STUDIES OF OH AND HO$_2$ IN THE REGION OF
THE ARCTIC WINTER TROPOPAUSE

A Dissertation in
Meteorology
by
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ABSTRACT

This study is based on in situ measurements made on the NASA DC-8 during the SAGE III Ozone Loss and Validation Experiment/Third European Stratospheric Experiment on Ozone (SOLVE/THESEO) campaign which was conducted in the 1999-2000 Arctic winter (November, 1999 to April, 2000). The DC-8’s extensive coverage of the arctic winter tropopause region afforded the opportunity to probe more deeply into the unique chemistry of the upper troposphere/lower stratosphere (UTLS). Central to this analysis are the measurements of OH, HO₂ (collectively called HOₓ), and halogen oxides that play a crucial role in the chemistry of this region. We discuss the modified configuration of the Penn State Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS) in order to accommodate the University of Colorado ClO/BrO instrument, the salient points of the measurement profiles that were obtained by this unique instrument, the shifts of these profiles in the presence of cirrus clouds that may indicate heterogeneous processing/activation of halogen reservoir species, and the projected impact of the abundance of these species on the local chemical ozone budget in the region.
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Chapter 1

Introduction

The largest decrease in the seasonally normalized ozone concentration takes place in the lower stratosphere and amounts to up to 10 % per decade [WMO, 2003]. The loss of ozone in this region is of great concern not only because of its effect on the total ozone column, but also because of its impact on the radiative forcing of Earth’s climate system. Since the discovery of the Antarctic ozone hole [Farman et al., 1985], numerous studies have been made in order to explain this severe loss. These studies have established the importance of halogen compounds, particularly chlorine monoxide (ClO), that are formed when halogens are released from halogen reservoirs (e.g., chlorine nitrate (ClONO$_2$), and hydrogen chloride (HCl)) through heterogeneous chemistry on the surfaces of polar stratospheric clouds (PSCs) in the lower stratosphere (LS) at the low temperatures of the polar winters. Upon the return of sunlight to the region during the polar spring, these halogen oxides dramatically destroy ozone through catalytic cycles involving hydrogen and nitrogen oxides. This chemistry of the polar LS is presently relatively well understood [Solomon, 1999].

At the lower boundary of the LS region—the region of the tropopause—the chemistry is less apparent. This region is characterized by the interaction of air masses of different chemical and dynamical character through the process of stratosphere-troposphere exchange (STE) [Holton et al., 1995]. More recent model simulations of the effects of ozone and other trace gases on the mean stratospheric temperature trends bring into focus the importance of understanding the ozone variability in the tropopause region in relation to global warming. Uncertainties in the lower stratospheric cooling trend are mainly due to our poor understanding of the vertical profile of ozone loss near the tropopause [Ramaswamy et al., 2001].
There has also been speculation on the significant role cirrus clouds may play in the perturbations of the local chemistry of the midlatitude tropopause. There are irreconcilable discrepancies between observed and modeled ozone depletion profiles at the midlatitudes. It has been suggested that cirrus clouds could affect the abundance of key radicals in that region thus affecting ozone [Borrmann et al., 1996, 1997].

Solomon et al. [1997] examined the role cirrus clouds might play in ozone destruction in some detail using global satellite observations of cirrus clouds as input to a numerical model of stratospheric ozone chemistry and transport. This work was an extension of the work done by Borrmann et al. [1996, 1997]. They concluded that it is indeed highly likely that cirrus clouds perturb chemical composition in the tropopause region and that the magnitude of such perturbations depends upon season, altitude, and latitude. The main concern is that these perturbations enhance a mechanism for the destruction of ozone through key catalytic reactions involving the radicals chlorine monoxide (ClO), bromine monoxide (BrO), and reactive hydrogen (HO_x), which is the sum of hydroxyl (OH) and hydroperoxyl (HO_2). Speculations have been made that actual concentrations of these key radicals within the region of the tropopause may be higher than what most present models predict [Avallone et al., 1993].

Ice and liquid surfaces facilitate reactions of long-lived compounds, such as chlorine nitrate (ClONO_2), that are not possible in the gas phase [Solomon et al., 1986; Solomon, 1999; Jaegle et al., 1997]. Such a process releases species that become more active in reacting with other molecules in its environment—hence, it is called “activation” of the species. In cirrus clouds, the heterogeneous reactions of interest are:

\[ \text{ClONO}_2 + \text{H}_2\text{O(ice)} \rightarrow \text{HOCl} + \text{HNO}_3 \]

\[ \text{BrONO}_2 + \text{H}_2\text{O(ice)} \rightarrow \text{HOBr} + \text{HNO}_3 \]

Furthermore, by photolysis,

\[ \text{HOCl} + h\nu \rightarrow \text{OH} + \text{Cl} \]
$\text{HOBr} + h\nu \rightarrow \text{OH} + \text{Br}$

Figure 1-1 illustrates this process schematically for the chlorine species—bromine species behave analogously.

![Diagram of chlorine activation on water ice and its effect on HOx.](image)

**Figure 1-1:** Schematic of chlorine activation on water ice and its effect on HO\textsubscript{x}.

The region of the tropopause straddles two atmospheric regimes—the upper troposphere and the lowermost stratosphere (UTLS)—wherein HO\textsubscript{x} chemistry has different net effects. In the upper troposphere (UT), the reactions of HO\textsubscript{x} with nitrogen oxides (NO\textsubscript{x}), which is the sum of nitric oxide (NO) and nitrogen dioxide (NO\textsubscript{2}), mainly result in a net production of ozone. In the lowermost stratosphere (LS), the greater abundance of halogen oxides (i.e. ClO, BrO) and ozone and the dearth of volatile organic compounds (VOCs) lead to the net destruction of ozone by catalytic cycles involving NO\textsubscript{x}, HO\textsubscript{x}, and halogens. The primary source of OH in the UTLS is the
photolysis of ozone to O($^1D$) followed by the reaction with water vapor. In the LS, this is also the primary source of all HO$_x$ (i.e. P(OH) ~ P(HO$_x$)). It has been shown that the concentration of OH in the lower stratosphere (a region above the lowermost stratosphere defined by $M < 2.5 \times 10^{18}$ molecules cm$^{-3}$) can be accurately parameterized in terms of a linear combination of secant functions based on the photolysis frequencies of ozone to O($^1D$) and formaldehyde to HCO [Hanisco et al., 2001]. This behavior results in a relatively tight agreement between measurements and model calculations of HO$_x$ in the lower stratosphere.

In the UTLS, however, as yet irreconcilable discrepancies exist between measurements and model calculations. Models constrained by ample suites of measured species known to affect HO$_x$ concentrations consistently and systematically underpredict HO$_x$ measurements in this region. Furthermore, uncertainties in present models of tropospheric chemistry are largest in the high altitudes and low temperatures of the UT. Lastly, HO$_x$ production throughout the troposphere is generally found to be dominated by ozone-water reaction (i.e. O$_3$ + hv $\rightarrow$ O($^1D$) + O$_2$; O($^1D$) + H$_2$O $\rightarrow$ 2OH) except in the region of the UT, where photolyses of oxygenated hydrocarbons and peroxides have been shown to be a significant source [Crawford et al., 1999].

This region is also the locale for the formation and persistence of cirrus clouds which have been suggested to be possible sites for activation of halogen species through heterogeneous chemistry—similar to that which occurs in polar stratospheric clouds (PSCs). Chemical perturbations due to heterogeneous chemistry on these clouds have been calculated to deplete the ozone column by an additional 1-2% [Borrmann et al., 1996; Solomon et al., 1997; Bregman et al., 2002], and the ozone in the lowermost stratosphere by considerably more.

During the SAGE III Ozone Loss and Validation Experiment and Third European Stratospheric Experiment on Ozone (SOLVE/THESAO, hereinafter, SOLVE) campaign held during the 1999-2000 Arctic winter (November, 1999 to April, 2000), extensive in situ measurements of HO$_x$ were made on the NASA DC-8 in the tropopause region. SOLVE has been
the largest international field campaign deployed to date to study Arctic ozone. The focus of the campaign was mainly on the stratospheric circumpolar vortex—where formation of polar stratospheric clouds facilitates ozone depletion through the heterogeneous conversion of halogen reservoir species (e.g., ClONO$_2$, HCl, etc.) to active halogen species (e.g., Cl$_2$, ClO) and subsequent catalytic reactions resulting in ozone loss upon the onset of sunlight [Newman et al., 2002].

Although the dynamics and chemistry of the Arctic vortex are less pronounced than its Antarctic counterpart, the effects of ozone loss in the Arctic would have greater direct effects on the relatively greater human population density in the Northern Hemisphere. Furthermore, it could be expected that anthropogenic contributions to vortex chemistry would be greater in the Arctic than in the Antarctic. Past Arctic stratospheric campaigns had focused more on the late winter to summer periods—during which more active photochemistry may be observed. One of the objectives of SOLVE was to augment the dearth of in situ data in the early and middle winter phases of the development of the Arctic vortex. These measurements would be essential in order to explore more exhaustively the dynamics (e.g. thermal evolution that governs the formation and extent of polar stratospheric clouds and that dictates the scope of diabatic descent of vortex air) and chemistry (e.g. the evolution and the partitioning of the inorganic chlorine, bromine, and nitrogen families) that set the stage for rapid ozone depletion in the spring [Newman et al., 2002].

The DC-8 in situ measurements during SOLVE were unique in that they were probably the most extensive in situ measurements to date in the region of the winter arctic tropopause. The measurement milieu was characterized mainly by little or no sunlight (solar zenith angle > 68°) in a region which is chemically in between or a mixture of the upper tropospheric and lower stratospheric regimes. This is a region that is photochemically relatively inactive and in which production of HO$_x$ from secondary sources may mitigate any loss from active halogen species.
Hence, the present understanding of the chemistry of this region is relatively limited and there have been consistent discrepancies of models and measurements in this region.

During SOLVE, enhancements of ClO averaging 15-20 pptv were indeed observed and 2-4 ppt of BrO was inferred [Thornton et al., 2003]. Cirrus clouds and stratospheric aerosols may play a major role in these increases in concentration.

Measurements of hydroxyl radicals (OH) have been, until around a decade ago, arguably one of the holy grails of atmospheric measurements. The difficulty in measuring OH comes about because of its extreme reactivity (lifetime on the order of a second or less) and its consequent low mixing ratio in the atmosphere (a fraction of a part per trillion per volume—or pptv). The related hydroperoxyl radical (HO$_2$) has a typical lifetime and abundance of around an order of magnitude more than OH and is coupled to OH as its primary reservoir in the atmosphere—thus, OH and HO$_2$ are collectively called HO$_x$. Furthermore, the reaction HO$_2$ with NO is one of the most important precursors of ozone—and this reaction also couples HO$_x$ with NO$_x$ (NO + NO$_2$). Hence, the simultaneous and collocated measurement of HO$_2$ with OH is similarly sought after. The importance of measurements of HO$_x$ lies in the primacy of this radical family in determining the oxidative capacity of the atmosphere. Because of this, there have been numerous efforts to measure HO$_x$ over the past two decades [Hard et al., 1984, 1992a, 1992b; Stevens et al., 1994; Wennberg et al., 1995; Kanaya et al., 2001; Tan et al., 2001; Faloona et al., 2004; Martinez et al., 2010].

The abundance and distribution of HO$_x$ in the atmosphere depends on its sources, sinks, and exchange reactions. The other chemical species and the complexity of the reaction sequences that contribute to the HO$_x$ profiles depend justifiably on the unique properties of the atmosphere in the region of interest. For example, the chemistry that controls HO$_x$ in the lower troposphere is more complex and involves a different, much larger set of key reactions than the chemical
scheme for the lower stratosphere. The chemical schemes pertinent to the different vertical
regimes of the atmosphere (i.e. troposphere, stratosphere, etc.) have been unveiled and are
continually being refined through the application of the classic scientific method—the cycle of
theory being verified by measurements and of measurements advancing theory.

In the subsequent sections, we present with more detail what is known about the basic
hydrogen, nitrogen, and halogen chemistry of the UTLS.

1.1 Photochemistry of Ozone in the Upper Troposphere/Lower Stratosphere (UTLS)

The mechanism for the steady-state concentration of ozone in the stratosphere was first
proposed by Chapman [1930] in what is now known as the Chapman cycle:

\[ \text{O}_2 + h\nu (\lambda < 242 \text{ nm}) \rightarrow \text{O} + \text{O} \quad \text{(R1.1)} \]

\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \quad \text{(R1.2)} \]

\[ \text{O}_3 + h\nu (\lambda < 315 \text{ nm}) \rightarrow \text{O}_2 + \text{O} \quad \text{(R1.3)} \]

\[ \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \quad \text{(R1.4)} \]

It is pedagogical to think of O and O\(_3\) as a family—odd oxygen or O\(_x\)—that allows us to
view reactions (R1.1) to (R1.4) as a complete scheme of production (R1.1), rapid exchange
reactions or cycling ((R1.2) and (R1.3)), and loss (R1.4) of odd oxygen that consequently should
define steady-state concentrations of ozone in the unperturbed stratosphere.

Reaction (R1.3), however, may be seen as the result of two fast reactions which quickly
generate and deactivate the highly reactive photofragment O(\(^1\text{D}\)):

\[ \text{O}_3 + h\nu (\lambda < 315 \text{ nm}) \rightarrow \text{O}_2 + \text{O} (\(^1\text{D}\)) \quad \text{(R1.3a)} \]

\[ \text{O}(\(^1\text{D}\)) \rightarrow \text{O}(\(^3\text{P}\)) \quad \text{(R1.3b)} \]

In the presence of H\(_2\)O, a minute fraction of the O(\(^1\text{D}\)) leads to the formation of the
hydroxyl radical, OH:
\[ \text{O}^1(\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \]  
(R1.5)

This is both a primary source of \( \text{OH} \) and a sink of ozone.

The highly reactive \( \text{OH} \) radical combines with available \( \text{CO} \), \( \text{CH}_4 \), and \( \text{VOCs} \) to generate peroxyl radicals \( \text{HO}_2 \) and higher \( \text{RO}_2 \). In the presence of ample \( \text{NO} \), these peroxyl radicals react to form \( \text{NO}_2 \):

\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2
\end{align*}
\]  
(R1.6) \hspace{2cm} (R1.7)

The photolabile \( \text{NO}_2 \) is readily photolysed into \( \text{NO} \) and \( \text{O}^3(\text{P}) \) which, through reaction (R1.2), leads to ozone formation:

\[
\begin{align*}
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3
\end{align*}
\]  
(R1.8) \hspace{2cm} (R1.2)

These catalytic reactions between \( \text{HO}_x \) (\( \text{OH} \) and \( \text{HO}_2 \)) and \( \text{NO}_x \) (\( \text{NO} \) and \( \text{NO}_2 \)) can produce many ozone molecules per \( \text{OH} \) molecule formed through (R1.5). Hence, in the presence of sufficient \( \text{NO} \), each ozone molecule lost to the formation of \( \text{OH} \) begets more ozone molecules in return. The efficiency with which this occurs is sometimes referred to as the ozone production efficiency but is more fundamentally called the chain length—which is the number of times a \( \text{HO}_x \) molecule is cycled before it is lost. In a \( \text{NO}_x \)-laden environment, \( \text{HO}_x \) is lost mainly through its reaction with \( \text{NO}_2 \) to form nitric acid:

\[
\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3
\]  
(R1.9)

Hence, quantitatively, the \( \text{HO}_x \) chain length may be expressed as:

\[
\frac{k_{\text{R1.6}}[\text{HO}_2][\text{NO}]}{k_{\text{R1.9}}[\text{OH}][\text{NO}_2]} \]  
(1.1)

where \( k_{\text{R}x.x} \) is the temperature-dependent rate constant of reaction \( x.x \).

