

The Role of Halogen Chemistry in Polar Stratospheric Ozone Depletion

Report from the June 2008 Cambridge, UK Workshop for an Initiative under the Stratospheric Processes and Their Role in Climate (SPARC) Project of the World Climate Research Programme

1. Introduction

Background

The scientific understanding of ozone loss in the Arctic and Antarctic stratosphere is built upon a combination of scientific discoveries and tested hypotheses extending from laboratory studies of reaction mechanisms, to *in situ* and remotely sensed atmospheric observations, global satellite measurements, and coordinated modeling results. The depth of this understanding has created a strong scientific link between the emissions of organic chlorine and bromine containing compounds via human activities and the catalytic loss of ozone over polar regions in the late winter and spring of each year since the 1970s. The chain of tested hypotheses linking the reactions of specific radicals and molecules to the direct observation of stratospheric ozone loss has played an important role in the formulation of international policy via the Montreal Protocol and its subsequent Amendments and Adjustments.

Recent laboratory results from Pope *et al.* [2007] have raised questions about one of the crucial steps in the chlorine-catalyzed loss of ozone in the polar stratosphere. The report of significantly smaller cross sections for the photodissociation of the chlorine monoxide (ClO) dimer, ClOCl, than previously measured has challenged the quantitative analysis of ozone loss rates in the winter/spring Antarctic and Arctic lower stratosphere. To address these issues, a new SPARC initiative was installed in the fall of 2007 with the specific objectives of:

- Evaluating the consequences of the new laboratory data for the ClO dimer photolysis rate on simulations of stratospheric ozone depletion, particularly in winter polar regions.
- Evaluating old and new laboratory results for the photolysis rate and determining the type of further studies that are necessary to resolve current differences.
- Assessing qualitative and quantitative evidence from the laboratory, field observations, and models linking polar ozone depletion to stratospheric active chlorine and bromine amounts.

An important step in addressing the initiative objectives was the organization of a workshop bringing together expertise from the laboratory, theory, atmospheric observations, and atmospheric modeling communities. The workshop was held in Cambridge, UK, during 17 – 19 June 2008, with more than 50 participants (see Section 11 – Appendix). In this report we summarize the results of this workshop, which examined five separate topics.

1. An analysis of the laboratory measurements the ClOOCl cross sections and related quantities as well as the challenges associated with the various studies.
2. A discussion of the *in situ* and remote observations of ClO, ClOOCl, and related species and the associated modeling analyses that have been used to place constraints on the photodissociation frequency of ClOOCl.
3. An analysis of measured and modeled polar ozone loss rates, including an analysis of the uncertainties that affect each quantity, in order to assess our understanding of the rate limiting steps of ozone loss by the dominant catalytic cycles.
4. An analysis of potential missing chemistry that explores a manifold of possible processes that could satisfy the constraints placed on the problem by theoretical analysis, laboratory observations, measurements of radical concentrations, and observed ozone loss rates.
5. A review of results from modeling efforts using global model simulations that incorporate the Pope *et al.* ClOOCl cross section.

To place things in perspective, we briefly review the key evidence linking the release of halogen compounds at the Earth's surface to the catalytic destruction of ozone in the polar stratosphere.

The Antarctic

The discovery by Farman *et al.* [1985] of large reductions in the abundance of total column ozone over the Antarctic in the late winter and early spring is shown in Figure 1.1. Plots shown in Chubachi *et al.* [1984] first documented the altitude dependence of the region of depleted ozone. Satellite measurements of the geographic distribution of total column ozone defined the horizontal extent of the region of highly depleted ozone [Stolarski *et al.*, 1986]. These measurements resulted in common use of the term "Antarctic Ozone Hole" to describe this phenomenon.

Several hypotheses were proposed to explain the Antarctic Ozone Hole, ranging from the dynamical redistribution of ozone [e.g., Tung *et al.*, 1986], to nitrogen catalyzed chemical loss of ozone [Callis and Natarajan, 1986], to halogen catalyzed ozone loss [Solomon *et al.*, 1986; McElroy *et al.*, 1986; Molina and Molina, 1987]. A combination of ground-based, aircraft, and satellite observations was shown to be inconsistent with the dynamical and nitrogen catalysis theories of polar ozone loss. Ground-based measurements of ClO, HCl, ClONO₂, and OClO obtained in Antarctica during 1986 [de Zafra *et al.*, 1987; P. Solomon *et al.*, 1987; Farmer *et al.*, 1987; S. Solomon *et al.*, 1987] indicated that ozone depletion is associated with elevated abundances of ClO. Compelling evidence that stratospheric ozone is destroyed by anthropogenic halogens resulted from the simultaneous *in situ* observation of the time evolution of ClO and O₃, which displayed a strong anti-correlation across the wall of the Antarctic vortex circulation system [Anderson *et al.*, 1991] (Figure 1.2).

Synoptic-scale observations of the column abundances of ClO and ozone above ~16 km in the Antarctic in September 1992 were subsequently provided by the Microwave Limb Sounder (MLS) on the Upper Atmosphere Research Satellite (UARS) [Waters *et al.*, 1993] (Figure 1.3). These observations again showed the coincidence of elevated ClO and depleted O₃. The region of elevated ClO observed by MLS is confined to the Antarctic vortex [e.g., Santee *et al.*, 1995], which is characterized by air that has experienced temperatures cold enough to form polar stratospheric clouds (PSCs) [McCormick *et al.*, 1985]. Reactions on the surface of PSCs convert chlorine from nonreactive forms (HCl and ClONO₂) to highly reactive ClO [Solomon *et al.*, 1986; McElroy *et al.*, 1986] and the sedimentation of PSC particles removes nitrogen oxides from the stratosphere, allowing chlorine to remain in reactive form until late spring [Crutzen and Arnold, 1986; Toon *et al.*, 1986; Fahey *et al.*, 1990].

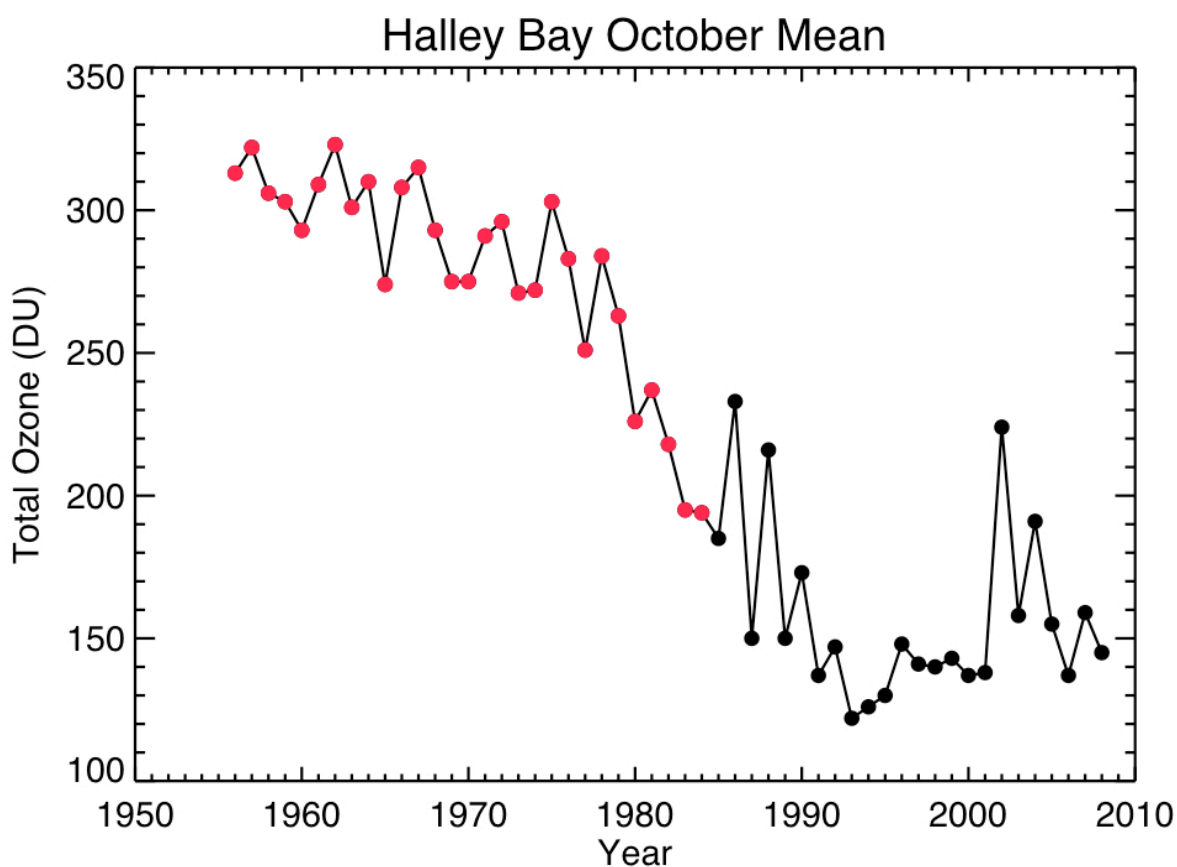


Figure 1.1. October mean total column ozone abundance from Dobson spectrometer measurements at Halley Bay, Antarctica (75.35°S, 26.34°W). Updated from Jones *et al.* [1995]. The data originally published by Farman *et al.* [1985] are shown in red. Data courtesy of J. Shanklin, British Antarctic Survey.

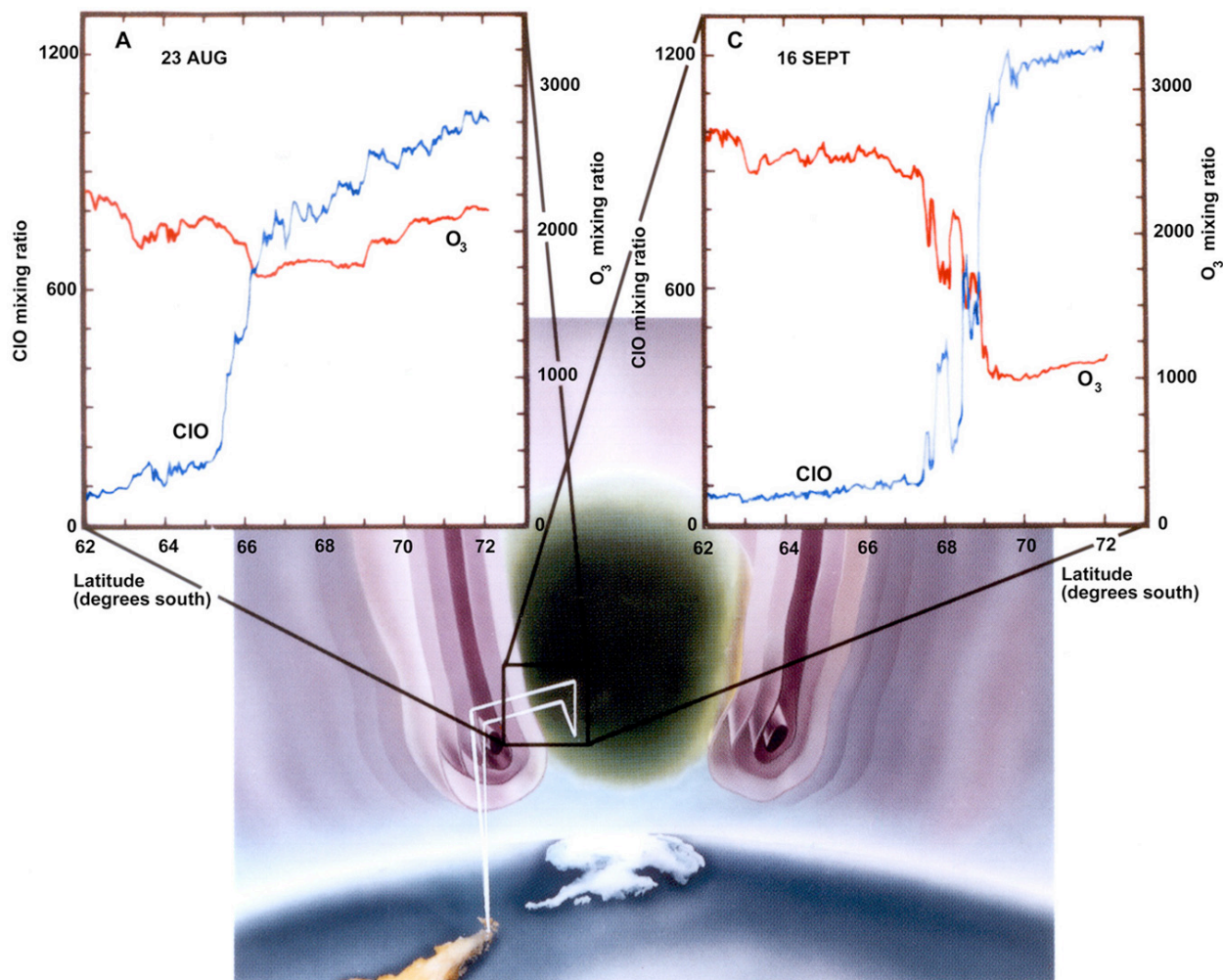


Figure 1.2. Rendering of the containment provided by the circumpolar jet that isolates the region of highly enhanced CIO (shown in green) over the Antarctic continent. Evolution of the anticorrelation between CIO and O₃ across the vortex transition is traced from the initial condition observed on 23 August 1987 to that observed on 16 September 1987 resulting from three weeks of exposure to elevated levels of CIO. From Anderson *et al.* [1991].

