2. Scientific Objectives

2.1 Background
2.2 Inorganic Chlorine chemistry
2.3 Bromine budget
2.4 HO\textsubscript{x} budget
2.5 Cirrus clouds
Stratospheric ozone trend

35N–60N 1979 – 2004

Contribution to the column O$_3$ trend in 1979–2004

-1%

-2%

0%

(-3% for 1992–1995 deficit)

WMO, 2006

Further needs of systematic understandings of O$_3$ chemistry and transport processes

Background

Controlling factors

Gas phase photochemistry

Dynamics & gas & het. photochemistry

(1/3 is due to export of vortex air)
Species and altitude range of SMILES measurement

* Single scan with 3 km altitude resolution.
** Zonal mean average with 5 km altitude resolution

Day and night Within clouds, too
Scientific targets of SMILES

1. Inorganic Chlorine chemistry
   - ClO to HCl ratio (O₃ trend in the US)
   - HOCl production (O₃ trend in the LS)
   - Global ClO (background ClO)
2. Bromine budget (very short-lived source gas)
3. HOₓ budget (HOₓ dilemma)
4. Cirrus clouds (Het. reactions & Rad. budget)
5. O₃ isotope (mass independent chemistry)
(6. UT/LS mixing (O₃ flux))
**Partitioning within Cl\(_y\) in US**

Inclusion of the reaction (2) results in a better agreement with observed [ClO]/[HCl] ratio (balloon) and O\(_3\) trend in the upper stratosphere.

\[
\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2 \quad (1)
\]

\[
6\%
\]

\[
\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2 \quad (2)
\]

SMILES [ClO]/[HCl] measurements can be utilized further systematic test on Cl\(_y\) partitioning.
There is a factor of 2 uncertainty in the rate constant for this reaction. It directly affects HOCl levels, while it does not affect ClO and HO₂ levels.
ClO + HO₂ → HOCl + O₂
HOCl + hv → OH + Cl
Cl + O₃ → ClO + O₂
OH + O₃ → HO₂ + O₂
net 2O₃ → 3O₂

ClO+HO₂ cycle can be the most efficient O₃ loss processes within the cycles involving ClO in the LS, and therefore important for O₃ trend.

SMILES HOCl measurements together with ClO and HO₂ measurements can be used to assess importance of the ClO+HO₂ cycle.
Global ClO distribution

The background ClO_x level is important to quantify the in-situ O_3 loss at mid-latitudes. However, its global distribution has not been observed with high precision.

SMILES provides global ClO distribution with high precision. Furthermore, measurements of ClO, HCl, HOCl, and HO_2 can provide important insights into the Cl_y chemistry.
BrO measurements suggest that in addition to long-lived source gases (halons and methyl bromide), very short-lived ($\tau < 6$ months) source gases likely contribute to Br$_y$ by about 5 pptv. This difference can be important for O$_3$ in the LS. (Salawitch et al., 2005)
**Bromine budget**

**Bry from CH$_3$Br & Halons**

MLS-derived **Br$_y$**

+ 5 pptv

**BrO + ClO & BrO + HO$_2$ cycles**

(WMO, 2006)

**Br$_y$ from CH$_3$Br & Halons**

(Livesey et al., 2006)

SMILES BrO measurements provide further constraints to Br$_y$ level, which affects O$_3$ chemistry in the LS.
SMILES measurements will provide vertical profiles of HO₂, which can be used to test our understanding of HOₓ chemistry.
Cirrus clouds: Heterogeneous reactions and radiation budget

MLS–derived IWC at 147 hPa

January

July

(Wu et al., 2008)
Cirrus Clouds: Heterogeneous reactions and radiation budget

Cirrus clouds

-65°C

(Thornton et al., 2005)
Stratospheric $O_3$ chemistry

Production

$O_2 \xrightarrow{hv} O_x = O + O_3$

Loss

$O_x \rightarrow O_3, HNO_3, HO_2, ClO, HCl, HOCl, BrO, BrO_x$

Coupling between radicals

+ analyses on dynamics
+ data from other satellites
+ 3D CTM calculations

Better understandings of $O_3$ trend

Wennberg et al., 1994

SPADE, May 1993

(Hetongers, HO_x, NO_x)

Increasing ozone loss

Increasing NO_x

(Wennberg et al., 1994)
**Summary**

- **Inorganic chlorine chemistry**

Chlorine is the key species for $O_3$ trend. SMILES provide major $Cl_y$ species, including $ClO$, $HCl$, and $HOCl$. These data set will be utilized to test our understanding in $Cl_y$ chemistry, especially that affects $O_3$ trend in the US and LS.

- **Bromine budget**

Very short-lived ($\tau<6$ months) bromine containing species likely to be important for the budget of bromine, which plays significant role in $O_3$ chemistry. SMILES will provide useful constraint to study bromine budget.

- **$HO_x$ budget**

SMILES $HO_2$ data can be utilized to test our understanding of $HO_x$ chemistry.

- **Systematic understanding of $O_3$ chemistry and transport**

Combination of high precision $O_3$ data and those of related species will be utilized for overall test for the $O_3$ chemistry ($O_3$– $NO_x$–$ClO_x$–$BrO_x$) and transport (low–mid–latitudes) processes that control $O_3$ levels.