When \( \text{NO} \) is scarce, however, the self-reactions of \( \text{HO}_x \) become more important:

\[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2
\]  
(R1.10)
\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  \hspace{1cm} (R1.11)

These latter reactions also constitute a net loss of \( \text{HO}_x \).

In the presence of ozone, with little or no \( \text{NO}_x \), the reactions of \( \text{HO}_x \) with ozone contribute to ozone loss:

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]  \hspace{1cm} (R1.12)
\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]  \hspace{1cm} (R1.13)

In view of the above key reactions between \( \text{O}_x \), \( \text{HO}_x \), and \( \text{NO}_x \), we define the ozone tendency \( P(\text{O}_3) \) which may be expressed as the difference between the rates of the rate-limiting reactions that form or deplete ozone. Ozone formation \( F(\text{O}_3) \) is rate-limited by (R1.6) and (R1.7) so that:

\[ F(\text{O}_3) = k_{\text{R1.6}}[\text{HO}_2][\text{NO}] + k_{\text{R1.7}}[\text{RO}_2][\text{NO}] \]  \hspace{1cm} (1.2)

Ozone destruction \( D(\text{O}_3) \) is rate-limited by (R1.5), (R1.12), and (R1.13) so that:

\[ D(\text{O}_3) = k_{\text{R1.5}}[\text{O}(^1\text{D})][\text{H}_2\text{O}] + k_{\text{R1.12}}[\text{OH}][\text{O}_3] + k_{\text{R1.13}}[\text{HO}_2][\text{O}_3] \]  \hspace{1cm} (1.3)

In the lower stratosphere, reactions of halogen species contribute to a net destruction of ozone through their interaction with \( \text{HO}_x \):

\[ \text{HO}_2 + \text{XO} \rightarrow \text{HOX} + \text{O}_2, \hspace{0.5cm} \text{X} = \text{Cl}, \text{Br} \]  \hspace{1cm} (R1.14)
\[ \text{HOX} + h\nu \rightarrow \text{OH} + \text{X} \]  \hspace{1cm} (R1.15)
\[ \text{X} + \text{O}_3 \rightarrow \text{XO} + \text{O}_2 \]  \hspace{1cm} (R1.16)

Or interaction with each other:

\[ \text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OCIO} \]  \hspace{1cm} (R1.17)
\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]  \hspace{1cm} (R1.18)

Or with themselves:

\[ \text{ClO} + \text{ClO} \rightarrow \text{M} \rightarrow (\text{ClO})_2 \]  \hspace{1cm} (R1.19)
\[ (\text{ClO})_2 + h\nu \rightarrow \text{Cl} + \text{ClOO} \]  \hspace{1cm} (R1.20)
ClOO $\rightarrow^{M} \text{Cl} + \text{O}_2$ \hspace{1cm} (R1.21)

$2 \times (\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2)$ \hspace{1cm} (R1.22)

The BrO + BrO reaction, which yields either Br + Br + O$_2$ or Br$_2$ + O$_2$, is negligible when compared with the other halogen cycles in this region.

Hence, taking these halogen reactions into consideration, we may augment the ozone destruction expression (1.3) accordingly:

$$D(O_3) = k_{R1.5}[O(1D)][H_2O] + k_{R1.12}[OH][O_3]$$
$$+ k_{R1.13}[HO_2][O_3] + k_{R1.14a}[ClO][HO_2] + k_{R1.14b}[BrO][HO_2]$$
$$+ k_{R1.17}[BrO][ClO] + k_{R1.19}[ClO][ClO]$$ \hspace{1cm} (1.4)

Lastly, we note that NO$_x$ catalytic cycles have been omitted in (1.4). Though NO$_x$ cycles dominate ozone loss in the lower stratosphere above 25 km [Osterman et al. 1997], they are negligible at around 10 – 15 km (which includes the region which we are examining in this dissertation). HO$_x$ and halogen cycles dominate this region of the lowermost stratosphere. [WMO, 1998; Wennberg et al., 1994; Seinfeld and Pandis, 2006].

1.2 Basic HO$_x$ Chemistry of the UTLS

The primary source of HO$_x$ in the lower stratosphere (LS) is the photolysis of ozone and the subsequent reaction with water:

$$\text{O}_3 + h\nu \rightarrow O(1D) + \text{O}_2$$ \hspace{1cm} (R1.23)

$$O(1D) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$$ \hspace{1cm} (R1.24)

In the presence of ozone, carbon monoxide, methane, and chlorine monoxide, OH is efficiently shifted into HO$_2$:

$$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$$ \hspace{1cm} (R1.25)
The HO$_2$ that is formed is similarly efficiently reduced back to OH by reaction with ozone, nitric oxide, chlorine monoxide, and bromine monoxide:

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \quad \text{(R1.30)}
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R1.31)}
\]

\[
\text{HO}_2 + \text{ClO} \rightarrow \text{HOCl} + \text{O}_2 \quad \text{(R1.32)}
\]

\[
\text{HOCl} + h\nu \rightarrow \text{OH} + \text{Cl} \quad \text{(R1.33)}
\]

\[
\text{HO}_2 + \text{BrO} \rightarrow \text{HOBr} + \text{O}_2 \quad \text{(R1.34)}
\]

\[
\text{HOBr} + h\nu \rightarrow \text{OH} + \text{Br} \quad \text{(R1.35)}
\]

Reactions (1.25) to (1.35) above exchange OH and HO$_2$ much faster than they are produced or lost. Moreover, these exchange reactions are intimately coupled with odd oxygen and halogen species to act in catalytic sequences that ultimately result in efficient ozone loss:

**Sequence 1:**

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(R1.25)}
\]

\[
\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \quad \text{(R1.30)}
\]

Net: 2\text{O}_3 \rightarrow 3\text{O}_2

**Sequence 2:**

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(R1.25)}
\]

\[
\text{HO}_2 + \text{XO} \rightarrow \text{HOX} + \text{O}_2, \ X = \text{Cl, Br} \quad \text{(R1.32, R1.34)}
\]

\[
\text{HOX} + h\nu \rightarrow \text{OH} + \text{X} \quad \text{(R1.33, R1.35)}
\]

\[
\text{X} + \text{O}_3 \rightarrow \text{XO} + \text{O}_2 \quad \text{(R1.36)}
\]

Net: 2\text{O}_3 + h\nu \rightarrow 3\text{O}_2
On the other hand, the coupling of HO\(_x\) with CO and NO\(_x\) results in ozone production:

Sequence 3:

\[
\begin{align*}
\text{OH + CO} & \xrightarrow{\alpha} \text{HO}_2 + \text{CO}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 & \xrightarrow{M} \text{O}_3 \\
\text{Net: CO} + 2\text{O}_2 & \rightarrow \text{CO}_2 + \text{O}_3
\end{align*}
\]

The above sequence also applies for non-methane hydrocarbons (NMHCs) in place of CO except for an extra step wherein an organic peroxy radical (RO\(_2\)) is formed initially before being further reduced by NO into HO\(_2\).

Not all of the reactions of HO\(_x\) with ozone and NO\(_x\) result in ozone loss.

\[
\begin{align*}
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 & \rightarrow \text{O}_3
\end{align*}
\]

Finally, loss of HO\(_x\) is mainly due to self reactions and/or heterogeneous uptake onto cloud or aerosol surfaces:

\[
\begin{align*}
\text{OH} + \text{HO}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2 \\
\text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\end{align*}
\]

We see, therefore, that OH and HO\(_2\) beget each other in a series of exchange reactions that rapidly establishes equilibrium between them. The exchange sequences above (Sequences 1 to 4) thus determine the instantaneous ambient concentrations of HO\(_x\) more than their sources and sinks. Assuming that reactions (1.25) to (1.35) are indeed the main exchange reactions for HO\(_x\), we can write the steady-state HO\(_x\) ratio (HO\(_2\)/OH) in the LS as:
This ratio reflects the instantaneous state of the HO$_x$ system when the rates of the source and sink reactions of HO$_x$ are negligible compared to that of the exchange reactions.

In the UT, however, the dearth of ozone and halogens results in CO dominating OH-to-HO$_2$ conversion and NO dominating the reverse conversion (except when NO is small so that ozone dominates). In this case, the HO$_x$ ratio may be simplified to:

\[
\frac{[\text{HO}_2]}{[\text{OH}]} = \frac{k_{\text{OH}, CO}[\text{CO}]}{k_{\text{OH}, O_3}[\text{O}_3] + k_{\text{OH}, NO}[\text{NO}]} \approx k_{\text{OH}, CO}[\text{CO}]
\]

(1.6)

However, Eq. (1.6) above may not generally be assumed to reflect the instantaneous state of HO$_x$ in the UT because primary sources other than the O($^1\text{D}$) reaction with water (R1.24) (i.e., photolyses of aldehydes and peroxides) may have rates competitive with the main HO$_x$ exchange reactions.

Nevertheless, we can divide the UTLS into particular chemical regimes governed by the dominant HO$_x$ exchange reaction. The upper troposphere, for example, could be defined chemically by the region where the (HO$_2$-producing) reaction of OH with CO (R1.26) dominates the reaction of OH with O$_3$ (R1.25) (e.g. by a factor of 5 to 10), whereas the lower stratosphere could be defined as the region where this dominance reverses. Similarly, ozone loss in the lower stratosphere could be diagnosed by examining regimes that are based on the conversion of HO$_2$ to OH. Regimes with high ozone loss efficiency would be regions in which the reaction of HO$_2$ and O$_3$ (R1.30) dominates the reaction of HO$_2$ and NO (R1.31) (ozone-dominated) and regions in which the reaction of HO$_2$ and ClO (R1.32) dominates the reaction of HO$_2$ and O$_3$ (R1.8) (ClO-dominated). On the other hand, regions of low ozone loss efficiency would be regions where the reaction of HO$_2$ and NO (R1.31) dominates the reaction of HO$_2$ and O$_3$ (R1.30) (NO-dominated) [Lanzendorf et al., 2001].
Lastly, if heterogeneous chemistry of halogen compounds on cirrus clouds is significant in the UTLS, HO\textsubscript{x} measurements should be a sensitive indicator of this chemistry and of the nature of the surfaces that affects the halogen activation [Jaeglé et al., 1997]. The most important heterogeneous reactions that are known to convert chlorine reservoir species ClONO\textsubscript{2} and HCl to active chlorine on stratospheric particles are:

\[
\begin{align*}
\text{ClONO}_2 + \text{HCl}(a) & \rightarrow_{\text{het}} \text{HNO}_3(a) + \text{Cl}_2 & \text{(R1.41)} \\
\text{ClONO}_2 + \text{H}_2\text{O}(a) & \rightarrow_{\text{het}} \text{HNO}_3(a) + \text{HOCl} & \text{(R1.42)} \\
\text{HOCl} + \text{HCl}(a) & \rightarrow_{\text{het}} \text{H}_2\text{O} + \text{Cl}_2 & \text{(R1.43)}
\end{align*}
\]

where (a) indicates that this species is adsorbed onto the aerosol surface that effects the heterogeneous reaction. (see Fig. 1-1)

The latter two reactions above, (R1.42) and (R1.43), are strongly coupled to HO\textsubscript{x} through the loss of ozone and the gas-phase production and loss of HOCl via:

\[
\begin{align*}
\text{HOCl} + h\nu & \rightarrow \text{OH} + \text{Cl} & \text{(R1.33)} \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 & \text{(R1.36)} \\
\text{HO}_2 + \text{ClO} & \rightarrow \text{HOCl} + \text{O}_2 & \text{(R1.32)}
\end{align*}
\]

The signature of heterogeneous processing via reaction R1.42 should manifest itself in additional gas-phase loss of HO\textsubscript{2} and extra production of OH during sunrise. The net effect of such heterogeneous processing would be to decrease ozone and the HO\textsubscript{2}/OH ratio.

Hence, even a small enhancement of the chemical ozone loss mechanism through heterogeneous processing in the UTLS region can have an appreciable effect on the trends in the total ozone column.
1.3 Scope and objectives of this dissertation

The environment of the winter Arctic tropopause is an ideal test bed for further understanding the causes of currently observed Arctic ozone loss trends. The greatest uncertainties in the chemistry of the ozone column lie in this region of relatively mixed nature—the region of the Arctic upper troposphere/lower stratosphere (UTLS). In this dissertation, we will present the first extensive measurements of HO\(_x\) in the Arctic winter tropopause and illustrate and analyze the important mechanisms that involve HO\(_x\) in the general chemistry of the Arctic tropopause region.

In this region, using a collocated measurement, a curious enhancement of chlorine monoxide has been observed (and a similar enhancement of bromine monoxide has been inferred) which points to a possible heterogeneous mechanism on cirrus clouds that are prevalent in this region. Using the measurements of HO\(_x\) and a simple box model, we will explore what can and cannot be concluded about the heterogeneous chemistry in this region.

Lastly, we will calculate the (photochemical) ozone loss and the local ozone budget for the region using the observations of HO\(_x\) and halogens in order to gain a quantitative understanding of the contribution of the ozone chemistry in the UTLS to the total ozone column.

To do this, we will first describe the unique attributes of the instrument used to make these measurements and the general environment in which it was deployed (Chapter 2), compare and differentiate HO\(_x\) chemistry in the regions of the upper troposphere (UT) and the lowermost stratosphere (LS), which the tropopause separates, and discuss how the measurements agree or disagree with our present understanding (Chapter 3), probe the effects of cirrus clouds on HO\(_x\) using simple box models (Chapter 4), and project the effects this would have on the local ozone budget in this region (Chapter 5).
Chapter 2

*In Situ* Measurements and Measurement Milieu for SOLVE

2.1 Instrument Description

During SOLVE, OH and HO$_2$ were measured *in situ* on the NASA DC-8 by the Penn State Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS). The instrument is based on the fluorescence assay by gas expansion (FAGE) method in which the sample gas is expanded under low pressure in order to extend the fluorescence lifetime [Hard *et al.*, 1984]. The instrument is mounted in the forward cargo bay of the DC-8 and the sample air is drawn by a vacuum pump and a Roots supercharger through an aerodynamic concentric double-nacelle projecting out of the underside of the aircraft. The nacelle is designed to protrude sufficiently outside the aircraft boundary layer and to decelerate the incident ambient air sample from around 200 m/s to 10-20 m/s without any contact with the nacelle surface. The sample flow velocity may be adjusted with an axial centerbody within the smaller concentric nacelle to verify any velocity dependencies of the measurement, which may be used to diagnose contact of the sampled air with the surface of the nacelle. Variable pitch and yaw maneuvers during one of the engineering test flights of the PEM-Tropics B mission verified that measurements were not affected by aircraft angle-of-attack except during a few periods where the inlet was most likely sampling the aircraft boundary layer.

The inlet extends by around 35 cm (14”) beyond the skin of the aircraft. The inlet tube is 5 cm (2”) in diameter and is heated actively to mitigate temperature fluctuations and to prevent icing of the inlet which would throttle or clog the flow. An inlet with a larger aperture (relative to past airborne missions)—2.0 mm (0.078”)—was used for SOLVE to effect internal pressures of around 4-8 hPa in the relatively low external pressures of the tropopause region. These relatively
higher internal pressures were also more suitable for the University of Colorado ClO/BrO instrument which was piggybacked onto ATHOS and which will be discussed shortly.