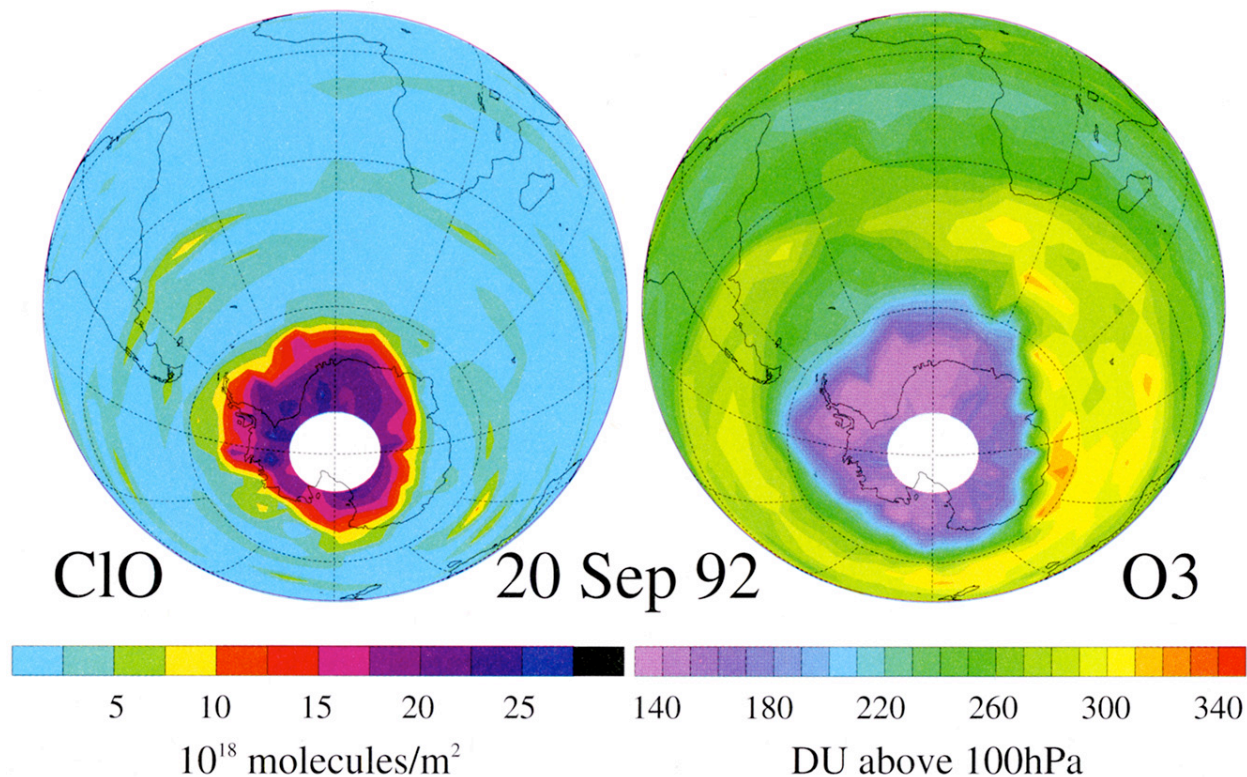
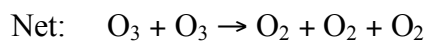
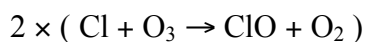
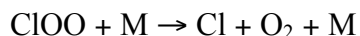
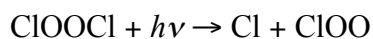
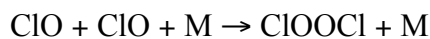


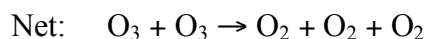
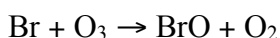
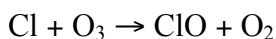
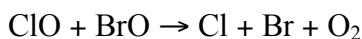
Figure 1.3. Observations of column abundances of ClO (10^{18} molecules m^{-2}) and ozone (Dobson units) above 100 hPa (about 16 km) in the Antarctic in September 1992, from the UARS Microwave Limb Sounder (MLS) satellite instrument. From Waters *et al.* [1993].

Observations of ClO and BrO provide mechanistic insight into the rate of ozone loss by various rate-limiting steps. The rate of ozone loss by the ClO dimer mechanism [Molina and Molina, 1987] can be calculated from knowledge of the concentration of ClO and the rate constant for the three-body recombination of ClO, $k_{\text{ClO}+\text{ClO}+\text{M}}$ [Sander *et al.*, 1989]:



Ozone loss rates calculated from the product $k_{\text{ClO}+\text{ClO}+\text{M}}[\text{ClO}][\text{ClO}][\text{M}]$ are valid only if loss of ClOOC l occurs by photolysis rather than by thermal decomposition, because photolysis breaks the Cl–OOCl bond (leading to reformation of O_2 , and loss of O_3 , following thermal decomposition of ClOO) [Molina and Molina, 1987]. Thermal decomposition of the dimer

breaks the weaker ClO–OCl bond, resulting in a null cycle. The rate of ozone loss by the bromine-chlorine mechanism [McElroy *et al.*, 1986] can likewise be computed from observations of concentrations BrO and ClO, together with the rate constant ($k_{\text{ClO+BrO}}$) for the branches of the ClO + BrO reaction that lead to ozone loss [Sander and Friedl, 1988]:



Numerous studies have shown very good quantitative agreement between measured Antarctic ozone loss rates and modeled loss rates based on the observed concentrations of ClO and BrO and laboratory values of $k_{\text{ClO+ClO+M}}$ and $k_{\text{ClO+BrO}}$ [e.g., Anderson *et al.*, 1991; MacKenzie *et al.*, 1996; Wu and Dessler, 2001; Frieler *et al.*, 2006]. A comparison for three Antarctic winter/springs is shown in Figure 1.4. Various simulations indicate that the ClO dimer mechanism contributes about 55 to 70% of the total loss of Antarctic ozone, with the remainder due mainly to the ClO + BrO mechanism.

The Arctic

Chemical loss of polar ozone occurs in the Arctic during winters cold enough to sustain significant abundances of PSCs [e.g., Newman *et al.*, 1997; Rex *et al.*, 2006; Tilmes *et al.*, 2004; Tilmes *et al.*, 2006]. Levels of total column ozone in the Arctic have not yet approached the low amounts seen in the Antarctic, due to more vigorous poleward transport of O₃ and also warmer conditions that are less conducive to PSCs in the NH. The quantification of chemical loss of Arctic ozone is more involved than for the Antarctic, but numerous techniques have been developed that provide reliable empirical estimates of ozone loss rates [e.g., Newman *et al.*, 2002, and references therein]. A number of studies show good agreement between measured and modeled values of Arctic ozone loss rates [e.g., Salawitch *et al.*, 1990; MacKenzie *et al.*, 1996; Frieler *et al.*, 2006]. However, the lack of complete quantitative reproduction of observed ozone loss rates by model calculations has been noted [Becker *et al.*, 2000; Kilbane-Dawe *et al.*, 2001; Rex *et al.*, 2003; Vogel *et al.*, 2006]. The consistency between field measurements of ozone, ClO, and BrO, laboratory determinations of the reaction rate constants for ClO + ClO + M and ClO + BrO, and the fundamental chemical mechanisms that affect polar ozone loss is discussed in detail in Sections 3 and 4.

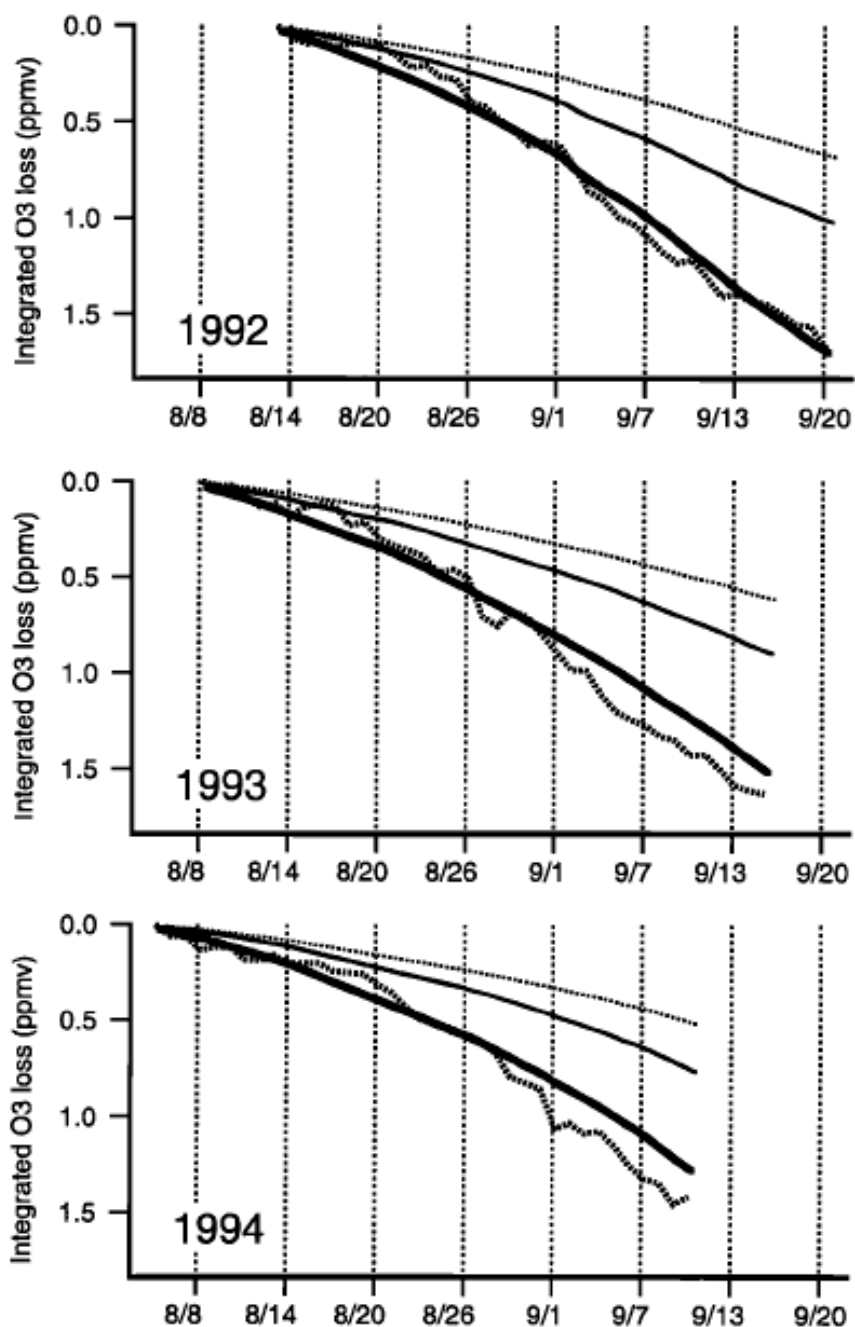


Figure 1.4. Antarctic vortex-averaged chemical loss of O_3 , for August-September of 1992, 1993, and 1994, for the ClO dimer cycle (light solid line), the ClO + BrO cycle (light dotted), and total modeled loss (heavy solid) compared to observed ozone loss (heavy dotted). The model calculations have been constrained by MLS measurements of ClO and DOAS balloon observations of BrO, and used values for $k_{ClO+ClO+M}$ and $k_{ClO+BrO}$ from DeMore *et al.* [1997]. The recommended values of $k_{ClO+ClO+M}$ and $k_{ClO+BrO}$ at 190 K given in Sander *et al.* [2006] are 34% and 2.5% larger, respectively, than values given in DeMore *et al.* [1997]. From Wu and Dessler [2001].

