fast rate constant (Stimpfle et al.)
- New spectroscopy changes the story!
  - Updated spectroscopic constants for HOCl in HITRAN 2004
  - Line strengths for mid-infrared lines, relevant to MkIV, decreased
    - thus increasing retrieved MkIV HOCl by about 60%
  - Broadening coefficients increased, which at these altitudes affects rotational lines (FIRS-2) but not vibrational lines (MkIV)
    - thus increasing retrieved FIRS-2 HOCl by about 10%



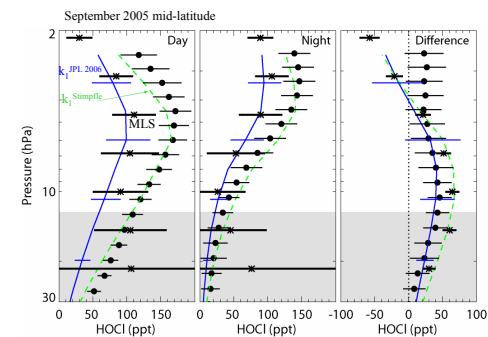
- As a result, for the first time, MkIV and FIRS-2 HOCl agree
  - However, they disagree with current models (blue)
  - They agree better with the model that uses Stimpfle et al. rate constant
- Diurnal variation of observed and modeled HOCl and its precursors ClO and HO<sub>2</sub>:



- Calculated precursors (ClO and HO<sub>2</sub>) agree with field measurements
  - Thus the discrepancy between measured and modeled HOCl is likely not due to error in model precursor abundances
- Unlike HOCl, ClO and HO<sub>2</sub> are insensitive to the choice of rate constant for HOCl formation, as this is a minor loss channel for both

## Part II. Satellite-borne MLS observations of HOCl

- MLS (Microwave Limb Sounder) on Aura satellite has been measuring vertical profiles of HOCl since August 2004
  - Range of latitudes sampled: 82°S to 82°N
  - About 3,500 vertical scans each day, half of sunlight atmosphere, half of dark atmosphere
  - Local solar time of MLS measurements is ~ 1:45 pm and 1:45 am
  - We consider the most recent publicly available retrieval version, v2.2
- Preliminary vertical profiles of MLS HOCl for daytime, nighttime, and day/night difference, compared with FIRS-2 and model:
  - MLS measurements are a zonal monthly mean for September 2005, from 30°N to 40°N
  - Unshaded regions indicate MLS measurements of HOCl are suitable for scientific use
  - Error bars represent both precision and accuracy



- For the day/night difference (removes potential systematic biases in the MLS HOCl signal)
  - MLS HOCl agrees with the model using the faster rate constant (green)
  - MLS HOCl agrees with FIRS-2 for pressures of 4.6 hPa and greater

## Summary

- With the update of FIRS-2 and MkIV retrieval spectroscopy to HITRAN 2004, HOCl measurements now agree with each other
  - However, these two field measurements of HOCl disagree with current models
  - Model agrees better with observations if  $k$  is increased by ~ a factor-of-two
    - either via a faster rate constant (comparable to that of Stimpfle et al.),
    - or via some other, as yet unknown, HOCl formation process
- Model predictions of the HOCl precursors, ClO and HO<sub>2</sub>, agree with field measurements obtained by FIRS-2, SLS, and MLS
  - They are insensitive to the value of the rate constant for HOCl formation
- Now that the spectroscopy behind the remote sensing observations is consistent, and the balloon data sets are in agreement, we use them to evaluate the accuracy of MLS retrievals of HOCl
- Preliminary comparison of MLS observations of HOCl with measurements obtained by balloon-borne FIRS-2 shows MLS is lower than FIRS-2 by about 35%
  - However, for pressures  $\geq 4.6$  hPa, the day/night differences (which remove potential biases in the MLS HOCl) are in agreement