The sampled air from the external inlet expands under low pressure into a detection block mounted on the aircraft nadir plate inside the aircraft. The distance from the inlet to the center of the detection block is around 43 cm (17”). The sample is irradiated by laser light in the detection block through a White cell configuration that causes the input laser beam to pass through the sample 36 times. The laser is a folded-cavity, frequency-doubled, YAG-pumped dye laser that was run at a 3 kHz pulse repetition rate and was tuned by an intracavity etalon on and off the OH Q1(2) line near 308 nm with a 15-10-5-10 s duty cycle—where the 15-s period was online for OH detection, the 5-s period was online for HO2 detection, and the 10-s periods were offline periods on both sides (minima) of the absorption peak for background measurement. This asymmetric duty cycle was implemented in order to effect a relatively higher sensitivity for OH. This is because in all other configurations of ATHOS the laser power in the OH detection cell is around two to three times that of the HO2 detection cell but in the SOLVE configuration, a single detection cell, and consequently, the same amount of laser power was used to measure both OH and HO2.

This laser light is delivered into the White cell via a 1-m optical fiber (200 µm dia.). The average UV power output ranged from 8-20 mW (typically around 12 mW) and the average UV power exiting the White cells ranged from 5.5-11 mW (typically around 7 mW).

A fraction of the resulting resonance fluorescence is collected and focused by condenser optics onto a narrowband UV filter and is subsequently detected by a time-gated microchannel plate detector. The time-gating of the detector gain allows detection of both the more intense Rayleigh scattering of the input laser light (in low-gain mode) and the relatively weaker ensuing resonance fluorescence (in high-gain mode) after the laser pulse exits the detection cell a few nanoseconds later. The number of detector counts per second is proportional to the OH mixing
ratio and the White cell UV power via a calibration factor that is diagnosed empirically before and after each flight series. The Rayleigh signal is an indicator of the real-time stability of the detection sensitivity.

The flow, White cell, and detection axes are mutually perpendicular and are mounted on the three pairs of opposing faces of the detection cell. For SOLVE, the detection block was modified to accommodate a port for the NO injector. \( \mathrm{HO}_2 \) is not measurable directly by LIF but the conversion of \( \mathrm{HO}_2 \) to OH by titration with NO—with a conversion efficiency of greater than 95%—allows ATHOS to measure total OH and determine \( \mathrm{HO}_2 \) by differencing the signals with and without NO addition. Normally, the \( \mathrm{HO}_2 \) measurement is done in a second detection cell (the \( \mathrm{HO}_2 \) axis) downstream from the first detection cell (the OH axis) and NO is added in between the two axes. For SOLVE, however, the same axis was used to measure both OH and \( \mathrm{HO}_2 \) and the detection cell was modified to allow an NO injector to be incorporated before this first axis. NO injection into the flow was effected through a 2-cm diameter loop of 1/8” perforated stainless steel tubing centered within the inlet tube with its plane normal to the flow. The NO flow rates were regulated through an 8-port solenoid valve-controlled stainless steel manifold which allowed ascarite-scrubbed NO source gas at 20 psi to be flow-regulated into the NO injector through sintered stainless steel flow restrictors (frits). The flow rates chosen were 3 (NO1 port) and 5 (NO2 port) standard cubic centimeters per minute (sccm) and normally 5 sccm was used. This setup allowed a diagnostic of the conversion efficiency of \( \mathrm{HO}_2 \) to OH by allowing NO values to range from 3 to 8 sccm. The NO injector was opened for 10 seconds in each 40-second sampling period in order to obtain \( \mathrm{HO}_2 \) online signals and \( \mathrm{HO}_2 \) offline (background) signals for 5 seconds each. The main concern about this setup was that the OH signal may be contaminated by inadvertent NO addition in the event of any leak of the NO injector valve. This possible problem was addressed by using one of the manifold ports as a “vacuum” port—to evacuate the manifold
before and during the OH measurement. Further details of the operation of ATHOS that is common to this and all its past configurations are discussed by Faloona et al. [2004].

As mentioned above, normally a second identical detection block is used for the simultaneous detection of HO$_2$ but for SOLVE this block was replaced by the ClO/BrO instrument (Figure 2-1). In this instrument, ClO and BrO are measured by titration of sampled air with NO to produce Cl and Br atoms. The reagent NO for this instrument is introduced via a second NO injector situated on the mounting adapter plate between the HO$_2$ detection cell and the BrO detection cell. This NO injector was opened for 15 seconds for every 40-second sampling period which, followed by the additional 10-second NO injection of ATHOS, resulted in obtaining 25 seconds of Cl/Br signals and 15 seconds of background. The sample is irradiated in two axes with ultraviolet radiation at 118.9 nm and 131.7 nm from a RF low-frequency discharge of Cl$_2$ or Br$_2$, respectively, in helium. The resonant scattering that ensues is detected by a photomultiplier tube mounted perpendicular to the axis of the lamp beam and the difference between the signals detected with and without NO is proportional to the concentrations of ClO or BrO in the sample. This measurement also requires that the sampling pressure be less than 100 hPa—a threshold necessary to avoid O$_2$ absorption of the Br$_2$ discharge. Further details of this technique are described by Anderson et al. [1977], Brune et al. [1989a, 1989b], and Toohey et al. [1993].

The ClO/BrO instrument for SOLVE was constrained to operate at around 4-6 hPa—lower than its normal operating pressure of around at least 10 hPa—because of its coupling to the ATHOS flow system. An unfortunate consequence of this was that this caused the detection limit of the BrO detection axis to be higher than the expected BrO abundances—essentially rendering its measurement moot. Furthermore, the amount of reagent NO needed to convert HO$_2$ to OH was much greater than the amount needed to convert ClO into Cl atoms, such that OClO was also converted to Cl atoms by the reaction sequence OClO + NO → ClO + NO$_2$ and ClO + NO → Cl
+ NO₂. These additional reactions caused the instrument to become sensitive to OCIO for the DC-8 conditions in darkness. Hence, only measurements of the sum of ClO and OCIO were made by the instrument [Thornton et al., 2003].

Thus, unlike all other configurations of ATHOS, the configuration for SOLVE consisted of a single detection block in which OH and HO₂ were detected alternately over a 40-second period. At the median DC-8 air speed of 230 m/s, this corresponds to a spatial extent of 9.2 km. The measurements of this instrument version, therefore, may be considered simultaneous for averages over this 40-second period or over a distance of 9.2 km. These averages are reasonable for most of the DC-8 sampling area—where numerous constant-altitude flight legs provided long stretches of homogeneous air masses to sample (as gleaned from other trace species measured).
The accuracy for both OH and HO$_2$ is estimated to be ±40% at the 2σ confidence level. The detection limit for OH is 10 parts per quadrillion (ppqv) over 40 seconds (S/N = 2) or 3 ppqv over a 5-minute integration time. The detection limit for HO$_2$ is 0.1 parts per trillion (pptv) over 40 seconds (S/N = 2), based on both ATHOS’s lower detection sensitivity of HO$_2$ and a small signal that comes from the purified NO. These detection limits are adequate for the conditions of these studies.

2.2 HO$_x$ and ozone interference

Previous measurements of HO$_x$ using laser-induced fluorescence were fraught with artifacts from the photolytic production of OH within the instrument from ambient ozone and water vapor [Smith and Crosley, 1990]. This effect is more pronounced for instruments that use 282 nm for OH excitation [Shirinzadeh et al., 1987]. The use of 308 nm excitation in ATHOS reduces this effect by around a factor of 100 because of the combined lower absorption cross sections of ozone and OH at this wavelength—essentially rendering this interference negligible [Zeng et al., 1998]. However, a non-laser-generated ozone-water interference has also been observed and is postulated to be a dark reaction on the detection cell walls—an effect that seems to be related to the detection cell flow geometry and internal coatings [Holland et al., 2003].

The polar wintertime conditions during SOLVE—the numerous flight hours in darkness and in regions of elevated ozone in the lowermost stratosphere—afforded an excellent field opportunity to test ATHOS for ozone interferences. Figure 2-2 is a plot OH and HO$_2$ as a function of ozone in the nighttime cloud-free lowermost stratosphere. The visible scatter of the HO$_x$ concentrations (gray dots) in the positive and negative directions is characteristic of the Poisson-distributed measurements of ATHOS at concentrations near its detection limit. The diamond symbols are binned averages of the measurements in 50-ppb ozone bins.
Throughout the range of ozone from around 100-900 ppb, the value of OH in the dark (based on the photolysis frequency $J(O^1D)$) remains relatively constant at less than 0.010 pptv with no discernible trend with ozone. This confirms the insensitivity of the OH measurement of ATHOS to ozone interference. HO$_2$ stays at less than 0.2 pptv throughout this range of ozone but there is a slight linear relationship with ozone of around 0.2 ppqv per ppbv of ozone. However, because this trend is small and the change in HO$_2$ comparable to the background detection limit, both OH and HO$_2$ measurements are effectively free of an ozone interference for SOLVE.

Figure 2-2: HO$_x$ vs. O$_3$ plots in the cloud-free nighttime lower stratosphere. Gray dots are the 40-second HO$_x$ mixing ratios and the diamond symbols are binned averages of the species in 50-ppb ozone bins.
2.3 Other In Situ Measurements

Other measurements on the DC-8 provide the additional information needed for the analysis of the HOx and ClO measurements (Table 2-1). Pressure, temperature, and altitude are logged as flight data by the DC-8 data acquisition and distribution system (DADS) along with other pertinent flight data such as aircraft pitch, heading, true air speed, and other aircraft track information. Vertical temperature profiles and local tropopause heights are measured by the JPL microwave temperature profiler (MTP) that uses a scanning mirror to view ten elevation angles between -80 and 80 degrees from flight level. The thermal emission from oxygen molecules at 55.51, 56.66, and 58.79 GHz is measured at each angle and vertical temperature profile is made for each full scan (which takes about 17 seconds) [Mahoney, M. J., personal communication].

NO, NO2, and NOy were measured by chemiluminescence with NOy being converted catalytically to NO on heated gold tubes and with CO as a reducing agent. An aft-facing inlet that discriminates against particles larger than 1 µm is used to sample gas-phase NOy and a forward-facing inlet samples total NOy—i.e. both gas-phase and particulate NOy. Particulate NOy may be derived by taking the difference between the forward and aft-facing NOy measurements scaled by a suitable enhancement factor, a function of aircraft speed and particle size, that takes into account the anisokinetic nature of the particulate sampling [Kondo et al., 1997, 2003].

Ozone was measured by near-IR chemiluminescence of excited-state NO2 produced by the reaction of NO and ozone in the sampled air [Gregory et al., 1983]. Ozone was also measured by UV absorption.

Gas-phase H2O was measured by second-harmonic tunable laser diode spectroscopy at 1.37 µm in a 54-pass Herriott cell pod (optical absorption path length of 11.1 m) and also by external path differential absorption at 1.4007 µm. The external path method is unique in that differential absorption is used to detect H2O along a path always normal to the plane’s heading.
A compact laser transceiver is mounted to a window on the DC-8 and the beam is reflected off reflective material mounted on the DC-8 engine housing (optical absorption path length of 28.5 m)—negating wall and inlet effects normally encountered by other measurement methods [Collins et al., 1995]. A third instrument, a closed-path laser hygrometer (CLH) based on the Herriott cell instrument above, measured total H₂O (gas-phase + particulate) due to its forward-facing inlet design [Halar et al., 2004].

Table 2-1: In Situ Measurements on the NASA DC-8 during SOLVE.

<table>
<thead>
<tr>
<th>Species</th>
<th>Technique</th>
<th>Group</th>
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</thead>
<tbody>
<tr>
<td>Pressure, Temperature,</td>
<td>FAGE/LIF</td>
<td>Penn State University</td>
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<td>Altitude, Flight Data</td>
<td></td>
<td>DC-8 DADS</td>
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<td>resonance fluorescence</td>
<td>NASA of Colorado</td>
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<td>chemiluminescence, UV absorption</td>
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<tr>
<td>O₃</td>
<td></td>
<td>NASA Langley, Univ. of Colorado</td>
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<tr>
<td>NO, NO₂, NO₃y (gas-phase and</td>
<td>chemiluminescence</td>
<td>Univ. of Tokyo</td>
</tr>
<tr>
<td>particulate)</td>
<td></td>
<td></td>
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<td>non-dispersive IR spectrometry</td>
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<td>JPL, NASA Langley</td>
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<td>(gas-phase and particulate)</td>
<td>hygrometry</td>
<td></td>
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<tr>
<td>total H₂O</td>
<td>closed-path laser hygrometry</td>
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<tr>
<td>(gas-phase and particulate)</td>
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<td>HNO₃</td>
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<td>photolysis frequencies</td>
<td>spectral radiometry</td>
<td>NCAR</td>
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<tr>
<td>aerosol size distribution</td>
<td>FSSP/PCASP</td>
<td>NASA Langley</td>
</tr>
<tr>
<td>vertical temperature profile,</td>
<td>microwave temperature profiler</td>
<td>JPL</td>
</tr>
<tr>
<td>tropopause height</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CO, CH₄, and N₂O were measured by the Differential Absorption CO Measurement (DACOM) instrument which uses three tunable diode lasers at 3.3, 4.5, and 4.7 m to access the CH₄, N₂O, and CO absorption lines, respectively [Vay et al., 1998]. CO₂ is measured by a modified Licor Model 6252 non-dispersive infrared (NDIR) spectrometer [Vay et al., 1999].

Particle size distributions were determined by the Passive Cavity Aerosol Spectrometer Probe (PCASP) for 28 bins of particle diameters between 0.1 and 3 µm and by the Forward Scattering Spectrometer Probe (FSSP) for 28 bins of particle diameters between 0.4 to 20 µm [Anderson et al. 1996].

Photolysis frequencies from 280-420 nm were measured by the Scanning Actinic Flux Spectroradiometer (SAFS). This consisted of two hemispherical (2π steradian) mounted above and below the aircraft in order to collect the spherically-integrated actinic flux [Shetter and Müller, 1999]. Photolysis frequencies were calculated for 16 species.

### 2.4 Measurement Milieu

During SOLVE, the NASA DC-8 flight schedule was partitioned into three flight series spanning the Arctic winter. The first series was from 30 November to 16 December 1999 (8 flights), the second from 14 January to 29 January 2000 (7 flights), and the third from 27 February to 15 March 2000 (7 flights). The first and last flights of each series were transit flights to and from Kiruna, Sweden, respectively. Hence, a total of 16 flights were actually confined to the Arctic region—we will designate these as “science flights” as opposed to the “transit flights”. The difference is important as the flight plans for science flights are based on scientific objectives and meteorological forecasts (e.g. the position and extent of the polar vortex, the existence of PSCs or cirrus, etc.) while transit flights are mainly focused on getting to the destination (Dryden air base or Kiruna) without the need for refueling (although a refueling stop was required on the
last flight of the last flight series). Furthermore, the transit flights brought the DC-8 into the midlatitudes and into regions of greater insolation—regions which are photochemically dissimilar to the winter Arctic region.