Role of ClOOCl Photodissociation

A critical parameter for both the chlorine and bromine catalytic cycles is the photolysis rate or photodissociation frequency of ClOOCl, J_{ClOOCl} . It is the rate-limiting step in the ClO dimer cycle under twilight conditions, and also has a major influence on the rate of the ClO/BrO cycle by governing the amount of active chlorine present as ClO. J_{ClOOCl} is the product of the ClOOCl absorption cross section, σ_{ClOOCl} , and the solar irradiance. As noted earlier, the recent laboratory study by Pope *et al.* [2007] reported much lower values for σ_{ClOOCl} at atmospherically relevant wavelengths (cf. Section 2) than had been found by prior laboratory observations [Cox and Hayman, 1988; Burkholder *et al.*, 1990; DeMore and Tschuikow-Roux 1990; Vogt and Schindler, 1990; Huder and DeMore, 1995]. It should be emphasized, however, that differences in the ClOOCl absorption cross-section data at wavelengths longer than 300 nm from various laboratory studies have existed before 2007 and that the level of agreement between measured and modeled ozone loss rates is very dependant on the values of the ClO dimer cross sections. Calculations of ClO_x partitioning are similarly dependant on both the cross sections and the equilibrium constant associated with dimer formation and thermal dissociation. However, the new cross sections by Pope *et al.* [2007] dramatically reduce the value of J_{ClOOCl} in the stratosphere, making the agreement between observations and modeling impossible to attain: if the Pope *et al.* [2007] measurement of the dimer cross section is correct, then the quantitative understanding of polar ozone loss at the molecular level requires revision. Models using this new cross section, and no other kinetic change, result in much lower values of ClO than observed (due to titration of active chlorine from ClO to ClOOCl) and in calculated Antarctic ozone loss rates that are about a factor of 2 less than measured [von Hobe *et al.*, 2007]. Alternatively, maintaining the observed abundance of ClO in a model using $J_{\text{ClOOCl}}^{\text{Pope}}$ and no new chemistry results in ClOOCl concentrations that are factors of 3 to 5 times greater than total available stratospheric chlorine. To account for measured ClO from a variety of instruments, the value of $J_{\text{ClOOCl}}^{\text{Pope}}$ requires the existence of one or more “missing chemical processes” that mimic ClOOCl photolysis [von Hobe *et al.*, 2007; Schofield *et al.*, 2008].

2. Laboratory Measurements and Theoretical Calculations

As stated in the Introduction and discussed in more detail in Sections 3 and 4 of this report, our understanding of the ClO_x chemistry leading to polar ozone loss has, for some time, contained a number of discrepancies between the fundamental physical properties measured in the laboratory and the atmospheric observations [WMO, 2007; von Hobe *et al.*, 2007; Stimpfle *et al.*, 2006; Frieler *et al.*, 2006]. The laboratory and theoretical session of the Cambridge Workshop dealt with reviews of published studies as well as descriptions of techniques and preliminary results from a number of ongoing laboratory studies. In addition, progress in theoretical calculations describing the Cl₂O₂ system was presented. Generally, the discussion at the workshop provided a clearer picture of the uncertainties and constraints encountered in laboratory studies of halogen photochemical processes important to polar ozone depletion.

Analysis of Previous Studies

Discrepancies in the Cl_2O_2 absorption cross-section data at $\lambda > 300$ nm from various laboratory studies have existed before 2007 [Sander *et al.*, 2006; WMO, 2007] and, in fact, provided the motivation for Pope *et al.* [2007] to revisit this issue in their recent laboratory study of the Cl_2O_2 spectrum. These researchers developed a new method to prepare bulk ClOOCCl samples that reduced the abundance of several Cl_xO_y impurities that were present in many of the previous studies (see below). However, significant amounts of Cl_2 were still present in their gas-phase samples. They employed a new spectral analysis approach to correct for the Cl_2 impurity and subsequently obtained Cl_2O_2 UV absorption cross sections significantly lower than all previous measurements. Figure 2.1 shows the Cl_2O_2 absorption spectra and cross-section values reported in published studies to date as well as the NASA-JPL 20006 [Sander *et al.*, 2006] recommended values. (The IUPAC panel recommend the Huder and DeMore [1995] values, which are not marked separately). Figure 2.1 also shows the wavelength dependence of the atmospheric photolysis rate at 20 km and a solar zenith angle of 86° obtained using the ClO dimer cross-section values from Burkholder *et al.* [1990], Huder and DeMore [1995], NASA JPL-2006 and Pope *et al.* [2007]. Two points are readily apparent from the figure. First, the disagreement in the published cross sections is indeed large - a factor of ~ 4.5 at 330nm, 14 at 350nm and 100 at 380 nm. Second, the most important region for atmospheric photolysis is 310 – 400 nm. Hence, the disagreement in the Cl_2O_2 cross section is large where it is atmospherically most important. It is worth noting that the agreement at the absorption maximum at 245 nm ($\pm 15\%$) is based on four absolute measurements [Cox and Hayman, 1988; Burkholder *et al.*, 1990; DeMore and Tschuikow-Roux, 1990; Bloss *et al.*, 2001]. Other studies make relative measurements, which are normalized to the peak value. So why are the uncertainties in a critical atmospheric parameter so large? Historically, there have been four reasons:

1. It is very difficult to prepare pure ClOOCCl in the laboratory;
2. Its UV absorption spectrum contains broad diffuse band structure, but no clearly identifiable signature features;
3. There are a number of potential interferences from other Cl_xO_y species (e.g., Cl_2 and Cl_2O_3), whose presence in laboratory studies is almost unavoidable and hard to quantify; and
4. The cross sections in the region of atmospheric interest are small.

The biggest source of uncertainty in spectroscopic studies (including Pope *et al.* [2007]) is now thought to arise from the presence of Cl_2 , with the derived spectrum being very sensitive to how the Cl_2 interference is removed. Figure 2.2 shows the results of a sensitivity analysis of laboratory data in which different amounts of Cl_2 are assumed to be present in the Cl_2O_2 sample. A relatively small difference in the amount of Cl_2 assumed spans the range from the highest to the lowest published absorption cross sections, pointing to the need for very accurate quantification of the Cl_2 present in the system when the absorption cross section is determined. Absorption due to Cl_2 was assumed to make a significant contribution to the absorbance signal measured by Pope *et al.* [2007] and the dimer cross sections reported were derived by subtracting this contribution. A further problem is that not all the properties of the other Cl_xO_y species are known. For example, the significant disagreement among the published values of the Cl_2O_3 absorption spectrum leads to considerable uncertainty in accounting for its possible presence and impact on the derived ClOOCCl absorption cross sections, especially in the region between 300 and 340nm.

Section 2. Laboratory Measurements and Theoretical Calculations

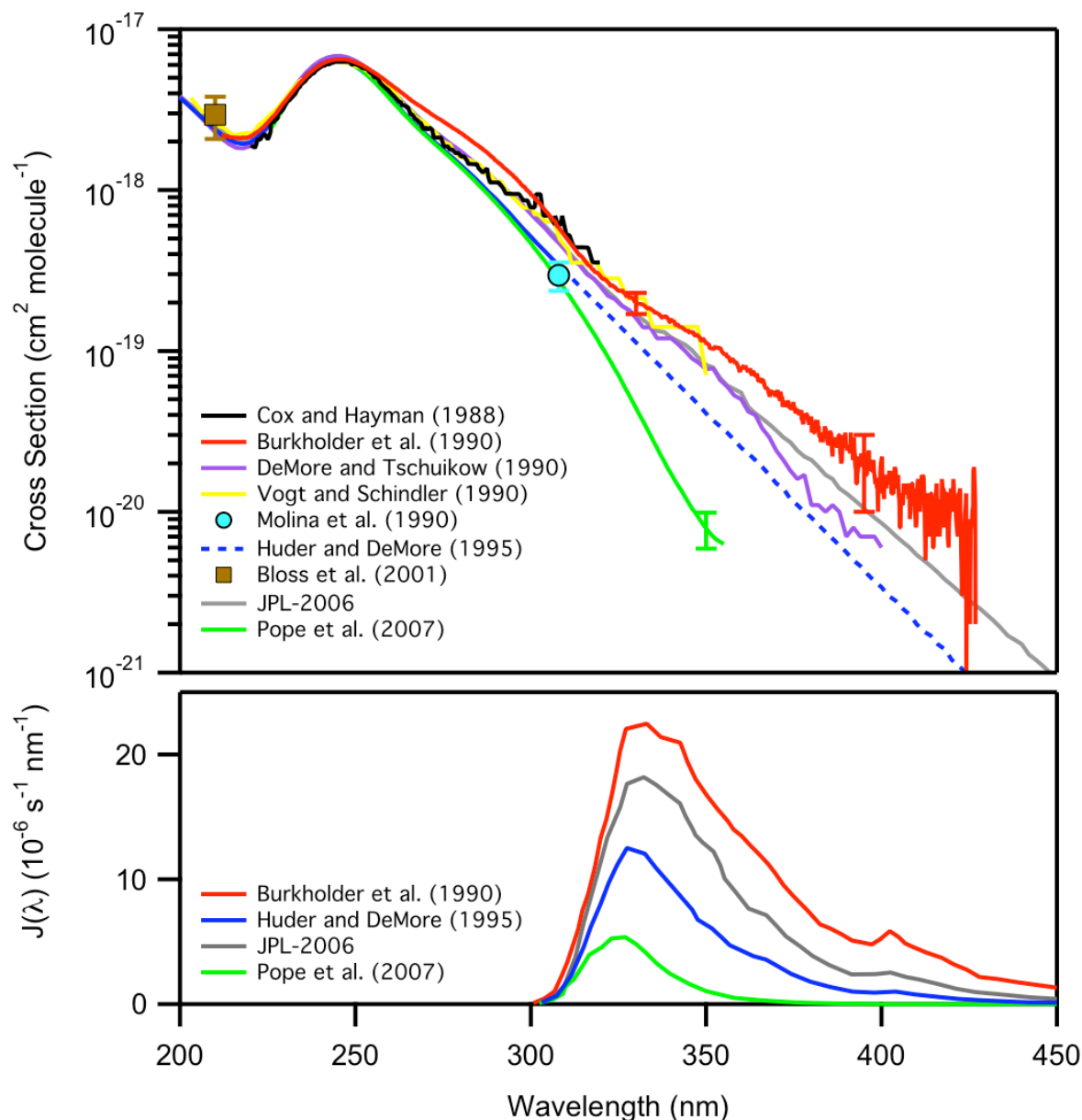


Figure 2.1. The upper panel shows a summary of results from ClOOCl absorption cross-section studies currently available. The current NASA-JPL recommendation is also shown while the IUPAC panel recommends the results from the Huder and DeMore [1995] study. The lower panel shows the wavelength dependence of the atmospheric photolysis rate constant at 20 km and a solar zenith angle of 86° obtained using the ClO dimer cross-section values from Burkholder *et al.* [1990], Huder and DeMore [1995], NASA JPL-2006 and Pope *et al.* [2007]. This shows the critical importance of the region between 310 and 400 nm and highlights the present level of uncertainty. Figure courtesy of J. Burkholder, NOAA-ESRL. Lower panel adapted from Pope *et al.* [2007].

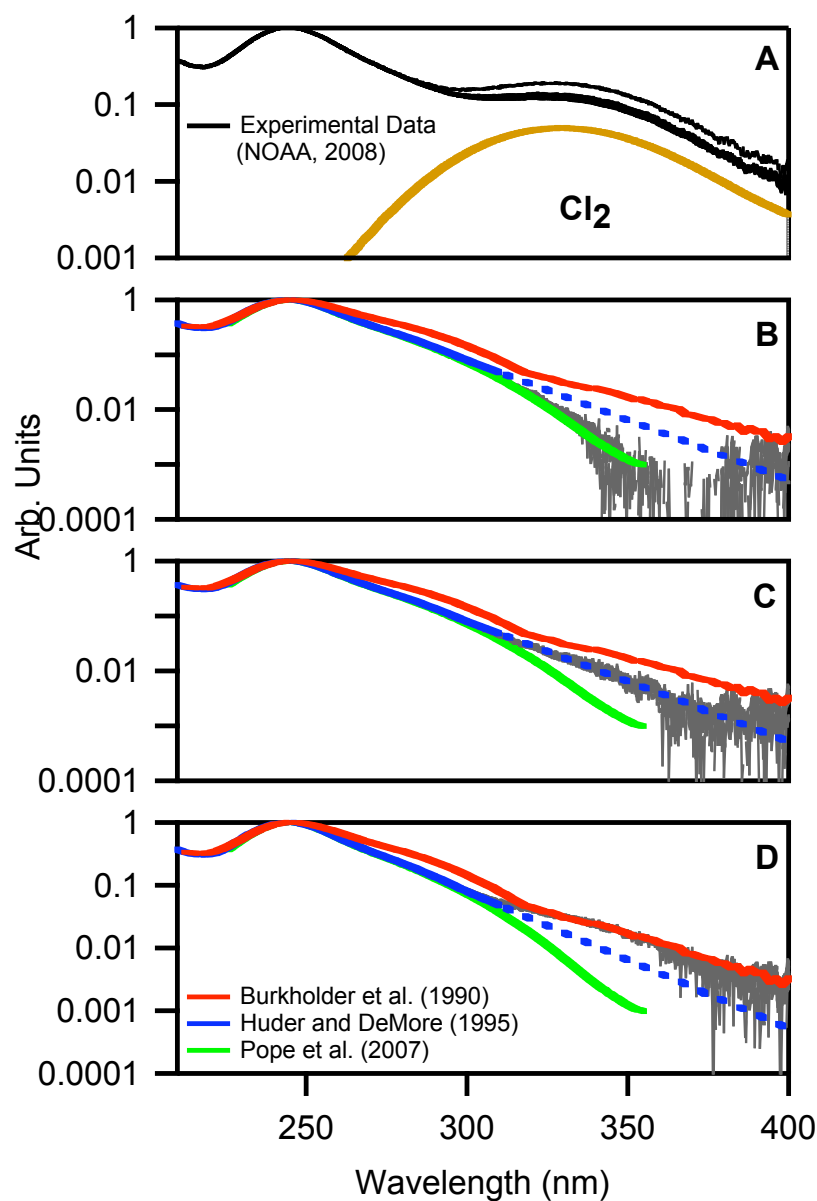


Figure 2.2. This figure illustrates the sensitivity in the determination of the ClOOC1 absorption spectrum at $\lambda > 310$ nm to corrections for unknown Cl₂ impurity levels. Panel (A) shows a sequence of absorption spectra measured in the NOAA laboratory following the 248 nm pulsed laser photolysis of a Cl₂O/Cl₂ gas-phase sample at 218 K and 720 Torr (He) total pressure. Cl₂O absorption has been subtracted and the spectra normalized at the peak of the ClOOC1 spectrum (245 nm). The differences in absorption near 330 nm are due primarily to the formation of Cl₂ during photolysis. The bottom panels show these spectra with varying amounts of Cl₂ subtracted. This demonstrates the high level of agreement that can be obtained with the shape of the ClOOC1 absorption spectra reported by (B) Pope *et al.* [2007], (C) Huder and DeMore [1995] and (D) Burkholder *et al.* [1990] by making small variations in the amount of Cl₂ subtracted from the experimental spectra. Figure courtesy of J. Burkholder, NOAA-ESRL.

New Laboratory Studies

Progress in four new on-going laboratory studies based on independent experimental approaches was reported. Encouragingly, the quantum yield for Cl production (currently recommended to be 0.9 for wavelengths >300nm, independent of wavelength, and unity for <300nm) will be measured. The techniques are described below. Preliminary results were reported at the workshop to illustrate the techniques; however it is too early to report specific results until thorough analyses have been carried out.

The NOAA Earth System Research Laboratory in Boulder, Colorado, is currently using pulsed laser photolysis combined with diode array absorption spectroscopy to investigate the Cl₂O₂ absorption spectrum and its absolute absorption cross sections over the wavelength range 210 – 450 nm. Pulsed laser photolysis of static Cl₂O/Cl₂ gas mixtures at temperatures in the range 200 – 235 K at 700 Torr total pressure are being used to produce ClO radicals and subsequently Cl₂O₂ in the gas-phase. UV absorption spectra (examples are shown in Figure 2.2) will be recorded following the completion of the gas phase chlorine chemistry. The stoichiometry and mass balance of the reaction system will be used to translate the measured Cl₂O₂ absorption spectrum into cross sections.

Groups from Forschungszentrum Juelich and the University of Wuppertal, Germany, are using infrared and UV spectroscopy to study ClOOCl isolated in a neon matrix. The matrix isolation technique has a number of advantages to gas phase studies: i) during matrix measurements no decomposition can occur; ii) the amount and purity of matrix isolated ClOOCl can be simultaneously tracked by IR and UV spectroscopy; and iii) any Cl₂ impurity in the ClOOCl sample can be removed by low temperature high vacuum sublimation. The complete removal of Cl₂ is independently checked by Raman spectroscopy. The neon matrix does affect the spectrum to some extent: light scattering occurs in the UV/Vis region, requiring a wavelength dependent correction to be made. Also, the low temperature and interaction of ClOOCl with the solid neon causes some distortion in its UV/Vis spectrum. Measurements are being made in the wavelength range 220 – 430 nm. The efficacy of the ClOOCl purification by cold trapping used in Pope *et al.* [2007] was confirmed. (Note: This study has been completed recently, and the results published [von Hobe *et al.*, 2009].)

A new laboratory experiment is underway at Harvard University to determine the product of the ClOOCl absorption cross section and the quantum yield of Cl atom production from ClOOCl laser photolysis. The experiment uses excimer lasers operating at 248 nm, 308 nm, and 351 nm to photodissociate ClOOCl, and the Cl atoms produced are detected with atomic resonance fluorescence. This technique has the advantage of high signal to noise even when the ClOOCl cross section is small. The concentration of ClOOCl necessary to perform this experiment is reduced with the improved sensitivity of resonance fluorescence detection relative to absorption, enabling operation in a flowing system with minimal wall interaction. The Harvard experiment is the first to study ClOOCl photolysis via a means other than absorption spectroscopy. The study is also providing a direct measure of Cl₂, the primary contaminant in previous studies. A variant of the experiment will determine the equilibrium constant K_{EQ} between ClO and ClOOCl.

Section 2. Laboratory Measurements and Theoretical Calculations

The experimental approach being undertaken at the University of Cambridge is to generate and measure the UV spectrum of the chlorine monoxide dimer, ClOOC1, and any Cl₂ impurity present in the same manner as detailed in Pope *et al.* [2007]. In addition, simultaneous measurement of the Cl₂ concentration will be achieved, in the same absorption cell, by using cavity enhanced absorption spectroscopy in the green region of the spectrum (~530 nm). Within this region the Cl₂ molecule has structured absorption features, and thus the Cl₂ concentration can be extracted by a differential approach. Precise knowledge of the Cl₂ concentration present in the experimental system will allow unambiguous subtraction of the Cl₂ peak from the ClOOC1/ Cl₂ UV spectrum.

The desired level of uncertainty in the Cl₂O₂ absorption cross section and quantum yield data was discussed in a general session, though without complete closure. From the laboratory perspective, it was felt that a 20% uncertainty would be a challenging target for individual experiments, and that 50% might be more realistic especially at longer wavelengths. It is apparent that the uncertainty in Cl₂O₂ cross-section experiments will most likely still be the result of systematic errors. However, the use of independent experimental methods, as described at this workshop, should significantly improve the overall level of certainty. It was not clear at this stage how to handle remaining systematic effects other than through the current NASA-JPL and IUPAC assessment process.

Theoretical Studies

New calculations by D. Dixon (University of Alabama) and co-workers [Matus *et al.*, 2008] of the energetics, structures and spectroscopic properties of the various isomers of Cl₂O₂ have been carried out with the latest Molecular Orbital Theory approaches. In contrast to some earlier studies, ClClO₂ is found to be the thermodynamically the most stable, 3.1 kcal/mol more so than ClOOC1. The weakest bond in ClClO₂ is calculated to be the Cl-Cl bond, while in ClOOC1 it is calculated to be the O-O bond. Further analysis and calculation is needed to produce the potential energy surfaces for Cl₂O₂ system and to provide insight into the kinetic barriers to formation and dissociation. The presence of any low-lying excited states will be important in this regard and their calculation might be challenging in this electron-rich system. New information about the electronic transitions and possible absorption features is also becoming available.

Alternative Reaction Mechanisms

The theoretical calculations should provide insight as to what reactions involving the Cl₂O₂ dimer are thermodynamically and kinetically possible and also serve as a guide in examining the role of various species in the search for missing chemistry. There was some discussion of what dimer reactions with other species might be important. If a chemical reaction causes ClOOC1 to be destroyed in the stratosphere, this could compete with its photolytic destruction. For a direct reaction of ClOOC1 with some atmospheric molecule X,



to be significant, several requirements would need to be satisfied in order to match atmospheric measurements. First, the product of the rate constant times the atmospheric concentration of X, $k[X]$, would have to be comparable to J_{ClOOCl} of Burkholder *et al.* [1990]. Second, the products of the reaction would have to cause the destruction of two O_3 molecules. Third, the reaction should have a diurnal variation, either directly or in the subsequent behavior of the initial products. A detailed discussion of alternative reaction mechanisms and their constraints is provided in Section 5 of this report.

One potential reaction, not previously investigated, was reported at the workshop.