The in situ measurements made by the NASA DC-8 during SOLVE were carried out mostly in the region of the winter arctic tropopause—a region that encompasses the arctic upper troposphere and lowermost stratosphere. The flight plans during SOLVE varied greatly according to the desired science objectives of each flight but a consistent pattern in all flights was the stair-stepping pattern in flight level or pressure altitude. Each flight would level off at a relatively lower altitude (around 10 km) and subsequently increase the flight level 3 to 5 times during the flight and ending at the ceiling of the DC-8 (around 12.5 km) before descending in order to land. This flight level pattern was modified at times when it was beneficial to the science objectives—e.g. to get out of lidar-obscreening clouds—but for almost all of the second and third flight series the stair-stepping pattern was followed. This resulted in the DC-8 sampling the lowermost stratosphere for about three-quarters of the flight time and the upper troposphere for the remaining quarter. The sampling coverage of the DC-8 flights is unprecedented in the tropopause region.

Distinguishing between the lowermost stratosphere and the lower stratosphere is important because the chemical makeup of each of these regions is quite distinct due to the episodic mixing of air from the upper troposphere into the lowermost stratosphere. The DC-8 flight ceiling of around 12.5 km (or around 180 hPa) confined it mostly to the lowermost stratosphere and did not allow it to penetrate into the lower stratosphere.

The horizontal spatial coverage of the DC-8 science flights (i.e. excluding transit flights between Kiruna and Dryden) is shown in Figure 2-3. From this figure we can glean the spatial extent of all the flights during SOLVE as the DC-8 was steered in and out (and along the edge) of the polar vortex—from its formation in late December 1999 to its breakup in mid-April 2000.
One of the crucial conditions for chlorine activation on cirrus is that the cirrus must penetrate into the lowermost stratosphere (or into air with characteristics of the lowermost stratosphere)—bringing its water-laden surface area into halogen-laden air. During SOLVE, the DC-8 science flights flew mostly in the lowermost stratosphere (~75%) and for the rest of the time in the upper troposphere (~25%)—based on tropopause heights determined by the JPL microwave temperature profiler. The measurements made thus provided a large data set to diagnose cirrus in the lowermost stratosphere.

**2.5 Cirrus in the lowermost stratosphere**

Figure 2-3: Flight tracks of the NASA DC-8 science flights during SOLVE.
The presence of cirrus clouds was determined from the University of Colorado closed-path laser hygrometer (CLH) data which measured total water content combined with an assiduous inspection of the periods of clear and cloudy skies from the time-stamped videos of the DC-8’s forward- and nadir-looking cameras during the science flights of 23 January, 25 January, and 8 March 2000 (these flights had the most extensive cirrus encounters). From this comparison, a threshold of 50 ppm of total water content (at temperatures at or below 230 K) was deemed to designate cirrus. Decreasing the threshold to 45 ppm would increase the extent of the cloud coverage but was found in the video observations to correspond to some regions that were cloud-free. Periods in which water vapor exceeded the threshold of 50 ppm were found in all video observations to be clearly within a cloud. The 50-ppm threshold is therefore actually a slight overestimate (which slightly underestimates the extent of the cloud) and thus gives a conservative indicator of the extent of the cloud. These measurements were also compared with the JPL laser hygrometer observations of supersaturation with respect to ice. Figure 2-4 shows the measurement coverage as a function of altitude relative to the local tropopause and the fraction of the measurements that indicated supersaturation with respect to ice. Figure 2-5 shows the same profile but uses the CLH total water measurement (gas-phase + particulate) using a threshold of 50 ppm to designate cirrus.

We note from these plots that the number of observations of ice saturation in the tropopause region greatly exceeds the number of observations of ice water content. This incongruity between ice saturation and ice water content measurements is not uncommon in the upper troposphere and may still be indicative of the presence of low optical depth (i.e. subvisible) cirrus that are not captured by the CLH total water content instrument [Jensen et al., 2001, 2005, 2010; Hallar et al., 2004; Gensch et al., 2008].

These observations indicate that most of the conditions for ice saturation and cirrus ice water content are localized within half a kilometer below the tropopause. Nevertheless, there is
an appreciable number of observations within half a kilometer above the tropopause—up to 20% of the observations in this region are supersaturated with respect to ice and a little more than 5% reveal enhanced ice water content. These observations are dissimilar to observations made by Smith et al. [2001] in the midlatitude lowermost stratosphere, who observed a sharply diminishing probability of ice saturation and heterogeneous reaction probability above the midlatitude tropopause and, hence, a negligible probability of activation of chlorine—supported by the absence of measurements of enhanced ClO above the tropopause. However, their observations in the tropopause were relatively limited as they were made mainly during ascent or descent legs of the NASA ER-2 while the observations made here are extensive in their horizontal spatial coverage of the same region. Furthermore, these differences in observations may be due to the differences in the dynamics of stratosphere-troposphere exchange (STE) in the wintertime polar region as compared to that of the midlatitudes [Holton et al., 1995]. The wintertime polar tropopause is also more likely to be richer in inorganic halogen species than the midlatitude tropopause. What we may infer from this particular situation, then, is that the blending of water-rich tropospheric air with inorganic halogen-bearing stratospheric air occurs with greater probability and to a larger extent in the wintertime polar region than in midlatitudes.

From the above analysis, we have put forth our evidence for the existence of cirrus above the thermal tropopause. Furthermore, the concentration of N$_2$O, which has its photolytic sink only in the stratosphere and is therefore well-mixed in the troposphere and tends only to decrease with height in the stratosphere, may also be used as a gauge of the stratospheric nature of the air (i.e. lower N$_2$O, more stratospheric). Global N$_2$O concentrations have been increasing slowly through the past years at the rate of around 1 ppbv/year (0.25-0.35%/year) [WMO, 1999]. The chemical tropopause during this 1999/2000 Arctic winter may be set at around N$_2$O = 315 ppbv.
Figure 2-4: Ice saturation (relative humidity with respect to ice >= 100%) as a function of altitude relative to the tropopause. The left panel shows the total number of (1-second) measurements made in each 0.5 km bin, the middle panel is the number of ice saturation observations, and the right panel is the ratio of the middle panel to the top panel.
Figure 2-5: *In situ* ice observations (indicated by total water enhancements above 50 ppm) as a function of altitude relative to the tropopause. The left panel shows the total number of (1-second) measurements made in each 0.5 km bin, the middle panel is the number of ice saturation observations, and the right panel is the ratio of the middle panel to the top panel.
One of the goals of this study is to examine the possibility of cirrus clouds forming in halogen-rich air. Unfortunately, the DC-8 had not measurement of organic or inorganic halogens, other than ClO and BrO. However, the DC-8 did have a measurement of nitrous oxide (N$_2$O). The utility of N$_2$O as an indicator of stratospheric nature is particularly important for estimating the inorganic (available) halogen content (Cl$_y$, Br$_y$) of the sampled air. Measurements of organic halogen species (CCl$_y$, CBr$_y$) along with estimates of total halogen content (Cl$_{tot}$, Br$_{tot}$) allow calculation of inorganic halogen content by difference (i.e. Cl$_y$ = Cl$_{tot}$ – CCl$_y$). Tight correlations between calculations of Cl$_y$ and N$_2$O have been established by such calculations [Woodbridge et al., 1995]. Using the data gathered during SOLVE from the NASA ER-2 Airborne Chromatograph for Atmospheric Tracer Species (ACATS) instrument [Elkins et al., 1996; Romashkin et al., 2001], we can calculate Cl$_{tot}$ and CCl$_y$ to come up with a relationship for Cl$_y$ as a function of N$_2$O. Figure 2-6 illustrates our calculated correlation for chlorine species.
The correlation between $N_2O$ and $Cl_y$ shows that regions of lower $N_2O$ are regions of higher inorganic chlorine. Hence, the presence of cirrus clouds in regions of lower $N_2O$ indicates more definitively the juxtaposition of the water-laden cloud surfaces and chlorine-rich air and is the more relevant indicator of potential processing of the available chlorine by cirrus. From the observations of $N_2O$ we had during SOLVE, we calculate that around 17% of all the cirrus encountered was in air with $Cl_y$ greater than at least 100 pptv (Figure 2-7). These regions with cirrus and $Cl_y > 200$ pptv are also the coldest regions where cirrus was observed ($T = 197-199$ K.).
Photochemical Box Model

A time-stepping photochemical box model adapted from the Chemical Lagrangian Model of the Stratosphere (CLaMS) gas-phase chemical mechanism [McKenna et al., 2002] was developed using JPL 2003 kinetics [Sander et al., 2003] in order to test our theoretical understanding of the HO₅ measurements. The gas-phase mechanism implemented herein consists

Figure 2-7: Observations of cirrus near the tropopause. Around 10% of the cirrus was observed within 0.5 km above the tropopause and around 17% was observed within chlorine-rich air (Cl₂ > 100 pptv)
of 77 gas-phase reactions and 19 photolysis reactions (Appendix). The model was written using Facsimile software [Curtis and Sweetenham, 1987]. The model was run on 5-minute averages of a 40-second-resolution merge file of simultaneous ancillary measurements of pressure, temperature, O₃, H₂O, CO, CH₄, NO, particle data, and photolysis frequencies based on the time stamp of the HOₓ measurements. The ancillary measurements were used to initialize the model at each data point and OH and HO₂ were calculated by running the model to (instantaneous) steady state for each data point. For the second and third flight series, a total of 690 data points were used.

In this photochemically-weak setting, where SZA-based calculations may be deficient in parameterizing the actual radiative environment, the availability of in situ measurements of photolysis frequencies ensured that the actual photolysis fields would be represented as accurately as possible. The accurate representation of these radiation fields is particularly important in, above, or below cloudy regions and at high SZA (SZA > 85°) where radiative extinction or enhancement is not generally well-represented by existing radiative transfer calculations based on SZA [Madronich, 1987; Madronich and Flocke, 1998].

The SOLVE DC-8 payload had a dearth of measurements of known HOₓ sources in the UT—namely peroxides, formaldehyde, and acetone—so the values of these species were set to values measured in similar conditions during the 1997 SONEX campaign [Faloona et al., 2000]. The values used for these species were typically the mean of the background measurement and the enhanced measurement from air that was most likely lofted convectively [Folkins et al., 1998]. Furthermore, the lack of measurements of chlorine species—except for ClO and some CFCs (for only four flights) [Linnea Avallone, unpublished data]—necessitated a general estimate of reactive chlorine from the ER-2 ACATS measurements correlations with ER-2 “unified” N₂O [Gaines, 2000; Hurst et al., 2002].

A summary of these model results will be presented in Chapter 3.
Chapter 3

**OH and HO\textsubscript{2} In the Region of the Winter Arctic Tropopause**

OH and HO\textsubscript{2} mixing ratios were measured throughout all the three flight series of the DC-8 with the exception of four science flights in the first flight series (i.e. flights on Dec 5, 7, 10, and 12, 1999) due to a laser power supply failure and logistical difficulties in the timely delivery of its replacement. However, almost all of the flights of interest in sunlight (i.e. of photochemical significance) occurred during the second and third flight series and complete measurements were made during these periods. Other *in situ* data included pressure, temperature, altitude, vertical temperature profiles (and local tropopause height), O\textsubscript{3}, NO, NO\textsubscript{2}, NO\textsubscript{y} (gas-phase and particulate), H\textsubscript{2}O (gas-phase and particulate), CO, CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O, ClO, SO\textsubscript{2}, HNO\textsubscript{3}, particle size distributions (from ultrafine to 20 µm), and photolysis frequencies (see Chapter 2 for details).

There are a number of ways in which the tropopause is currently defined: chemical (based on threshold values of ozone), dynamical (~2.0 potential vorticity units), potential temperature (380 K, but mainly applicable for the tropics), and temperature lapse rate (the WMO definition—lowest level at which the lapse-rate decreases to 2 K/km or less, and the average lapse-rate from this level to any level within the next higher 2 km does not exceed 2 K/km). For purposes of this analysis, the temperature lapse rate tropopause height, based on the vertical temperature profile measurements made simultaneously with the HO\textsubscript{x} measurements onboard the NASA DC-8, will be used to designate the level of the tropopause and to separate the upper troposphere from the lowermost stratosphere.
3.1 HO₃ in the UTLS

Figure 3-1 and Figure 3-2 are scatter plots of HO₃ versus CO, NO, O₃, and N₂O—separated into upper troposphere and lower stratosphere, respectively, by MTP tropopause heights. The data was filtered for solar zenith angles (SZA) less than 90 degrees. This bound the data to an SZA range of 69 to 90 degrees—which is indicative of the low-light environment during SOLVE. The data illustrated here are for the second and third flight series (Jan and Mar, 2000) and exclude transit flights between Dryden and Kiruna. The data are furthermore segregated by indicating measurements made in cloud-free conditions (blue) and measurements in cirrus (red) based on FSSP and CLH total H₂O data.

From the upper troposphere plot (Figure 3-1), we can glean that there is a general decrease in HO₃ mixing ratios as the air masses become more stratospheric in nature—i.e. lower CO, higher O₃, lower N₂O. The plot also illustrates the well-known anti-correlation between O₃ and N₂O. Furthermore, the maximum value of O₃ is above 600 ppbv and the minimum value of N₂O is around 290 ppbv—values that would be expected well into the lowermost stratosphere. This indicates the presence of air masses of both chemically tropospheric and stratospheric nature in the region of the thermal tropopause.
The values of NO are generally below 100 pptv which puts the HO\textsubscript{x} measurements in the “NO\textsubscript{x}-limited” regime with respect to ozone production [Jaegle \textit{et al.}, 2001]—wherein HO\textsubscript{x} self-reactions and peroxide formation are the main sinks of HO\textsubscript{x}.

Measurements in cirrus clouds occur generally in tropospheric air masses (also see Figure 2-7)—i.e. higher CO, lower O\textsubscript{3}, higher N\textsubscript{2}O—and are also the regions of elevated HO\textsubscript{x}. These measurements in cirrus clouds will be discussed further in Chapter 4.
From the lowermost stratosphere plot (Figure 3-2), HO\textsubscript{x} decreases similarly in air masses of increasing stratospheric nature, and the range of the HO\textsubscript{x} concentrations is also lower by around a factor of two relative to the upper-tropospheric plot. Variation between air masses of tropospheric and stratospheric nature is similarly apparent as in the upper troposphere plot. NO concentrations in the lowermost stratosphere are not significantly different from the upper tropospheric values. An appreciable amount of cirrus is also present in this region—albeit mostly in air masses of tropospheric nature. Hence, the main differences between the regions in this atmospheric “slab” separated by the local thermal tropopause are the range of HO\textsubscript{x} concentrations and the frequency of cirrus clouds.

Figure 3-2: Scatter plots of HO\textsubscript{x} as a function of CO, NO, O\textsubscript{3}, and N\textsubscript{2}O above the local tropopause. Blue dots are measurements in cloud-free conditions and red dots are measurements in cirrus clouds. Data are filtered for SZA < 90.
Note that though we are using a precisely-defined definition of the thermal tropopause—which gives an ostensibly definite boundary height—the transition between troposphere and the stratosphere actually occurs over a more spread-out layer that may span tens to hundreds of meters [Fueglistaler et al., 2009]. Furthermore, even with the WMO lapse rate definition of the tropopause we used, there are instances that there may be more than one tropopause at the same location [Gettelman et al., 2002; Randel et al., 2007]. This indistinctness notwithstanding, a precise definition of the tropopause is not vital to the analyses herein as we have illustrated that the tropopause region is indeed replete with the variation of species of both tropospheric and stratospheric character. Nevertheless, regardless of the prescribed height of the thermal tropopause, there is interesting variability in HO\textsubscript{x} and other species measurements as a function of height. We proceed to discuss these altitude profiles in the following section.