In the polar stratosphere, the $\text{O}_2(\text{a}^1\Delta)$ molecules would be formed by absorption of solar radiation in the near infrared to form $\text{O}_2(\text{b}^1\Sigma)$, which would then be collisionally deactivated to $\text{O}_2(\text{a}^1\Delta)$. Thus, reaction (2) would show a diurnal dependence. The two ClOO radicals would rapidly dissociate to form two Cl atoms, which would subsequently react with ozone. Laboratory measurements reported at the workshop suggest that reaction (2) does occur, but the rate constant is too slow, by at least a factor of 10^3 , to be significant in the chlorine catalyzed destruction of ozone. A survey of molecules known to be present in the stratosphere (including NO_2 , CO , N_2O , H_2O , and CH_4), using either measured rate constants if known, or assuming reaction at every collision, did not reveal any other good candidates that might have $k[X]$ comparable to J_{ClOOCl} .

Other Issues

While the calculation of ozone loss is more sensitive to the uncertainty in the ClOOCl photolysis rate than to an uncertainty associated with any other reaction rate, a few other issues were identified. First, there is the possibility of an additional absorption at wavelengths greater than 450 nm since the photo-dissociation limit for ClOOCl is around $1\mu\text{m}$. The theoretical calculations should allow an assessment of the likelihood of this process. The other reaction whose uncertainty leads to significant uncertainty in ozone loss calculations is $\text{ClO} + \text{BrO}$, in particular the branching ratios for the three reaction channels (cf. Section 4 of this report). Recent results for this reaction support the current NASA-JPL recommendation, but they do not reduce the uncertainties significantly.

An independent measurement of the heat of formation of ClOOCl (i.e., not calculated from measurements of the equilibrium constant) would enhance our confidence in the understanding of the ClOOCl system and provide valuable information to the theoretical calculations. In addition, there was some discussion of the mass deficit observed in kinetic measurements of the $\text{ClO} + \text{ClO} + \text{M}$ reaction. It is not clear whether the deficit is significant or within the limits of the measurement uncertainty. The general issue of the overall estimation of uncertainties was discussed. The JPL and IUPAC panels for the evaluation of photochemical data solely consider laboratory measurements in reaching their recommendations for each reaction. This was contrasted with one of the purposes of this SPARC initiative, namely the consideration of all relevant information (particularly analyses of field measurements) to provide a more broadly based set of constraints on what might be occurring in the atmosphere.

Section 2. Laboratory Measurements and Theoretical Calculations

3. Chlorine Partitioning

Literature Synthesis

Many studies published during the past several decades have focused on the quantitative understanding of the partitioning of [ClO] and [ClOOCl], the active chlorine species that participate in ozone loss by the ClO dimer mechanism. There was considerable discussion of this literature at the workshop; of course, many of the presentations were made by authors of these studies. Here, we present a succinct overview of these discussions.

The chemistry linking ClO and ClOOCl is thought to be rather simple. During daytime when temperatures are low enough that loss of ClOOCl occurs mainly by photolysis, the ratio $[M][\text{ClO}]^2/[\text{ClOOCl}]$ equals $J_{\text{ClOOCl}}/k_{\text{ClO}+\text{ClO}+\text{M}}$. During night, when loss of ClOOCl occurs exclusively by thermal decomposition, this ratio equals $k_{\text{THERMAL}}/k_{\text{ClO}+\text{ClO}+\text{M}}$, where k_{THERMAL} denotes the rate constant for thermal decomposition of ClOOCl. The quantity $k_{\text{ClO}+\text{ClO}+\text{M}}/k_{\text{THERMAL}}$ is termed K_{EQ} , the equilibrium constant between ClO and ClOOCl. A theoretical overview of $k_{\text{ClO}+\text{ClO}+\text{M}}$ is given by Golden [2003] and a recent review of the consistency among laboratory measurements of various aspects of the ClO/ClOOCl kinetics is given by von Hobe *et al.* [2007]. Since the rate of ozone loss by the ClO dimer mechanism cycle is controlled by the parameters J_{ClOOCl} and $k_{\text{ClO}+\text{ClO}+\text{M}}$, comparisons of measured and modeled daytime values of [ClO] and [ClOOCl] provide a quantitative measure of the speed of this cycle in the atmosphere. As noted in Section 1, thermal decomposition of ClOOCl completes a null cycle that does not affect ozone. However, precise knowledge of K_{EQ} and an accurate measurement of nighttime [ClO] enable an accurate estimate of $[\text{ClO}_x]$, defined as $[\text{ClO}] + 2[\text{ClOOCl}]$, to be made that is independent of the ClOOCl cross section (σ_{ClOOCl}). Accurate estimates of $[\text{ClO}_x]$ from nighttime observations are useful for evaluating the behavior of the chemical system as air is exposed to sunlight.

It is beyond the scope of this report to describe, in detail, all of the studies that have evaluated consistency between atmospheric observations of [ClO] (or [ClO] and [ClOOCl]) and the kinetic parameters that govern the partitioning of ClO and ClOOCl. Rather, we summarize in Figures 3.1 and 3.2 the high level findings of these studies, particularly as they relate to the discussions at the workshop. Figure 3.1 shows the value of $J_{\text{ClOOCl}}/k_{\text{ClO}+\text{ClO}+\text{M}}$ inferred from seven studies relative to the recommended value of this ratio, found using the kinetic parameters provided by the most recent NASA-JPL Evaluation [Sander *et al.*, 2006] (hereafter JPL 2006). These seven studies suggest the photodissociation frequency of ClOOCl is as large as, or larger than, the value found using the JPL 2006 value of σ_{ClOOCl} . Of course, this finding is contingent upon how well the value of $k_{\text{ClO}+\text{ClO}+\text{M}}$ is known. At 190 K, the largest reported value of $k_{\text{ClO}+\text{ClO}+\text{M}}$ [from Boakes *et al.*, 2005] is 17% larger than the JPL 2006 value, and the smallest reported value [Troler *et al.*, 1990] is 33% smaller than the JPL 2006. Thus, the range of uncertainty in $k_{\text{ClO}+\text{ClO}+\text{M}}$ (red bars) does not come close to encompassing the value of $J_{\text{ClOOCl}}^{\text{Pope}}$ (green line) indicated on Figure 3.1. Hence, the existing literature, either implicitly (pre-Pope *et al.* [2007] studies) or explicitly (von Hobe *et al.* [2007] and Schofield *et al.* [2008]), both of which consider Pope *et al.* [2007]), indicates that the Pope *et al.* [2007] cross sections require the existence of one or more “missing chemical processes” to account for the observed abundance of [ClO] (or, the observed partitioning of [ClO] and [ClOOCl]).

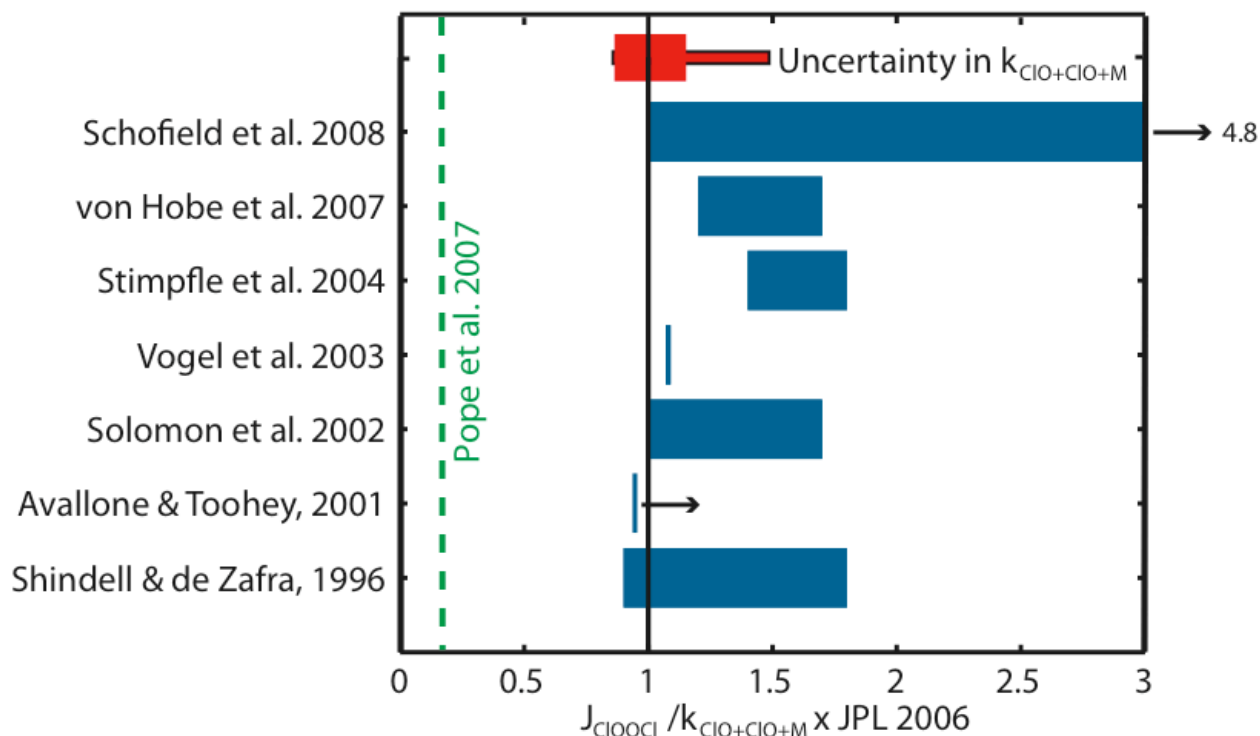


Figure 3.1. The value of $J_{\text{ClOOCl}}/k_{\text{ClO}+\text{ClO}+\text{M}}$ inferred from analysis of daytime measurements of [ClO] or of [ClO] and [ClOOCl] divided by the value of $J_{\text{ClOOCl}}/k_{\text{ClO}+\text{ClO}+\text{M}}$ based on the latest NASA-JPL recommendation [Sander *et al.*, 2006] from various studies (blue bars). The two horizontal arrows denote the fact these studies determined lower limits. The value of $J_{\text{ClOOCl}}^{\text{Pope}}/k_{\text{ClO}+\text{ClO}+\text{M}}^{\text{JPL 2006}}$ is shown by the green dashed vertical line. The effect of uncertainties in $k_{\text{ClO}+\text{ClO}+\text{M}}$ on J/k is shown by the red bars: the thick red bar shows the Sander *et al.* [2006] uncertainty evaluated at 190 K, and the thin red bar shows the range of various laboratory determinations of k . A value of unity indicates consistency between field observations and the laboratory determination of J/k . Figure courtesy of R. Schofield, AWI-Potsdam.

It is apparent from Figure 3.2 that the value of K_{EQ} inferred from atmospheric observations generally lies below the value for K_{EQ} recommended by JPL 2006. The use of a logarithmic scale for the figure tends to obscure the level of disagreement between analysis of field observations and laboratory estimates. Stimpfle *et al.* [2004] concluded that the value of K_{EQ} inferred from their observations is ~50% less than the JPL 2006 value. The analysis of nighttime ClO reported by Berthet *et al.* [2005] concluded that K_{EQ} was smaller than, or perhaps equal to, the value for K_{EQ} reported by Cox and Hayman [1988] and that their data are not consistent with the JPL 2006 value. Results from earlier airborne observations of nighttime ClO yielded similar findings [Eyring, 1999]. Numerous presentations at the workshop showed the presence of higher values of nighttime [ClO] than predicted by standard theory using the JPL 2006 value of K_{EQ} . In contrast, no observations of nighttime [ClO] presented at the workshop indicate “agreement” with standard theory and the JPL 2006 value of K_{EQ} . Nevertheless, it should be emphasized that the lower limit of the JPL 2006 value for K_{EQ} lies close to the mid-point of the value of K_{EQ}

needed for general, overall consistency with field observations (Figure 3.2). Also, we note that the laboratory determination of K_{EQ} typically involves a considerable extrapolation from observations obtained at temperatures higher than those of the polar stratosphere. Indeed, the laboratory-based recommendation for K_{EQ} continues to be re-evaluated, given this need for extrapolation. There was considerable discussion at the workshop regarding the consistency between field observations and a suite of theoretical aspects of the ClO and ClOOCl reaction system. Overall, workshop participants expressed a need for continued work on many aspects of this reaction system to reduce present uncertainties in the fundamental processes that link these two critical species. The recent review by von Hobe *et al.* [2007] encapsulates some of the discussion that took place at the workshop.

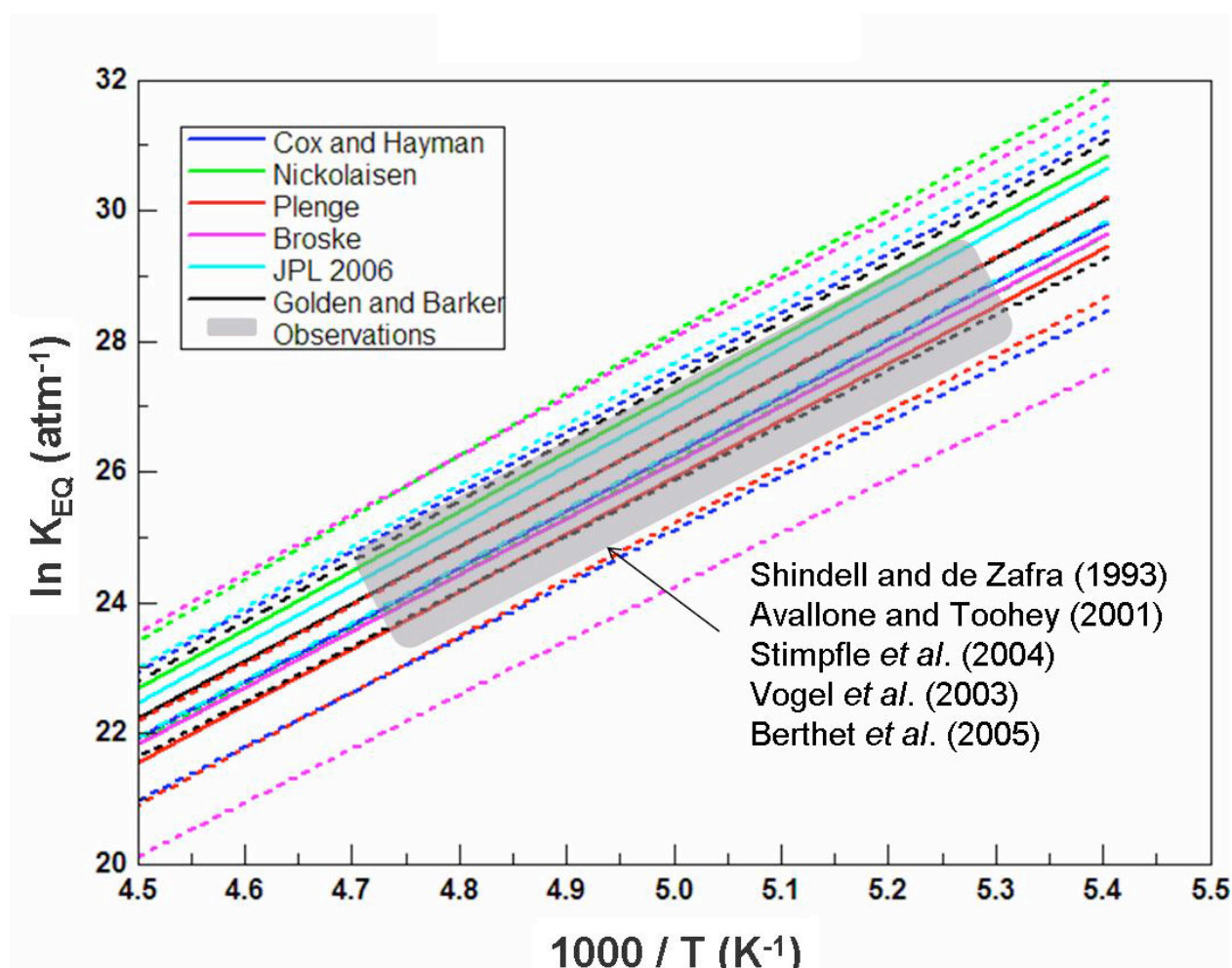


Figure 3.2. The value of K_{EQ} found from 4 laboratory studies, the JPL 2006 recommendation, and a new re-analysis of laboratory data that was circulated by D. Golden and J. Barker prior to the workshop (solid-colored lines) as well as associated uncertainties with each determination (dotted lines) compared to the range of values for K_{EQ} inferred from analysis of atmospheric measurements of [ClO] (all studies except Stimpfle *et al.*) or measurements of [ClO] and [ClOOCl] [Stimpfle *et al.*, 2004]. Figure courtesy of D. Toohey, University of Colorado.

Recent Advances

The workshop featured numerous presentations of the observations of [ClO], [ClOOCl], and related species and associated modeling analyses used to place constraints on the photodissociation frequency of ClOOCl. These talks either updated the literature by repeating model/measurement comparisons using the Pope *et al.* [2007] value for σ_{ClOOCl} , or highlighted new model/measurement comparisons that shed light on the impact of the new σ_{ClOOCl} measurement on our understanding of polar ozone photochemistry.

Stimpfle *et al.* [2004] introduced a comparison of the ratio of modeled $[\text{ClO}]^2/[\text{ClOOCl}]$ to the measured value of this quantity, which they termed β , to quantify how well models represent the kinetic factors that govern the partitioning of ClO and ClOOCl. Figure 3.3 shows an update to the β ratio plot that includes an analysis of β for the Pope *et al.* [2007] value of σ_{ClOOCl} . This analysis, based on *in situ* measurements of [ClO] and [ClOOCl] obtained using resonance fluorescence, indicates that models and measurements of the $[\text{ClO}]^2/[\text{ClOOCl}]$ ratio are completely inconsistent if the Pope *et al.* [2007] cross section is used to compute J_{ClOOCl} and no other kinetics change (or process) is invoked. The importance of the morning versus afternoon comparisons is discussed in Section 5. *In situ* observations of [ClO] and [ClOOCl] obtained by another instrument were also shown at the meeting, with the analysis demonstrating the same conclusion (i.e., see Figure 7 of von Hobe *et al.* [2007]).

This conclusion was also supported by observations of daytime ClO obtained by a satellite instrument, shown in Figure 3.4, that reveal considerably larger abundances than found by a 3D Chemical Transport Model (CTM) using recommended kinetic parameters and J_{ClOOCl} based on the Pope *et al.* [2007] value for σ_{ClOOCl} . Observations of HCl do not provide as strong of a test because, for the Pope *et al.* [2007] run, ClO_x becomes activated in a manner similar to the other run, but a greater fraction is present as ClOOCl. However, the timing of HCl recovery (following ozone loss and cessation of heterogeneous processing) is simulated significantly better by the standard run (Figure 3.4). The comparison of measured and modeled O_3 shown in Figure 3.4 is discussed in Section 4.

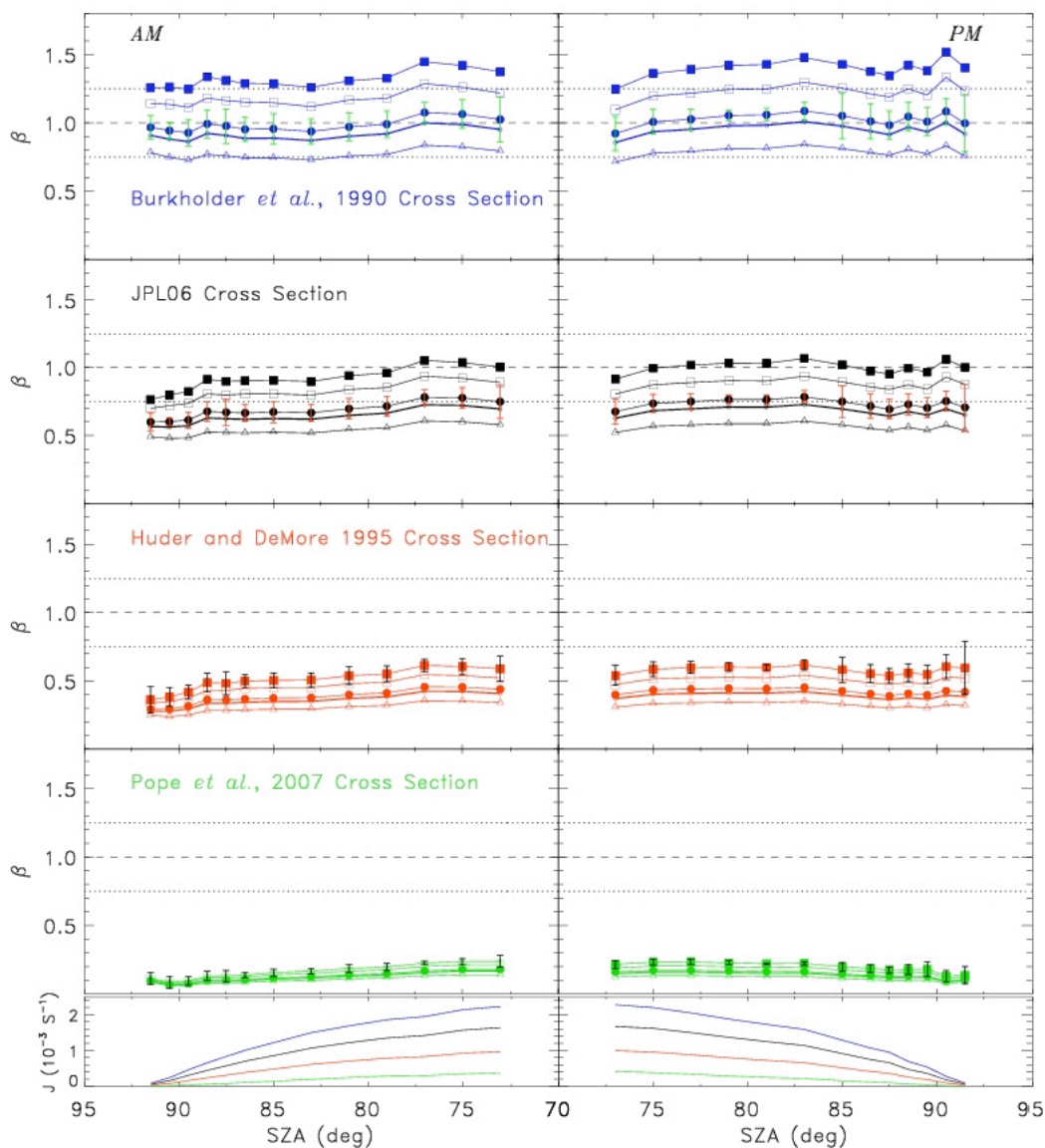


Figure 3.3. Analysis of daytime measurements of $[\text{ClO}]$ and $[\text{ClOOCl}]$ obtained during the SAGE III Ozone Loss and Validation Experiment (SOLVE). Values of β (see text) are shown as a function of solar zenith angle (SZA), for measurements made prior to local solar noon (left panels, labeled “AM”) and for measurements made after noon (right panels, “PM”). Each panel represents model results for a different value of the ClOOCl absorption cross section, as indicated. The five lines on the top four panels for both AM and PM show results for five values of $k_{\text{ClO}+\text{ClO}+\text{M}}$: Troiler *et al.* [1990], JPL 2000 (Sander *et al.* [2000]), Bloss *et al.* [2002], JPL 2002 (Sander *et al.* [2003]), and Boakes *et al.* [2005]. The lower panel shows the SZA dependence of J_{ClOOCl} , for the four values of σ_{ClOOCl} used in the analysis. Error bars on the model results depict the standard deviation about the mean of the individual data points that fall within the various SZA bins. The dotted horizontal lines depict the $\pm 25\%$ uncertainty in β attributable to uncertainties in the observations of ClO and ClOOCl . After Stimpfle *et al.* [2004] and Figure 4-15 of WMO [2007]. Figure courtesy of T. Canty and R. Salawitch, University of Maryland.