### 3.2 Altitude Profiles

Median altitude profiles and interquartile ranges of HO\textsubscript{x} and SZA relative to the tropopause are shown in Figure 3-3. The variation of HO\textsubscript{x} clearly tracks that of the SZA. This is demonstrative of general relationship between HO\textsubscript{x} and insolation described by Hanisco et al. [2001] that showed that OH in the LS could be accurately parameterized in terms of a linear combination of secant functions based on the photolysis frequencies of ozone to O(\textsuperscript{1}D) and formaldehyde to HCO. This relationship is also illustrated further in the next section on sunlight transitions. Furthermore, this relationship is remarkable considering that HO\textsubscript{x} radicals are highly reactive—and is therefore indicative of the highly buffered nature of the HO\textsubscript{x} system.

Figure 3-4 illustrates median altitude profiles of NO\textsubscript{y} and total NO\textsubscript{y} relative to the local tropopause. Though lower gas-phase NO\textsubscript{y} is consistent with tropospheric air, the gas-phase NO\textsubscript{y} is consistently lower in concentration in the presence of cirrus than in cloud-free conditions.
Total NO\textsubscript{y} (i.e. gas-phase and particulate) is largest slightly below the tropopause—at the altitude where cirrus clouds are most prevalent (see Chapter 4). The profiles of gas-phase and total NO\textsubscript{y} in cirrus—i.e. that gas-phase NO\textsubscript{y} is relatively depleted and total NO\textsubscript{y} is enhanced in cirrus—are consistent with uptake of NO\textsubscript{y} (which is mainly HNO\textsubscript{3}) on the cirrus particles [Kondo \textit{et al.}, 2003]. These \textit{in situ} measurements confirm that most of the cirrus particles contain HNO\textsubscript{3}. The absence of \textit{in situ} measurements of H\textsubscript{2}SO\textsubscript{4} precludes any verification of the ternary (i.e. H\textsubscript{2}SO\textsubscript{4}/HNO\textsubscript{3}/H\textsubscript{2}O) nature of the cirrus particles. However, for the median temperature and H\textsubscript{2}O vapor pressure of the regions in which cirrus clouds were observed (~204 K and 15 ppmv, respectively), an approximate maximum value of around 65 % by weight of H\textsubscript{2}SO\textsubscript{4} may be inferred [Carslaw \textit{et al.}, 1995]

Median altitude profiles of CO, O\textsubscript{3}, NO, and N\textsubscript{2}O relative to the tropopause are shown in Figure 3-5. The CO, O\textsubscript{3}, and N\textsubscript{2}O medians follow expected trends—with CO and N\textsubscript{2}O decreasing with height and O\textsubscript{3} increasing with height. The median values of CO, O\textsubscript{3}, and N\textsubscript{2}O in cirrus are consistent with the tropospheric nature of the cirrus clouds. Lastly, the NO profile is not significantly different in or out of cirrus—except for the region around 1 km below the thermal tropopause where the majority of cirrus encounters were observed (see Figure 2-5).
Figure 3-3: Median profiles of HO$_x$ and solar zenith angle as a function of altitude relative to the local tropopause (0.5-km bin). Blue circles are in cloud-free conditions, red squares are in cirrus cloud. Horizontal bars indicate interquartile range (25 to 75 percentile).
Figure 3-4: Median profiles of NO\textsubscript{y} as a function of altitude relative to the local tropopause (0.5-km bin). Blue circles are in cloud-free conditions, red squares are in cirrus cloud. Horizontal bars indicate interquartile range (25 to 75 percentile).
3.3 HO$_x$ in Sunlight transitions

Although previous models of the UTLS already tend to underpredict HO$_x$ measurements [Jaegle et al., 1998; Wennberg et al., 1998; Brune et al., 1998]; the disparity between model calculations and measured values in this region becomes even greater at higher solar zenith angles (SZA)—i.e. near sunlight transitions. One of the processes thought to explain this discrepancy is the nighttime conversion of NO$_x$ to nitrous acid, HONO, on sulfate aerosols and the subsequent photolysis of HONO to produce OH [Salawitch et al., 1994]. Another postulated mechanism is
overtone-initiated photodissociation of atmospheric chromophores of hydrogen and nitrogen [Donaldson et al., 1997]—in particular, the photolysis of peroxy nitric acid (HO$_2$NO$_2$) at high SZAs [Wennberg et al., 1999; Salawitch et al., 2002; Evans et al., 2003; Stark et al., 2008]. This mechanism was demonstrated to increase atmospheric photolysis rates by 11% mainly impacting HO$_2$ production and negligibly producing OH [Stark et al., 2008]. Furthermore, if halogens are activated on clouds and aerosol in this region, we would expect a similar enhancement of OH in the sunrise transition due to the heterogeneous reaction:

$$\text{XONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOX} + \text{HNO}_3$$  \hspace{1cm} (R3.1)

followed by photolysis,

$$\text{HOX} + h\nu \rightarrow \text{OH} + \text{X}$$  \hspace{1cm} (R3.2)

where X = Cl, Br

This process would enhance both HO$_x$ and ClO$_x$ budgets and are of great interest because of the crucial role these species play in local chemical ozone loss in the region. The influence of clouds and aerosol on HO$_x$ is discussed in greater detail in Chapter 4.

Figure 3-6 and Figure 3-7 illustrate mean HO$_x$ profiles as a function of sunrise and sunset SZAs for the upper troposphere and lower stratosphere, respectively. Sunrise and sunset are determined by SZAs before and after local solar noon, respectively, at the longitude of the point of measurement. The measurement profiles illustrate the small range of high SZAs that characterized the observations over this winter campaign—especially for sunrise measurements. Furthermore, there is a gap of around ten SZAs (-80 to -70 degrees) in the sunrise measurements over which no measurements were made. The lowest SZA sunrise measurements were actually made just before local solar noon on the 8 March 2000 flight—and were thus the only data selected as sunrise data for that flight. Hence, these dissimilar sunrise values seem to fit more with the sunset values than with the sunrise ones. Nevertheless, we see that for the upper troposphere data in particular (Figure 3-6), HO$_x$ is slightly greater at each SZA during sunrise
than at sunset. This observation confirms earlier results from the Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE) [Salawitch et al., 1994] and the Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) campaigns [Wennberg et al., 1999; Salawitch et al., 2002]. The lowermost stratosphere data (Figure 3-7), however, do not exhibit these relative enhancements between sunrise and sunset.

Figure 3-6: Mean HOx profiles below the local tropopause as a function of solar zenith angle. Blue circles are cloud-free measurements; red asterisks are in cirrus cloud. Error bars indicate 1σ precision.
FIGURE 3-7: Mean HOx profiles above the local tropopause as a function of solar zenith angle. Blue circles are cloud-free measurements; red asterisks are in cirrus cloud. Error bars indicate 1σ precision.
3.4 Hydrogen, Nitrogen, and Halogen Oxides

We can infer the potential concentrations of halogen oxides from the measured HO\textsubscript{x} ratio (HO\textsubscript{2}/OH) by calculating the HO\textsubscript{x} ratio from Eq. (1.1) while neglecting the contribution of the halogen oxides, comparing the resulting calculation with the measured HO\textsubscript{x} ratio, and calculating the amount of halogen oxides required to bring the calculation and measurement into exact agreement. We begin by considering Figure 3-8. Figure 3-8 illustrates the relationship of the calculated HO\textsubscript{x} ratio to the measured HO\textsubscript{x} ratio as a function of NO, CO, and O\textsubscript{3}. The blue dots are median values of the ratio of the calculated HO\textsubscript{x} ratio to the measured HO\textsubscript{x} ratio binned by constant intervals of NO, CO, and O\textsubscript{3}. Note that the clustering of the dots on the semilog plot is the consequence of displaying a linearly-binned value on a logarithmic scale. The calculated HO\textsubscript{x} ratio agrees with the measured HO\textsubscript{x} ratio only when NO is around 100 pptv and overestimates the measured ratio as NO decreases (left uppermost panel). Since most of the NO measurements are below 10 pptv (right uppermost panel), the calculated HO\textsubscript{x} ratio is clearly higher than the measured ratio for almost all the measurements. On the other hand, the calculated HO\textsubscript{x} ratio is also seen to be around 1.5 times the measured value when plotted as a function of CO and around 2 times the measured value when plotted as a function of O\textsubscript{3} but this calculated-to-measured ratio is not dependent on the concentrations of CO and O\textsubscript{3}. 
The University of Colorado ClO/BrO instrument was integrated with ATHOS in order to measure both halogen and hydrogen oxides simultaneously. Significant enhancements of ClO of around 15 to 20 pptv were observed on the average in the UTLS region where ClO is expected to have concentrations of less than a few pptv [Thornton et al., 2003].

Recalling the HO\textsubscript{x} ratio given by Eq. (1.5):

\[
\frac{[\text{HO}_2]}{[\text{OH}]} = \frac{k_{\text{OH}+\text{NO}}[\text{O}_3] + k_{\text{OH}+\text{CO}}[\text{CO}] + k_{\text{OH}+\text{ClO}}[\text{ClO}] + 1.7 \times k_{\text{OH}+\text{CH}_4}[\text{CH}_4]}{k_{\text{HO}_2+\text{O}_3}[\text{O}_3] + k_{\text{HO}_2+\text{NO}}[\text{NO}] + k_{\text{HO}_2+\text{ClO}}[\text{ClO}] + k_{\text{HO}_2+\text{BrO}}[\text{BrO}]} \tag{1.5}
\]

we may derive a relationship that allows us to calculate ClO by reconciling the measured and the modeled HO\textsubscript{x} ratio (i.e. bringing the ratio of the calculated-to-measured HO\textsubscript{x} ratio back to 1):

Figure 3-8: The left panels show the ratio of the calculated HO\textsubscript{x} ratio (HO\textsubscript{2}/OH) to the measured HO\textsubscript{x} ratio binned by NO, CO, and O\textsubscript{3}. The right panels show the number of observations per bin.
\[
[\text{ClO}] = \frac{r_{\text{OH} + \text{CO}} + r_{\text{OH} + \text{O}_2} + 1.7 \cdot r_{\text{OH} + \text{CH}_3} - r_{\text{HO}_2 + \text{NO} - r_{\text{HO}_2 + \text{O}_2}}}{k_{\text{HO}_2 + \text{ClO}} [\text{HO}_2] - f \times k_{\text{HO}_2 + \text{BrO}} [\text{HO}_2] - k_{\text{OH} + \text{ClO}} [\text{OH}]} \tag{3.1}
\]

where \( r_{XY} = k_{XY} [X][Y] \) and \( f \) is an arbitrarily assumed ratio between ClO and BrO (i.e. BrO = \( f \) ClO).

This may be done in a similar manner for BrO:

\[
[\text{BrO}] = \frac{r_{\text{OH} + \text{CO}} + r_{\text{OH} + \text{O}_2} + 1.7 \cdot r_{\text{OH} + \text{CH}_3} - r_{\text{HO}_2 + \text{NO} - r_{\text{HO}_2 + \text{O}_2}}}{k_{\text{HO}_2 + \text{BrO}} [\text{HO}_2] - \frac{1}{f} (k_{\text{OH} + \text{ClO}} [\text{OH}] - k_{\text{HO}_2 + \text{ClO}} [\text{HO}_2])} \tag{3.2}
\]

It is therefore possible to put upper limits on the abundances of ClO and BrO based on Eq. (3.1) and (3.2) by neglecting the contribution of the other halogen:

\[
[\text{ClO}]_{\text{max}} = \frac{r_{\text{OH} + \text{CO}} + r_{\text{OH} + \text{O}_2} + 1.7 \cdot r_{\text{OH} + \text{CH}_3} - r_{\text{HO}_2 + \text{NO} - r_{\text{HO}_2 + \text{O}_2}}}{k_{\text{HO}_2 + \text{ClO}} [\text{HO}_2] - k_{\text{OH} + \text{ClO}} [\text{OH}]} \tag{3.3}
\]

\[
[\text{BrO}]_{\text{max}} = \frac{r_{\text{OH} + \text{CO}} + r_{\text{OH} + \text{O}_2} + 1.7 \cdot r_{\text{OH} + \text{CH}_3} - r_{\text{HO}_2 + \text{NO} - r_{\text{HO}_2 + \text{O}_2}}}{k_{\text{HO}_2 + \text{BrO}} [\text{HO}_2]} \tag{3.4}
\]

Figure 3-9 shows plots of maximum ClO, maximum BrO, and ClO calculated with \( f = 0.1 \) and median binned by NO and Figure 3-10 shows binned averages of the same with solar zenith angle (SZA). We cannot deduce from the HOx ratio whether the halogen oxide involved is ClO or BrO. However, if the putative halogen is all ClO, its abundance should be around 50 pptv and if it is all BrO, its abundance should be around 8 pptv.

Furthermore, enhanced column BrO of up to 30 ppt was observed by the GOME satellite in the 1996 winter Arctic troposphere [Wagner and Platt, 1998; Richter et al., 1998]. Though the column BrO enhancements in the Arctic have been traditionally attributed to emissions from ground-based sources (tropospheric origin) [Simpson et al., 2007], more recent observations and analyses of Arctic BrO column “hotspots” during the 2008 ARCTAS and ARCPAC campaigns have pointed to BrO enhancements of between 5 to 10 pptv of stratospheric origin [Salawitch et
...al., 2010]. The upper limit of 8 pptv of BrO based on the HOx measurements here is consistent with these estimates.

Assuming that [BrO] = 0.1*[ClO], the [ClO] derived from the HOx ratio is approximately 15 pptv (Figure 3-9, second panel) and [BrO] is ~2 pptv. These values are consistent with measured [ClO] and inferred [BrO] [Thornton et al., 2003] during SOLVE (Figure 3-9, top panel). The assumption of the halogen partitioning, the ClO measurements, and, at high SZA’s, the HO2/OH ratios have large uncertainties. However, despite these uncertainties, the [ClO] derived from the HOx ratio confirms the direct simultaneous measurement of enhanced [ClO] by Thornton et al. [2003].

These measured and derived enhancements of reactive halogens have a significant impact on the calculated ozone loss in the UTLS region, as will be discussed in Chapter 5.
Figure 3-9: Calculated values of maximum ClO, maximum BrO and ClO for $f = 0.1$ from Eq. (3.1) bin averaged by NO.
Figure 3-10: Measured ClO and calculated values (from Eq. 3.1) of maximum ClO, maximum BrO and ClO for $f = 0.1$ from all science flights in January and March 2000 bin averaged by solar zenith angle.
3.5 Model results

A photochemical box model (Chapter 2) was run in two cases for comparison of modeled-to-measured HO\textsubscript{x}. The first ‘base case’ run (Figure 3-11) was constrained only to the measured species O\textsubscript{3}, H\textsubscript{2}O, CO, CH\textsubscript{4}, NO, and photolysis frequencies while the second ‘param case’ run (Figure 3-12) was constrained further to the estimated peroxides, formaldehyde, acetone, and ClO.

Clearly, the ‘base’ case is greatly insufficient in reproducing the measured HO\textsubscript{x} values—indicating that the ozone-water reaction is not the main source of HO\textsubscript{x} for this environment. Not only does this model case severely underestimate the measurements (captures only around 30% of the measured values), this case cannot even reproduce the variance of the measurements satisfactorily ($R^2 \approx 0.59$).

The ‘param case’, however, is an improvement. The absolute measured values are reproduced to around 80% with a much tighter correlation ($R^2 \approx 0.7$ and 0.8 for OH and HO\textsubscript{2}, respectively). This suggests that the unmeasured (and therefore parameterized) HO\textsubscript{x} sources are indeed more significant in this region. Sensitivity tests of the model to the parameterized species revealed no definite “sweet spot” for the concentrations of the parameterized species—i.e. for this model, there is no optimum combination of the parameterized species that will reproduce the measured values. This indicates that increases in any of the parameterized species will always cause increases in HO\textsubscript{x} and the choice of which species to increase is arbitrary. Hence, it seems reasonable to stay with these SONEX-based estimates of the unmeasured species for the model analysis of specific flights in the next chapter.
Figure 3-11: ‘Base case’ This case is the model constrained with only the available in situ measurements. Axes depict mixing ratios in pptv. See text for details.
Figure 3-12: ‘Param case’ The Param case is the base case plus inclusion of parameterized peroxides, aldehydes, acetone, and ClO. Axes depict mixing ratios in pptv. See Chapter 2 for details.
3.6 Summary

We have described herein the region of the wintertime Arctic UTLS from the standpoint of the measurements of HO\(_x\) and the known (modeled) behavior of HO\(_x\) in the presence of other measured species like NO, O\(_3\), H\(_2\)O, CO, CH\(_4\), and photolysis frequencies. We have pointed out significant deviations of the HO\(_x\) measurements from its expected behavior and have likewise attempted to reconcile the two using parameterized (unmeasured) species known to produce HO\(_x\). Finally, we have illustrated using a calculation with the HO\(_x\) ratio (HO\(_2\)/OH) and its constraining species (Eq. 1.5) in order to derive the amounts of reactive halogens ClO and BrO required to reconcile the calculations with the measurements.

The key result to be taken away from this is that the reconciliation of the calculated HO\(_x\) ratio to the measured HO\(_x\) ratio points to a more chemically-active UTLS region with reactive halogens significantly higher than previously observed or predicted for this region. While it is possible that some unmeasured species in this region that shifts OH to HO\(_2\) with the same efficiency as ClO and BrO, it is much more likely that ClO an BrO are responsible. The inferred values of around 20 pptv for ClO and 2 pptv for BrO (i.e. 0.1 * ClO) from our calculations are remarkably consistent with the findings of Thornton et al. [2003] in the same region.

Having established the plausibility of these significant enhancements in reactive halogens, the next question is “What is causing these enhancements?” One of the hypotheses put forward by Solomon et al. [1997] is the activation of such by heterogeneous processing of inorganic chlorine in cirrus clouds.

We proceed to investigate this hypothesis with actual case studies in the Chapter 4.
Chapter 4

OH and HO$_2$ In The Presence of Cirrus Clouds

A measurement of HO$_2$ levels in the midlatitude upper troposphere during the SUCCESS mission showed that HO$_2$ concentrations decreased by 40 to 60 percent in the presence of cirrus clouds—and that the decrease is highly correlated to ice crystal surface area [Faloona et al., 1998]. These results point to heterogeneous loss of HO$_2$ in clouds. OH, however, was not found to be affected by such because the other losses of OH are already large compared to heterogeneous loss of OH while the other losses of HO$_2$ are not large compared to the heterogeneous loss. Because OH and HO$_2$ (collectively called HO$_x$) reactions lead to ozone production or loss, understanding the effects of cirrus clouds on HO$_x$ is important for understanding the ozone balance of the upper troposphere.

Heterogeneous reactions in clouds can affect both the halogen and HO$_x$ budgets and increases in reactive halogens are indicators of these reactions. HO$_x$ is also of particular importance because it dominates ozone loss rates in the lower stratosphere. This effect is potentially important if halogens are indeed activated by cirrus clouds in the region.

An analysis of the abundance of radicals near the tropopause for 49°N in summer and the monthly averaged composition perturbations caused by cirrus clouds imply ozone loss rates on the order of 10 ppbv/month [Solomon et al., 1997]. Since the ozone abundance in this region is only of the order of a few hundred ppbv and transport is slow, the calculated enhancements to ClO$_x$/BrO$_x$ and HO$_x$-driven ozone destruction can result in ozone trends over the decade of the 1980s on the order of several percent.

Measurements of these key radicals have been made in the lower stratosphere and upper troposphere [Stimpfle and Anderson, 1988; Stimpfle et al., 1989], but these measurements do not
provide a test of this heterogeneous chemistry. Thus, the measurements of these radicals in cirrus clouds near the tropopause would provide valuable input to present models of stratospheric chemical dynamics and transport.

During the SOLVE campaign, the DC-8 flight plans afforded the opportunity to make heretofore unprecedented extensive in situ aircraft measurements in the mid-to-high latitude upper troposphere/lower stratosphere (UTLS). On the DC-8, cirrus clouds were identified in situ by measurements of aerosol size distribution of up to 20 µm using a Forward Scattering Spectrometer Probe (FSSP), total water content (gas-phase H₂O + particulate H₂O) from a forward-facing probe inlet on the University of Colorado Tropospheric Ozone and Tracers from Commercial Aircraft Platforms (TOTCAP) instrument, and by reviewing the forward and nadir-viewing videos of the pertinent flights through cirrus.

For heterogeneous reactions, the relevant measurement is the total surface area (SA) of the ice crystals and the instruments above give only underestimates of SA because of the configurations of their sampling systems and the largest size bin of the aerosol size distribution measurement. As cirrus particle sizes normally extend beyond 20 µm, a parameterization is required to extend the size distribution (and hence, SA) to account for this undersampling. The size distribution of cirrus particles with characteristic diameters greater than 20 µm were estimated by using the number densities from the FSSP and the total ice water content (measured volume of particulate H₂O)—assuming a log-normal size distribution [Heymsfield and McFarquhar, 1996; Heymsfield et al., 2002]. From these estimates, a more realistic value of the SA was computed. The addition of these estimated values tended to double the total SA, on average, though this value is still an underestimate of the SA [Kondo et al., 2003].
4.1 General Observations in Cirrus

Median values of in situ measurements for all science flights classified by being inside and outside cirrus clouds are listed in Table 4-1. From these median values, we can glean the following general observations about cirrus clouds in contrast with cloud-free regions. Firstly, cirrus form slightly below the tropopause (~0.4 km below)—in regions where the tropopause is higher (1.5 km higher) and therefore colder (~4 K lower temperature). Secondly, cirrus clouds form in air masses of tropospheric nature—as indicated by higher values of NO, CO, and N₂O, and lower values of O₃. Cirrus particles take up copious amounts of HNO₃/NOₓ—as indicated by the relative depletion of gas-phase HNO₃ and NOₓ and the relative enhancement of total NOₓ.

Notably, HO₂ is enhanced in cirrus regions while OH remains relatively unaffected. ClO also appears to be enhanced in cirrus, but the broad 20-80 percentile range of these measurements does not signify much difference between cloud-free and in-cloud observations.
Table 4-1: Median observations for all SOLVE Science Flights (i.e. excluding transit flights)

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Cloud-Free Median Value</th>
<th>20-80 Percentile</th>
<th>In Cirrus Cloud Median Value</th>
<th>20-80 Percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O vapor, ppmv</td>
<td>10</td>
<td>8.4-11.2</td>
<td>15</td>
<td>9.9-22.9</td>
</tr>
<tr>
<td>RH (ice), %</td>
<td>31</td>
<td>20.0-43.8</td>
<td>104</td>
<td>91.3-117.2</td>
</tr>
<tr>
<td>OH, pptv</td>
<td>0.026</td>
<td>-0.005-0.067</td>
<td>0.026</td>
<td>-0.006-0.093</td>
</tr>
<tr>
<td>HO$_2$, pptv</td>
<td>0.25</td>
<td>0.02-1.1</td>
<td>0.36</td>
<td>0.02-2.46</td>
</tr>
<tr>
<td>ClO, pptv</td>
<td>11.8</td>
<td>-32.9-58.8</td>
<td>20.1</td>
<td>-40.4-58.3</td>
</tr>
<tr>
<td>NO, pptv</td>
<td>2.4</td>
<td>0.76-13.2</td>
<td>11.9</td>
<td>2.2-32.1</td>
</tr>
<tr>
<td>NO$_2$, pptv</td>
<td>18.4</td>
<td>6.48-44.9</td>
<td>24</td>
<td>4.65-58.0</td>
</tr>
<tr>
<td>HNO$_3$, pptv</td>
<td>1886</td>
<td>1485-2322</td>
<td>105</td>
<td>62.4-268.7</td>
</tr>
<tr>
<td>NO$_3$, pptv</td>
<td>1608</td>
<td>1278-2044</td>
<td>262</td>
<td>158-450</td>
</tr>
<tr>
<td>O$_3$, ppbv</td>
<td>359</td>
<td>285-445</td>
<td>66</td>
<td>47-106</td>
</tr>
<tr>
<td>CH$_4$, ppbv</td>
<td>1711</td>
<td>1689-1727</td>
<td>1777</td>
<td>1767-1792</td>
</tr>
<tr>
<td>CO, ppbv</td>
<td>36</td>
<td>29.9-35.7</td>
<td>92</td>
<td>84.0-106.3</td>
</tr>
<tr>
<td>SO$_2$, pptv</td>
<td>35</td>
<td>29-41.5</td>
<td>31</td>
<td>21.7-43</td>
</tr>
<tr>
<td>N$_2$O, ppbv</td>
<td>305</td>
<td>301-308</td>
<td>315.9</td>
<td>315.9-316.4</td>
</tr>
<tr>
<td>Total NO$_2$, pptv</td>
<td>1706</td>
<td>1350-2131</td>
<td>3588</td>
<td>904-7305</td>
</tr>
<tr>
<td>Total H$_2$O, ppmv</td>
<td>20</td>
<td>13.3-28.0</td>
<td>294</td>
<td>115.6-593.1</td>
</tr>
<tr>
<td>J(NO$_2$), 10$^{-3}$ s$^{-1}$</td>
<td>21.6</td>
<td>0.026-524.5</td>
<td>42.8</td>
<td>0.75-391.5</td>
</tr>
<tr>
<td>J(O$^1$D), 10$^8$ s$^{-1}$</td>
<td>4.2</td>
<td>1.2-72.2</td>
<td>10</td>
<td>1.2-64.3</td>
</tr>
<tr>
<td>Aerosol Surface Area, $\mu$m$^2$ cm$^{-3}$</td>
<td>3.2</td>
<td>2.7-3.8</td>
<td>86</td>
<td>34.9-172.1</td>
</tr>
<tr>
<td>Tropopause height, km</td>
<td>10.3</td>
<td>9.8-11.3</td>
<td>11.8</td>
<td>11.5-12.6</td>
</tr>
<tr>
<td>Altitude relative to tropopause, km</td>
<td>1.0</td>
<td>0.3-1.5</td>
<td>-0.4</td>
<td>-1.0--0.2</td>
</tr>
<tr>
<td>Pressure, mbar</td>
<td>216.6</td>
<td>196.5-238.4</td>
<td>216.5</td>
<td>196.6-240.4</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>210.1</td>
<td>207.7-213.0</td>
<td>204.0</td>
<td>200.2-208.2</td>
</tr>
<tr>
<td>SZA, degrees</td>
<td>91</td>
<td>82.6-102.2</td>
<td>89.5</td>
<td>83.5-94.6</td>
</tr>
<tr>
<td>Latitude, °N</td>
<td>69.6</td>
<td>63.1-77.6</td>
<td>68.5</td>
<td>65.8-71.6</td>
</tr>
</tbody>
</table>
4.2 Flights in cirrus

In this section we discuss HO\textsubscript{x} measurements in two of the NASA DC-8 flights that were characterized by the most extensive encounters with cirrus clouds during the whole campaign. During SOLVE, the priority was on polar stratospheric clouds (PSCs) in the lower stratosphere—which were observable only by the remote sensing instruments (e.g. lidars) on the DC-8. Hence, flights in cirrus were less desirable as they obscured or scattered the probing lasers. Nevertheless, there were three flights in which the DC-8 encountered an appreciable amount of clouds—the flights of 23 January, 25 January, and 8 March 2000. Out of these three, we pick the two most noteworthy ones—mainly because of the extent in which the clouds during these flights were in sunlight and in sunlight transitions. The first is the flight of 23 January 2000, which was within the second flight series of the DC-8 in the SOLVE campaign; and the second is the flight of 8 March 2000, which was within the third flight series.

The HO\textsubscript{x} measurements are compared with the modeled HO\textsubscript{x} discussed in the previous chapter using three cases: the ‘base’ case, which was constrained only to the measured species O\textsubscript{3}, H\textsubscript{2}O, CO, CH\textsubscript{4}, NO, and photolysis frequencies, the ‘param’ case, which is the “base case” but was constrained also by estimated peroxides, formaldehyde, acetone, and measured ClO, and a third case, JHNO\textsubscript{4}, which is the ‘base’ case with enhanced photolysis of HNO\textsubscript{4} [Wennberg \textit{et al}., 1999].

4.2.1 Flight 118—January 23, 2000 (ER-2 Intercomparison Flight)

One of this flight’s objectives was to underfly the ER-2 flight path over Scandinavia in order to remotely observe the sunrise evolution of ClO above the DC-8 along the ER-2 flight
curtain (using the Airborne Submillimeter Radiometer or ASUR [Bremer et al., 2002]). This flight path took the DC-8 out northwest from Kiruna over the Norwegian Sea and back southward over Sweden up to the middle of the Baltic Sea (at around 58°N, 20°E) then back towards Kiruna. At around 1000 UT over Sweden the DC-8 climbed to 11.3 km—rising above the local tropopause—at around the same time as the aircraft was breaking into sunlight.

From around 1000 UT to 1200 UT, the DC-8 was cruising above the local tropopause. At around 1200 UT, the aircraft reentered the troposphere and encountered cirrus that was observed to contain HNO$_3$ (nitric acid). The underflight duration was from around 0800 UT to 1230 UT and was also the period of most sunlight for this flight. After the ER-2 had landed (1230 UT), the DC-8 climbed to 12 km (above the tropopause) and turned westward to begin a two-hour sun run (i.e. flying along a relatively constant sunrise solar zenith angle of around 89°) toward Greenland to take solar occultation PSC spectra and to probe a predicted large mountain wave off its east coast. At around 1330 UT, the aircraft crossed the tropopause once again into the troposphere—upon which it intercepted cirrus. The cirrus persisted for the next hour or so until the aircraft flew into darkness.
Figure 4-1: Observations and model calculations of OH and HO$_2$ for the flight of 23 January 2000. Data are shown for SZA<90. The Base case is the model constrained with only the available in situ measurements. The J(HNO$_4$) case is the base case with enhanced HNO$_4$ photolysis included. The Param case is the base case plus inclusion of parameterized peroxides, aldehydes, acetone, and ClO. The HO$_2$/OH ratio ‘calc’ is calculated from Eq. (1.5) without ClO and BrO. Cirrus clouds are indicated by the enhancements in ‘Sfc Area’.
The measured and modeled profiles of OH and HO$_2$ during this time (1000 UT – 1500 UT) are shown in Figure 4-1, from which we can glean the following observations. Firstly, as the DC-8 broke into sunlight, the measurements rose faster than the ‘base’ model and the J(HNO$_4$) models but not as fast as the ‘param’ model—though the ‘param’ model seems to have the better fit with this ‘sunrise’ data. Conditions changed along the DC-8 flight track from 1000UT to 1100UT, with increasing insolation (decreasing solar zenith angle) and increasing stratospheric nature of air (decreasing NO, increasing Cl$_y$). For these changing conditions, the ‘param’ model is directly correlated with NO for both OH and HO$_2$ throughout the sunlit region before 1230 UT.