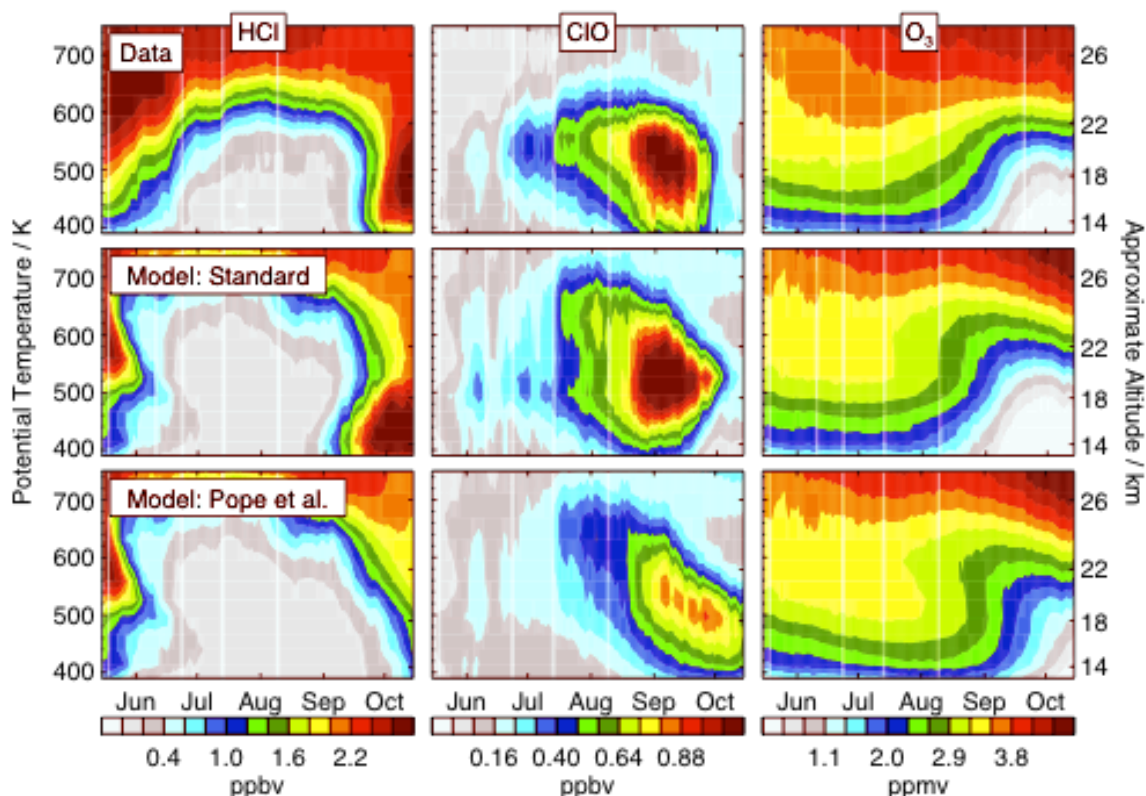


Figure 3.4. Measurement of HCl, ClO and O₃ obtained in the 2005 Antarctic vortex by the MLS instrument on Aura (top row) averaged within the $1.4 \times 10^{-4} \text{ s}^{-1}$ PV contour compared to SLIMCAT CTM calculations of these species, found using either kinetic parameters from JPL 2006 (middle row) or the Pope *et al.* [2007] value of σ_{ClOOCl} plus JPL 2006 values for all other kinetic parameters (bottom row). After Santee *et al.* [2008]. Figure courtesy of M. Santee, Jet Propulsion Laboratory, California Institute of Technology.

The workshop included detailed discussion of the uncertainties in the field measurements of [ClO] and it was concluded that the inconsistency between measurements and models using the Pope *et al.* [2007] cross section is robust in light of these uncertainties. Numerous presentations also examined the sensitivity of calculated [ClO] to various kinetic parameters and the clear message from these studies was that measured and modeled ClO could not be reconciled using the Pope *et al.* [2007] cross section without invoking some unknown chemical process that converts ClOOCl to ClO.

Several presentations examined the behavior of ClO and ClOOCl across the solar terminator (transition from dark to sunlit conditions, or vice versa). These studies were more detailed than previously published studies and highlighted the potential value of nighttime observations of [ClO] to constrain the abundance of [ClO_x] in a manner that is independent of σ_{ClOOCl} . Observations of nighttime [ClO] are available from several aircraft campaigns using numerous instruments as well as two satellite instruments. If [ClO_x] can be accurately specified from

nighttime observations of [ClO] for a particular air mass, then measurements of [ClO] have the potential to provide strong constraints on J_{ClOOCl} as that air mass experiences sunlight. The presentations that focused on the behavior of this chemical system across the terminator noted the intrinsic coupling of uncertainties in K_{EQ} and σ_{ClOOCl} . Basically, present uncertainties in K_{EQ} are too large to allow for much advance in our understanding of σ_{ClOOCl} using nighttime data. However, the existing data show promise for future use in assessing consistency of measurements of [ClO] with various values of σ_{ClOOCl} , provided the uncertainties in K_{EQ} can be reduced. These studies led to the following general conclusions regarding comparisons of modeled and field measurements of ClO and ClOOCl across the solar terminator:

- Best agreement was found using the Plenge *et al.* [1995] laboratory determination of K_{EQ}
 - Constant value of [ClO_x] inferred from observations of [ClO] across the terminator
 - Inferred [ClO_x] always < inferred [Cl_y]
- Good agreement was found using K_{EQ} derived from either the Cox and Hayman [1988] laboratory study or from the Avallone and Toohey [2001] field data analysis
 - Inferred [ClO_x] does not vary strongly across the terminator
 - Inferred [ClO_x] generally < [Cl_y]
- Poor agreement was found using the value for K_{EQ} suggested by the von Hobe *et al.* [2005] analysis of field data
 - Inferred [ClO_x] varies strongly across the terminator
 - Inferred [ClO_x] declines as SZA increases
- Very poor agreement was found using either the JPL [2006] or new Golden and Barker values of K_{EQ} calculated for the workshop
 - Inferred [ClO_x] varies strongly across the terminator
 - Inferred [ClO_x] generally > inferred [Cl_y] (i.e., inferred [ClO_x] violates Cl budget)

This discussion also noted that the uncertainties in the empirical determination of K_{EQ} from field observations may actually be considerably less than the uncertainties in the laboratory determination of K_{EQ} at the present time. This situation has arisen because of the need for extensive extrapolation of the laboratory data to low temperatures and the steep exponential temperature dependence of K_{EQ} . Thus, in addition to at least one new laboratory investigation planned for measuring K_{EQ} at low temperature, studies will also be conducted to re-examine the total uncertainty in K_{EQ} derived from field data. Of course, the empirical determination of K_{EQ} from field observations assumes that the chemical processes that link ClO and ClOOCl are all “known,” as outlined at the beginning of this section.

Several studies explored the sensitivity of chemistry climate model (CCM) simulations of polar ozone depletion to various kinetic parameters. In general, these studies concluded that polar ozone loss was more sensitive to J_{ClOOCl} than to any other kinetic or photochemical parameter, as expected based on the literature (discussed further in Section 4). The CCM simulations presented at the meeting showed that calculated values of [ClO] could not match measured [ClO] if the Pope *et al.* [2007] value of σ_{ClOOCl} was used in the CCM calculation, reinforcing the conclusions noted above.

The summary of the studies that examined atmospheric observations of [ClO], [ClOOCl], and related species was that the analyses suggest either: a) the mechanistic understanding of the ClO self reaction to form the dimer is incomplete; b) additional (unknown) processes influence the partitioning of ClO and ClOOCl; or c) perhaps ClOOCl photolyzes much faster than is suggested by the recent Pope *et al.* [2007] measurement of σ_{ClOOCl} . Clearly these conclusions have strong overlap with material discussed in Sections 2, 4, and 5 of this report.

4. Diagnostic Ozone Loss in Polar Regions

The ultimate test of our understanding of halogen-driven ozone loss chemistry is the ability to simulate the details of observed ozone change in polar regions. The decline of ozone in the springtime polar vortex of either hemisphere depends critically on the abundance, partitioning, and rates of reaction of chlorine and bromine species as described above. Ozone, however, can be a difficult diagnostic because it also depends on non-halogen chemical processes and transport, which cannot always be well constrained. Changes in the relatively isolated vortex, however, can be closely attributed to chemistry, particularly in the Antarctic, and trajectory-matching techniques minimize uncertainty in transport allowing us to quantitatively evaluate the chemical mechanisms and rates. Several perspectives on diagnostic ozone loss are discussed in this section. Comparisons to chemistry-transport models will be described further in Section 6.

Morphology of the Ozone Hole: South Pole and Hemispheric Perspective

Balloon-borne ozonesondes have been tracking the vertical profile of Antarctic Ozone loss at the South Pole Station since 1986. Figure 4.1A shows ozone profiles from the year 2006 before and after the annual austral springtime event. While typical of the magnitude and altitude range of ozone depletion, 2006 marked a record in both the 14-21 km integrated ozone loss and the geographical size of the ozone hole. Figure 4.1B shows the annual course of the 14-21 km ozone column for the 22 years of data. A smooth reduction in ozone is observed at the South Pole during September in each year except 2002, when the vortex was highly disturbed. A typical ozone loss rate profile is shown in Figure 4.1C for September 2006. The time history of September ozone loss rates for the 14-21 km and the total ozone column is shown in Figure 4.1D. In addition to a general increase in the magnitude of ozone loss rates from 1986 to 2000 (when Equivalent Effective Chlorine, EECI, should have peaked in the Antarctic stratosphere), a high degree of variability from year to year is observed. This variability has a strong quasi-biennial component, often correlated with the QBO in tropical winds, with the maximum ozone loss rate occurring in the austral spring following a descending easterly transition in the equatorial winds [Hofmann *et al.*, 1997].

Figure 4.2 shows that the ozone loss seen in the South Pole profiles is characteristic of a large area within the Southern vortex. MLS satellite data shows the characteristic chlorine chemical transformations that accompany extreme ozone loss: HCl is converted entirely to reactive forms ($\text{ClO} + \text{Cl}_2\text{O}_2 + \text{Cl}_2$) in mid-winter (July); a balance between HCl, ClO, and Cl_2O_2 is established in early spring depending on the amount of sunlight available (September - ozone is rapidly destroyed during this period); and finally, reactive Cl is nearly all converted back to HCl later in spring (October) after ozone loss is near complete (Santee *et al.* [2008] and references therein).