Secondly, an enhancement in HO$_2$ from around 1330 UT to 1430 UT is not reproduced by the ‘base’ model but is mimicked by the J(HNO$_4$) and ‘param’ models. The OH during this period, however, is better reproduced by the ‘param’ model—consequently causing the ‘param’ model to best simulate the measured HO$_x$ ratio. We note from the flight data (not shown) that the enhancement occurs during a constant flight level leg in the middle of the Norwegian sea between Scandinavia and Greenland wherein the tropopause sloped upward causing the aircraft to transition from stratosphere to troposphere at around 1330 UT—subsequently encountering thick cirrus clouds. The enhancement ended when the aircraft climbed to a new flight level (around 12.5 km) at 1430 UT just off the east coast of Greenland. The flight level change still did not allow the DC-8 to penetrate the stratosphere and escape the cirrus decks but, by this time, the aircraft was plunging into darkness.

Lastly, despite the differences in the absolute values of HO$_x$ calculated by the ‘base’ and the J(HNO$_4$) models, the HO$_x$ ratio calculations are remarkably similar—and similar, furthermore, to the HO$_x$ ratio calculation from Eq. (1.1) in Chapter 1 (without ClO and BrO). These three HO$_x$ ratio calculations are indistinguishable in the third panel of Figure 4-1. Nevertheless, the ‘param’ model still best reproduces the measured HO$_x$ ratios.
From the fourth panel of Figure 4-1, we note that the largest deviations between the modeled and measured HO$_x$ ratio (i.e. modeled HO$_2$/OH minus measured HO$_2$/OH) occur in the presence of cirrus clouds—and that the deviation in cirrus is even greater if the region also has depleted NO. From the middle and lower panels, we see that NO is anti-correlated with Cl$_y$—except in regions of cirrus where the NO tends to be depleted. This depletion of NO in the regions of cirrus is consistent with the observation of nitric acid uptake in cirrus that depletes the gas-phase NO$_y$ [Kondo et al., 2003].

4.2.2 Flight 126—March 8, 2000 (Sunlight and cirrus clouds)

The main objective of this flight was to remotely observe PSCs (using the lidar instruments) around the vortex on a streamline at 440 K. Following the downwind edge of PSCs along this Lagrangian trajectory would allow the study of both the PSC particle composition and its subsequent processing downwind.

This flight was notable for spending the longest amount of time in cirrus in sunlight—from around 1030 UT to 1230 UT. This cirrus deck was encountered along a northeastward run along the northwest coast of Russia and on a shorter northward leg along the peninsula of Poluostrov Yamal.
Figure 4-2: Same as Figure 4-1 but for the flight of 8 March 2000.
From Figure 4-2 we see that all the three models initially reproduce the HO\textsubscript{x} measurements quite well before 1030 UT. During this time, the DC-8 was in one of the brightest (i.e. highest insolation) regions of the campaign and was in stratospheric air. As the aircraft traveled further northeast along the Russian coast, the tropopause once again began to slope up, and at 1030 UT the DC-8 crossed into the troposphere and encountered extensive cirrus cloud decks. At this point, both OH and HO\textsubscript{2} began to increase and only the ‘param’ model is able to match the variation. At 1100 UT, the DC-8 climbed to the next flight level (11.1 km) but still remained below the tropopause. During this climb, HO\textsubscript{x} and all other tracers visibly shifted to more stratospheric values.

At around 1145 UT, the DC-8 dove down into the cirrus deck to an altitude of about 9.6 km and after about 5 minutes ascended once again to 11.1 km. Despite the diminishing sunlight during this dive, both OH and HO\textsubscript{2} show enhancements that are not captured by the models. The models calculate the largest HO\textsubscript{x} ratios during this dive but are in great disparity with the measurements. Finally, from the bottom three panels of Figure Error! Reference source not found. we can glean that the largest differences between modeled and measured HO\textsubscript{x} occur once again in regions of thin cirrus and depleted NO.

4.3 Summary

The common features of these two flights pertaining to HO\textsubscript{x} in the presence of cirrus clouds may thus be summarized as follows: 1) there are marked differences in the absolute amounts of HO\textsubscript{x} between the lowermost stratosphere and the upper troposphere—especially when transitioning through the tropopause in the presence of cirrus; 2) cirrus clouds form above the thermal tropopause in around 5% of the cirrus observations but around 17% of cirrus is present in air with Cl\textsubscript{y} > 100 pptv; 3) the greatest deviations in the modeled to measured HO\textsubscript{x} ratios tend to
occur in regions of thin cirrus with little NO; 4) models constrained solely by species involved in
the fast exchange between OH and HO$_2$ (i.e. ‘base’ and J(HNO$_4$) models) cannot adequately
reproduce the absolute measured HO$_x$ concentrations nor the measured HO$_x$ ratios in these
regions, and; 5) the ‘param’ model, with its estimated unmeasured HO$_x$ sources, consistently
represents the measurements best.

The absence of in situ measurements of primary HO$_x$ sources other than ozone and water
precludes a tightly-constrained quantitative analysis of the HO$_x$ budget in this region. Nevertheless, the use of estimated typical values of these unmeasured sources allows us to do
reasonably well. That the modeled HO$_x$ ratios have their greatest deviation from the
measurements in regions of thin cirrus with low NO points to a mechanism in these regions that
either depletes HO$_2$, enhances OH, or does both. While cirrus clouds can come into contact with
lowermost stratospheric air, the HO$_x$ measurements do not provide unambiguous evidence that
this hypothesized heterogeneous process is occurring. However, ClO enhancements averaging
15-20 pptv have been measured simultaneously in this region [Thornton et al., 2003]—as
compared to a pptv or less in the midlatitudes [Smith et al., 2001]. Furthermore, Thornton et al.
[2003] found the ClO/Cl$_y$ ratio (which is a measure of the extent of chlorine activation) to be
maximum (around 5%) just above the tropopause—a region which is also generally the coldest
part of the atmosphere sampled during the SOLVE flights. If heterogeneous processes are not
responsible for such enhancements, then the mechanism that generates these enhanced halogens
is yet unknown.
Chapter 5

In Situ Ozone Budget During SOLVE

The Penn State ATHOS instrument, which measures OH and HO$_2$ by laser-induced fluorescence at 308 nm, was deployed during the SOLVE mission on the NASA DC-8 aircraft to measure OH and HO$_2$ in the upper troposphere and lower stratosphere. Moreover, the University of Colorado ClO/BrO instrument was coupled to the ATHOS flow system during SOLVE in order to measure simultaneously ClO and BrO. Other groups measured NO$_x$, H$_2$O, and actinic fluxes (see Chapter 2).

These measurements enable the calculation of the ozone loss rates by halogens and hydrogen oxides in the wintertime Arctic upper troposphere and lowermost stratosphere (UTLS) (Equation 1.4). The loss of ozone in this region is of great concern not only because of its effect on the total ozone column, but also because of its impact on the radiative forcing of Earth’s climate system. Moreover, in the Arctic region (unlike the Antarctic region) ozone depletion is strongly modulated by variability in atmospheric dynamics, transport, and temperature but it has been established that the direct cause of ozone depletion is the high level of chlorine and bromine from ozone depleting substances (ODS) [WMO, 1991 to 2011]. Hence, it is befitting that we assess this halogen chemistry in this region we have observed. We will see that HO$_x$ also plays a significant role in this mechanism.

From Chapter 1, we recall that in the region of the UTLS, HO$_x$ chemistry (with NO$_x$) can result in a net production of ozone but HO$_x$ chemistry (with low NO$_x$ and halogens) can also result in a net loss of ozone. Furthermore, in this region HO$_x$ production itself is no longer simply dominated by the ozone-water reaction (R1.23, R1.24) but may be appreciably enhanced by contributions from the photolyses of aldehydes and peroxides. Hence, it is important to calculate
any net loss in order to gain a quantitative understanding of the contribution of chemistry to the ozone depletion in this region and to trends in the total ozone column.

We present here calculations of ozone production and loss rates derived from *in situ* measurements of actinic flux, OH, HO₂, NOₓ, H₂O, ClO, and inferred BrO in the lowermost stratosphere during SOLVE.

### 5.1 Data Analysis

OH, HO₂, and ClO binned averages are shown in Figure 5-1. At high solar zenith angles, the OH concentration drops below the detection limit of 10 ppqv or 4x10⁴ molecules/cm³. The measured ClO concentration drops slightly with lower sun elevation but the uncertainty of ±20 ppt in the ClO measurement does not allow a more rigorous observation. The high uncertainty in the ClO measurement is due to the lower-than-optimum operating pressure of the ClO/BrO instrument because of its coupling with the flow system of ATHOS. This lower pressure caused scattering on the detection chamber walls to dominate Rayleigh scatter from the sampled air, necessitating reduction of the field of view of the fluorescence-collecting optics and consequently reducing significantly the instrument’s precision. The relatively low operating pressures of the instrument during SOLVE also precluded the measurement of BrO because the BrO detection limit was at least 5 pptv for these operating conditions and the atmospheric BrO abundances were most likely below the detection limit. Nevertheless, nighttime abundances of OClO to which the instrument became sensitive (see Chapter 2) allowed BrO to be inferred. The inferred values ranged between 2 and 4 pptv [Thornton *et al.*, 2003].
From the discussion of ozone photochemistry in Chapter 1 (section 1.1), we see that the ozone tendency, $P(O_3)$ (i.e. the difference between Eqs. 1.2 and 1.4) is basically controlled by hydrogen, nitrogen, and halogen radicals. Thus, from these three measurements above, along with the ancillary measurement of NO, we can determine what the dominant reactions are in this region. Figure 5-1 shows the main reaction rates that convert HO$_2$ to OH as a function of altitude relative to the local tropopause. The reaction rates are calculated using the in situ measured pressure and temperature in the JPL-recommended

Figure 5-1: Mean OH, HO$_2$ and ClO concentrations measured at bins of ±1.5 degrees solar zenith angle. Measurements were filtered for N$_2$O less than 307 ppb. The error bars indicate the standard deviation.
Arrhenius form of the rate constant multiplied by the *in situ* measured concentrations of the reactants [Sander et al., 2003]:

\[ r_{X+Y} = k_{X+Y}[X][Y] \quad (5.1) \]

Recall that the \( \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \) and \( \text{HO}_2 + \text{ClO} \rightarrow \) products result in ozone loss while \( \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \) results in ozone production.

Figure 5-2: The top panels are the median values of the reaction rates (in molecules cm\(^{-3}\) s\(^{-1}\)) of \( \text{HO}_2 + \text{O}_3 \), \( \text{HO}_2 + \text{ClO} \), and \( \text{HO}_2 + \text{NO} \) as a function of altitude relative to the local tropopause. The bottom panels are the ratios of the reaction rates as labeled. The data used here are filtered for SZA < 90.
The ratios of these reaction rates illustrate the dominance of the reaction of $\text{HO}_2 + \text{O}_3$—which results in ozone loss—especially above the local tropopause. Above the tropopause, $r_{\text{HO}_2+\text{O}_3}$ increases by an order of magnitude over $r_{\text{HO}_2+\text{NO}}$ and $r_{\text{HO}_2+\text{O}_3}$ approaches two orders of magnitude above $r_{\text{HO}_2+\text{NO}}$ at the highest altitudes. This simple analysis gives us a semi-quantitative sense of the contributions of the various ozone loss and production cycles and, furthermore, clearly indicates that the ozone tendency in this region during this season was one of net loss. This negative ozone tendency (i.e. net loss) is not surprising because the UTLS region probed during the SOLVE science flights is generally NO$_x$-limited (NO$_x$ < 100 pptv) wherein the production of ozone is proportional to NO$_x$. Hence, for the generally low concentrations of NO$_x$ in this region, production of ozone is expected to be weaker and a net ozone loss is more likely.

This ozone loss is due to photochemistry as opposed to dynamics or transport. Hence, it is instructive to partition the data as a function of insolation or solar zenith angle (SZA). To visualize the individual contributions of the ozone loss and production cycles more clearly, we subdivide the data into SZA bins and calculate the mean contribution of each ozone cycle to the total bin. Figure 5-3 illustrates the same case we plotted in Figure 5-2 above—but now as a function of SZA instead of altitude. We see the same relationship between the loss cycles as HO$_x$ dominates the loss rates from the lower SZAs. As the environment becomes darker (higher SZA), the chlorine cycles begin to dominate. The HO$_x$ cycles contribute around 55%, the HO$_x$ and ClO cycle contributes 15%, and the ClO self-reaction contributes 30% to the total integrated loss rate (for all SZAs shown). The lower plot shows both ozone formation rates and ozone tendency (i.e., formation – loss). With the dearth of NO$_x$ and sunlight in this region, it is not surprising how much smaller ozone formation is than loss in this region. The total ozone loss rate at the lowest SZA is around 2.1 ppbv/day.
The preceding analysis is missing the reactions involving BrO, which have long been known to be important for ozone loss in the lower stratosphere [WMO, 2011; Simpson et al., 2007; Salawitch et al., 2005; Yung et al., 1980]. Although the BrO instrument was not sensitive enough to measure BrO in this study, the impact of this reaction on the ozone loss rate can be assessed by assuming 2 pptv of BrO in the analysis. This amount is on the lower end of the inferred BrO range in this region and is not an atypical value for the winter Arctic troposphere [Thornton et al., 2003; Burrows et al., 1999]. Figure 5-4 illustrates this case. The addition of this amount of BrO increases the highest loss rates by at least 30% with the dominance shifting to the

Figure 5-3: The top panel shows the contribution of each ozone loss cycle as a function of the solar zenith angle. The calculated loss rates are derived from a zero-order proxy in which BrO is neglected. The bottom panel shows ozone formation rates (blue) and the ozone tendency (red) which is the net loss.
halogens for most of the loss rates. This increase in ozone loss rate is not too surprising because adding BrO to the calculation instantly activates the two important ozone loss cycles, BrO + HO\textsubscript{2} and BrO + ClO. The cycle initiated by BrO + BrO is not important at this level of BrO and is included on the graph to demonstrate this. Hence, in this case, the HO\textsubscript{x} cycles contribute around 37%, the HO\textsubscript{x} and halogen cycles contribute 17% and the halogen self-reactions contribute 46% to the total integrated loss rate (for all SZAs shown). The total ozone loss rate at the lowest SZA is 2.8 ppbv/day, which is 0.7 ppbv/day greater than the case with no BrO reactions included.

Figure 5-4: Same as Figure 5-3 except for addition of 2 pptv of BrO.
5.2 Discussion and Conclusion

The SOLVE campaign during the Arctic winter of 1999/2000 had perhaps the best suite of measurements ever assembled to assess ozone loss in the tropopause region. For the same Arctic winter, several other methods were used to assess ozone loss in the lower stratosphere from the tropopause region and above. These methods determined extensive chemical loss of ozone. In the polar vortex at 450 K in March during SOLVE, the largest loss rate of around 61 ppbv/day was observed [Rex et al., 2002]. Given our calculations above, chemical loss in the region of the tropopause contributes to around 5% of this loss.

The ozone loss rates calculated herein are relatively high for this region of the UTLS—a situation that is brought about mainly by relatively enhanced halogen oxides in the region during this winter [Thornton et al., 2003] that contribute to around 63% of the calculated chemical ozone loss.

The calculations made (in Chapter 3) of the amount of halogen oxides required to bring the observed HOx ratio (HOx/OH) into accord with the computed HOx ratio from the known major sources and sinks of HOx point compellingly to the enhancement of these halogen species in quantities reported by Thornton et al. [2003]. Furthermore, the box model based on the CLaMS chemical mechanism used in Chapter 3 was demonstrated to match the observations better only after the enhanced halogens were included in the model.

The mechanism for the enhancement of these halogens was not observed by the \textit{in situ} measurements during SOLVE. Nevertheless, because the HOx ratios at low NOx do not preclude the existence of such enhancements, the absence of any gas-phase process to explain these enhancements points to the possible significance of heterogeneous processes in the region.
Modeling studies that evaluate the relative effect of transport to chemistry in the midlatitudes and the Arctic region (as opposed to the Antarctic region) [Fusco and Salby, 1999; Chipperfield and Jones, 1999] conclude that interannual variability of the ozone column is dominated by dynamical variations (planetary waves) rather than chemistry—by a ratio of roughly 70 to 30. Nevertheless, a small enhancement of the chemical ozone loss mechanism in the Arctic tropopause could increase the chemical contribution appreciably—despite the small mixing ratios of ozone in this region, the larger overall density of ozone contributes a sizable fraction of the trends in the total ozone column. From the calculations we have presented here, we have shown that the halogen reactions contribute around 63% to the chemical ozone loss of around 2.8 ppbv/day which, in turn, corresponds to around 5% of the largest loss rate of ozone observed (61 ppbv/day) in the lower stratosphere during the 1999-2000 Arctic winter [Rex et al., 2002].

The 5% contribution to the chemical loss rate of ozone loss computed here has relatively small impact on the total column ozone trend in the Arctic in wintertime. But this is for conditions where photochemistry is weak, transport dominates, and the recovery of active chlorine is slow. Solomon et al. [1997] calculated that the impact of cirrus on the ozone column trends at midlatitudes during summer would be less than 1.5% but if the enhancements we have calculated here are indeed due to heterogeneous chemistry on cirrus clouds, then we can expect HOx and halogen photochemistry in the tropopause region to have a much more significant contribution to ozone loss during summertime conditions in the lower latitudes.
Chapter 6

Summary and Conclusions

This study is based on the exposition of hydrogen oxide measurements in tandem with halogen oxide measurements made during the SOLVE campaign and their implications for unique chemistry of the wintertime Arctic tropopause. The measurement trends were profiled mainly by solar exposure and altitude in order to elucidate photochemical processes and spatial location and extent, respectively, of the crucial mechanisms that dictate abundances or imbalances between these measured species and its effect on ozone abundances or ozone production/depletion mechanisms.

Photochemically, the milieu of this measurement campaign was poor—the peak of solar exposure of the in situ measurements during this campaign is the low-end (or even cutoff) used in most photochemical models of polar chemistry. Nevertheless, the contribution of this campaign to the growing database of measurements in the wintertime Arctic UTLS region is necessary—as few extensive measurements of these crucial radicals have been made in this region and during this period so far. The highlight of the observations is the enhancement of the measured ratio of \( \text{HO}_2 \) to \( \text{OH} \)—as compared to a calculation of the same ratio based on the known non-halogen dominant reactions that control this ratio in the UTLS—and the prediction of the amount of ClO (and BrO) that would be required to reconcile the calculated ratio with the measured one. The prediction of an average of around 20 pptv ClO and 4 pptv BrO—based solely on the HO\(_x\) ratio—agrees to within statistical uncertainties with the observed enhancements in ClO (and inferred enhancements in BrO) of Thornton \textit{et al.} [2003].

Spatially, the sampling domain covered the lowermost stratosphere 75\% of the time and the upper troposphere 25\% of the time—frequently crossing the thermal tropopause. Most of the
time, such tropopause crossings would be sites for intercepting cirrus clouds. The measurements allowed a diagnosis of the frequency with which cirrus clouds exist in the lowermost stratosphere (bringing water-rich surfaces in contact with halogen-rich air)—an important prerequisite for activation of halogens on its surface by heterogeneous processes. Some of these tropopause crossings (in the periphery of cirrus “edges”) were also the regions where greater deviations between model calculations and measurements of HO\textsubscript{x} occurred—a deviation which was demonstrated to be reconcilable by the presence of enhanced halogen oxides in regions with little NO.

The contribution of our measured hydrogen and halogen oxides to chemical ozone loss is shown to be appreciable—as the contribution of these oxides to the total ozone loss during this Arctic winter is calculated to be around 5%—with the halogen reactions contributing around 63% of this loss. The measurements and analysis point to a more halogen-rich tropopause than was previously thought and—though it cannot be unequivocally established—that the possible role of heterogeneous chemistry on cirrus cannot be ignored.

In order to ascertain the possible effects of such heterogeneous chemistry with greater confidence, gas-phase and particulate measurements of HCl, ClONO\textsubscript{2}, and H\textsubscript{2}SO\textsubscript{4}, would be important—along with additional particle measurements of phase and perhaps 2D-imaging—in addition to the measurements we have presented here. Furthermore, measurements of the important precursors of HO\textsubscript{x} like formaldehyde and peroxydes—merely parameterized in the ‘param’ model presented here—would allow a tighter analysis of our understanding of the HO\textsubscript{x} budget in this region. These additional measurements, along with the measurements and modeling of NO\textsubscript{x} and halogen oxides, should provide a definitive representation of the contribution of chemistry to the ozone budget of this region.

Despite the time that has elapsed between the SOLVE campaign and this written dissertation, these measurements still provide unique valuable insights into the wintertime Arctic
polar tropopause region. This dissertation has demonstrated the observation that cirrus clouds form in halogen-rich air, that halogens are enhanced in this region, and that these halogens are responsible for a significant ozone loss during SOLVE. It is not yet known how increases in greenhouse gases and decreases in halogens will affect the ozone losses determined here. Another research project with at least the measurement suite recommended above will be required to answer this question.
Appendix

Adapted CLaMS Scheme

Adapted Chemical Lagrangian Model of the Stratosphere (CLaMS) Scheme
(77 gas-phase reactions—65 bimolecular, 12 termolecular, 19 photolysis reactions)

\[ \text{O}(^3\text{P}) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \]
\[ \text{O}(^1\text{D}) + \text{O}_2 \rightarrow \text{O}(^3\text{P}) + \text{O}_2 \]
\[ \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]
\[ \text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{HO}_2 \]
\[ \text{O}(^1\text{D}) + \text{N}_2 \rightarrow \text{O}(^3\text{P}) + \text{N}_2 \]
\[ \text{O}(^1\text{D}) + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3\text{O}_2 \]
\[ \text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 \]

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]
\[ \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2 \]
\[ \text{HO}_2 + \text{O}_2 \rightarrow \text{OH} + 2\text{O}_2 \]
\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

\[ \text{O}(^3\text{P}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \]
\[ \text{OH} + \text{NO}_3 \rightarrow \text{HO}_2 + \text{NO}_2 \]
\[ \text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3 \]
\[ \text{OH} + \text{HO}_2\text{NO}_2 \rightarrow \text{NO}_3 + \text{H}_2\text{O} + \text{O}_2 \]
\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \]
\[ \text{HO}_2 + \text{NO}_3 \rightarrow \text{NO}_2 + \text{OH} + \text{O}_2 \]
\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]
\[ \text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2 \]
\[ \text{NO}_2 + \text{O}_2 \rightarrow \text{NO}_3 + \text{O}_2 \]
\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 \]
\[ \text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 \]
\[ \text{HO}_2\text{NO}_2 + \text{M} \rightarrow \text{HO}_2 + \text{NO}_2 \]
\[ \text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 \]
\[ \text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 \]

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{HO}_2 \]
\[ \text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{O}_2 \]
\[ \text{OH} + \text{HCHO} \rightarrow \text{H}_2\text{O} + \text{HO}_2 + \text{CO} \]
\[ \text{OH} + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{O} + \text{HCHO} + \text{HO}_2 \]
\[ \text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{O} + \text{H}_2\text{O} \]
\[ \text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{CH}_2\text{O} + \text{OH} + \text{H}_2\text{O} \]
\[ \text{HO}_2 + \text{CH}_3\text{OO} \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 \]
\[ \text{CH}_3\text{OO} + \text{CH}_3\text{OO} \rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2 \]
\[
\begin{align*}
\text{CH}_3\text{OO} + \text{NO} &\rightarrow \text{NO}_2 + \text{HCHO} + \text{HO}_2 \\
\text{CH}_3\text{OO} + \text{NO}_2 + \text{M} &\rightarrow \text{CH}_2\text{O}_2\text{NO}_2 \\
\text{CH}_2\text{O}_2\text{NO}_2 + \text{M} &\rightarrow \text{CH}_3\text{OO} + \text{NO}_2 \\
\end{align*}
\]

\[(\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{CO}_3)\]
\[(\text{CH}_2\text{CO}_3 + \text{NO} \rightarrow \text{CH}_3\text{OO} + \text{CO}_2 + \text{NO}_2)\]

\[
\begin{align*}
\text{CH}_3\text{OOH} + \text{Cl} &\rightarrow \text{HCl} + \text{HCHO} + \text{OH} \\
\text{O}(^3\text{P}) + \text{ClO} &\rightarrow \text{Cl} + \text{O}_2 \\
\text{OH} + \text{Cl}_2 &\rightarrow \text{HOCl} + \text{Cl} \\
\text{OH} + \text{ClO} &\rightarrow \text{HO}_2 + \text{Cl} \\
\text{OH} + \text{HCl} &\rightarrow \text{H}_2\text{O} + \text{Cl} \\
\text{OH} + \text{HOCl} &\rightarrow \text{H}_2\text{O} + \text{ClO} \\
\text{HO}_2 + \text{Cl} &\rightarrow \text{HCl} + \text{O}_2 \\
\text{HO}_2 + \text{Cl} &\rightarrow \text{OH} + \text{ClO} \\
\text{HO}_2 + \text{ClO} &\rightarrow \text{HOCl} + \text{O}_2 \\
\text{Cl} + \text{O}_3 &\rightarrow \text{ClO} + \text{O}_2 \\
\text{Cl} + \text{H}_2 &\rightarrow \text{HCl} + \text{HO}_2 \\
\text{Cl} + \text{CH}_4 &\rightarrow \text{HCl} + \text{CH}_3\text{O}_2 \\
\text{Cl} + \text{HCHO} &\rightarrow \text{HCl} + \text{HO}_2 + \text{CO} \\
\text{Cl} + \text{CH}_3\text{OH} &\rightarrow \text{HCl} + \text{HCHO} + \text{HO}_2 \\
\text{Cl} + \text{OCIO} &\rightarrow \text{ClO} + \text{ClO} \\
\text{Cl} + \text{HOCl} &\rightarrow \text{Cl}_2 + \text{OH} \\
\text{Cl} + \text{HOCl} &\rightarrow \text{ClO} + \text{HCl} \\
\text{Cl} + \text{ClONO}_2 &\rightarrow \text{Cl}_2 + \text{NO}_3 \\
\text{ClO} + \text{NO} &\rightarrow \text{NO}_2 + \text{Cl} \\
\text{ClO} + \text{CH}_3\text{OO} &\rightarrow \text{Cl} + \text{HCHO} + \text{HO}_2 \\
\text{ClO} + \text{NO}_2 + \text{M} &\rightarrow \text{ClONO}_2 \\
\text{ClO} + \text{ClO} + \text{M} &\rightarrow \text{Cl}_2\text{O}_2 \\
\text{Cl}_2\text{O}_2 + \text{M} &\rightarrow 2\text{ClO} \\
\text{O}(^3\text{P}) + \text{BrO} &\rightarrow \text{Br} + \text{O}_2 \\
\text{OH} + \text{HBr} &\rightarrow \text{H}_2\text{O} + \text{Br} \\
\text{HO}_2 + \text{Br} &\rightarrow \text{HBr} + \text{O}_2 \\
\text{HO}_2 + \text{BrO} &\rightarrow \text{HOBr} + \text{O}_2 \\
\text{Br} + \text{O}_3 &\rightarrow \text{BrO} + \text{O}_2 \\
\text{Br} + \text{HCHO} &\rightarrow \text{HBr} + \text{HO}_2 + \text{CO} \\
\text{BrO} + \text{NO} &\rightarrow \text{NO}_2 + \text{Br} \\
\text{BrO} + \text{ClO} &\rightarrow \text{Br} + \text{OCIO} \\
\text{BrO} + \text{ClO} &\rightarrow \text{Br} + \text{Cl} + \text{O}_2 \\
\text{BrO} + \text{ClO} &\rightarrow \text{BrCl} + \text{O}_2 \\
\text{BrO} + \text{BrO} &\rightarrow \text{Br}_2 + \text{O}_2 \\
\text{O}(^3\text{P}) + \text{HOBr} &\rightarrow \text{OH} + \text{BrO} \\
\text{OH} + \text{Br}_2 &\rightarrow \text{HOBr} + \text{Br} \\
\text{BrO} + \text{NO}_2 + \text{M} &\rightarrow \text{BrONO}_2 \\
\text{BrONO}_2 + \text{hv} &\rightarrow \text{BrO} + \text{NO}_2 \\
\text{BrONO}_2 + \text{hv} &\rightarrow \text{Br} + \text{NO}_3
\end{align*}
\]
BrCl + hv → Br + Cl
Cl₂O₂ + hv → Cl + Cl + O₂
ClONO₂ + hv → Cl + NO₂
ClONO₂ + hv → ClO + NO₂
H₂O₂ + hv → 2OH
HCHO + hv → 2HO₂ + CO
HCHO + hv → H₂ + CO
HO₂NO₂ + hv → HO₂ + NO₂
HOBr + hv → OH + Br
HOC₁ + hv → OH + Cl
HNO₃ + hv → OH + NO₂
CH₃OOH + hv → HCHO + OH + HO₂
NO₂ + hv → NO + O(³P)
O₂ + hv → O₂ + O(¹D)
OClO + hv → O(³P) + ClO
Br₂ + hv → Br + Br

(CH₃COCH₃ + hv → CH₃CO + CH₃O₂)

HO₂ heterogeneous uptake
OH heterogeneous uptake
References


VITA

James Bernard B. Simpas

James was born in Quezon City, Philippines on the 21st day of August of the year that JFK was assassinated. He spent his first five years in Madison, WI while his parents were pursuing their graduate degrees there. He returned to begin his schooling in a Philippine Jesuit school—the Ateneo de Manila. He spent his entire elementary, secondary, and undergraduate life under this auspicious Jesuit tutelage, graduating in 1985 with a degree in Physics. He spent his first year after graduation as a Jesuit Volunteer in the south Philippine city of Cagayan de Oro—teaching undergraduate Physics to life science majors and co-moderating the school’s catechetical organization. There he was called upon to help organize a citizens’ election watchdog group during the sham election that then President Marcos called to legitimize his dictatorship. After Marcos fled the country after an historic bloodless “people’s power” revolt, James then went back to the Ateneo to continue teaching Physics and develop educational instrumentation for use in the University and for cheap fabrication by poorer rural high schools. In 1993, he left for studies in scientific instrumentation in Manchester, UK and returned to the Philippines a year later with a Master’s degree in the field. It was his interest in applied science and instrumentation that led him to pursue a degree in meteorology that had nothing to do with forecasting weather—as he was led into the fascinating field of atmospheric chemistry. Along this path of doctoral studies he has become happily married to Rina and is also, over the past decade, a doting father to Therese Danielle.