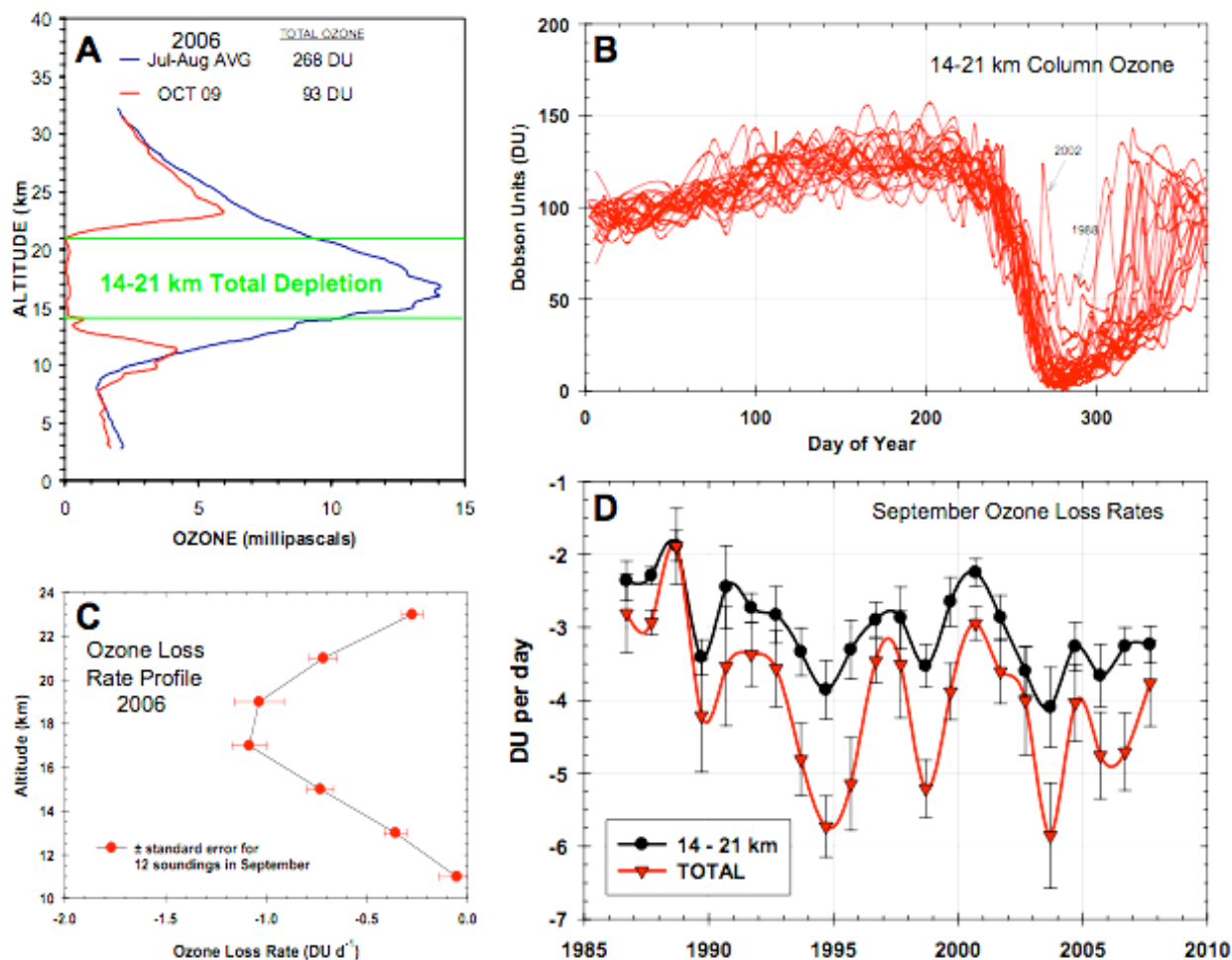


Figure 4.1. South Pole ozonesonde data related to September ozone loss rates. A) 2006 ozone profiles before and after the annual austral springtime events. The 14-21 km near-zero ozone region is delineated in the figure. B) Annual course of the 14-21 km column ozone amount for the 22 years of data. A highly disturbed vortex in 2002 resulted in an unusual disturbance in the normally smooth reduction in ozone observed during September at the South Pole. C) Vertical profiles of the September ozone loss rate during formation of the 2006 ozone hole. The data are for two km averages of 12 soundings in September 2006. Error bars are for plus and minus one standard deviation in the ozone loss rates. D) Time history of September ozone loss rates for the 14-21 km region and for total column ozone.

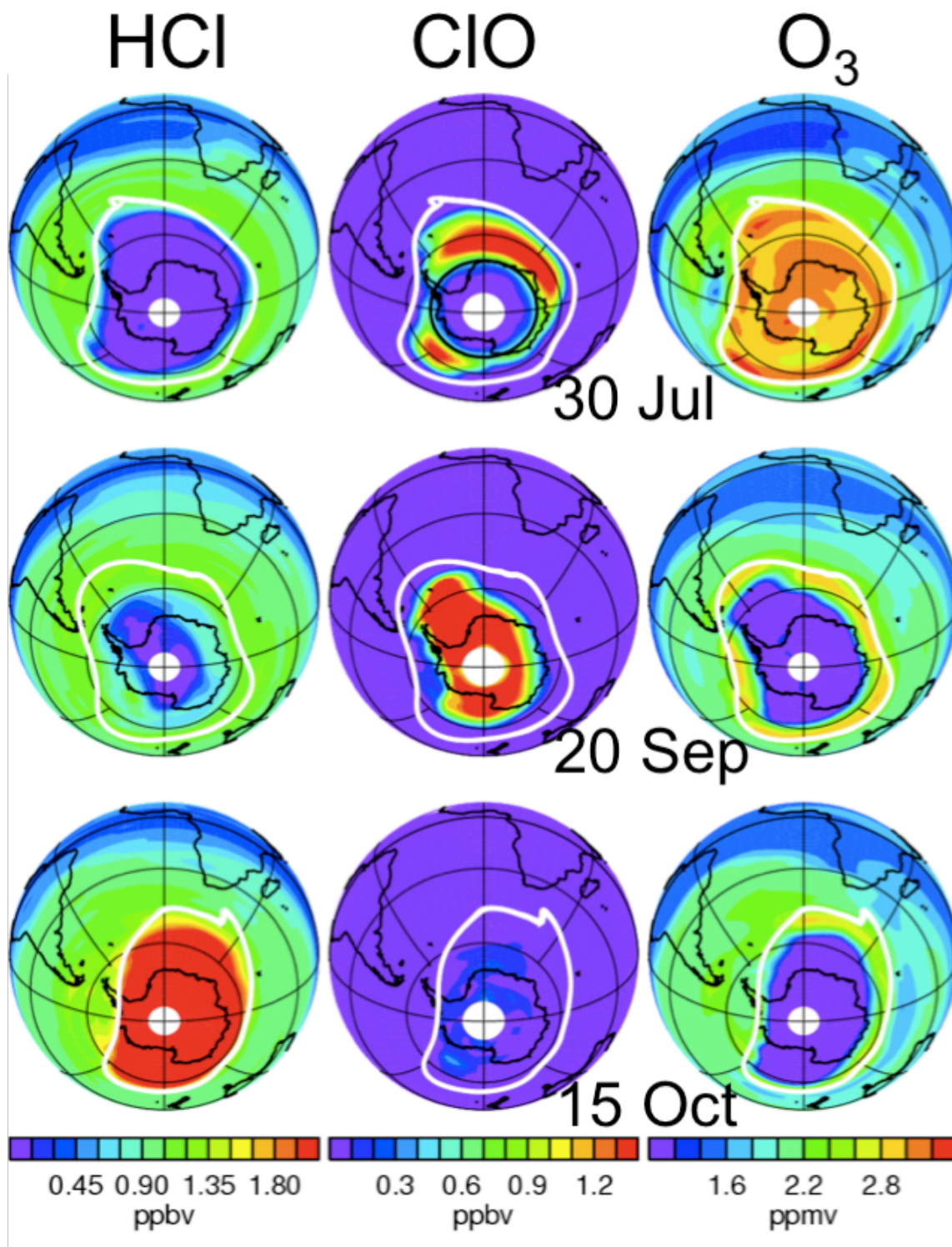


Figure 4.2. Hemispheric plots of HCl, ClO, and O₃ from MLS at three dates during the 2005 Southern Hemisphere winter/spring at 490 K (near 20 km).

To explore the impact of the Pope *et al.* [2007] dimer absorption cross sections on the agreement between modeled and measured chlorine partitioning and ozone loss, Santee *et al.* [2008] compared results from the SLIMCAT model using the new cross sections against results from the standard model (photochemical data from JPL 2003, except for the Cl_2O_2 photolysis rate, for which the values of Burkholder *et al.* [1990] were used, with a long-wavelength extrapolation to 450 nm [Stimpfle *et al.*, 2004]). The sensitivity tests show that, although modeled Cl_y and ClO_x are essentially unchanged, the partitioning between ClO , Cl_2O_2 , ClONO_2 , and HCl is altered throughout the winter relative to the standard run. The new cross sections result in a substantial reduction in modeled ClO (as shown also by von Hobe *et al.* [2007]), which severely underestimates that measured by Aura MLS during the period of peak activation in Antarctic winter (Figure 3.4). Modeled ClO remains significantly enhanced, and HCl reduced, well after MLS indicates that deactivation has taken place in late September, especially below the 500 K potential temperature altitude. As expected, the much lower ClO abundances in the test run lead to a substantial underestimation of ozone depletion (Figure 3.4). In addition, off-line calculations using the new cross sections yield unrealistically high values of ClO_x (> 6 ppbv) inferred from MLS ClO throughout much of the midwinter polar vortex (not shown). Similar, though less dramatic, reductions in ClO enhancement and chemical ozone loss and delay in chlorine deactivation are seen in Arctic model runs using the Pope *et al.* [2007] values [Santee *et al.*, 2008]. Tracking the temporal evolution of the chlorine species and ozone throughout the entire winter season provides a powerful tool for assessing theoretical understanding of chlorine partitioning and chemical ozone loss processes (see additional model comparisons in Section 6). Recent Arctic (and, to a lesser extent, Antarctic) winters have exhibited a large degree of interannual variability; such widely variable conditions provide a stringent test of model performance.

POAM and Match Ozone Loss/Sunlit Hour Observations

The Polar Ozone and Aerosol Measurement (POAM III) satellite instrument provided 8 years (1998-2005) of Antarctic ozone profile measurements. Figure 4.3 shows that vortex ozone declines sharply in late winter-early spring in each of these years except 2002, which had an anomalous level of dynamical disturbance [Newman and Nash, 2005], and 2004, which was also somewhat warmer than usual near 21 km in the vortex [Hoppel *et al.*, 2005a]. To isolate the chemical ozone loss, Hoppel *et al.* [2005b] applied the Match technique [Rex *et al.*, 1998] to five years of data using the photochemical box model of Salawitch *et al.* [1993] and Canty *et al.* [2005] to calculate ozone photochemical loss. The model calculates ozone loss from chlorine and bromine reactions using JPL 2002/2006 kinetics. To simulate maximum expected loss, total reactive bromine, BrO_x was set at 20 pptv, which equals the total inorganic bromine budget for the time period including shorter-lived bromocarbons [Wamsley *et al.*, 1998; Pfeilsticker *et al.*, 2000; WMO, 2003]. The abundance of reactive chlorine (ClO_x) was set to 3.7 ppbv. At a potential temperature of 469 K (~ 19 km altitude), the 5-year average loss rates were found to increase slowly from ~ 2 ppbv/sunlit-hour at the beginning of July to ~ 7 ppbv/sunlit-hour in the beginning of September, and then decrease rapidly. The peak loss rates compare well with the maximum loss rates of ~ 6 ppbv/sunlit-hour shown by Tripathi *et al.* [2007] for a Match analysis of Antarctic ozonesondes during 2003, and they are consistent with those observed at South Pole in Figure 4.1. When the Burkholder *et al.* [1990] ClOOCl cross sections are used in the box model, the simulated loss rate increases by $\sim 18\%$, which is still consistent with the observations

Section 4. Diagnostic Ozone Loss in Polar Regions

considering that the ClO_x and BrO_x may be overestimated in the model. When the Huder and DeMore [1995] cross sections are used, the September peak loss rate decreases to ~ 4.5 ppbv/sunlit-hour, significantly less than the observed value of ~ 7 ppbv/sunlit-hour. Finally, if the Pope *et al.* [2007] cross sections are used, the simulated loss rate is ~ 2.5 ppbv/sunlit-hour, less than half the observed value. The Match results are, however, sensitive to the choice of meteorological analysis used for the trajectory calculations. As discussed in Hoppel *et al.* [2005b], the ECMWF trajectories yielded the smallest peak loss rates, which are expected to be the most accurate because of the higher spatial and temporal resolution compared to the other meteorological data used in the study.

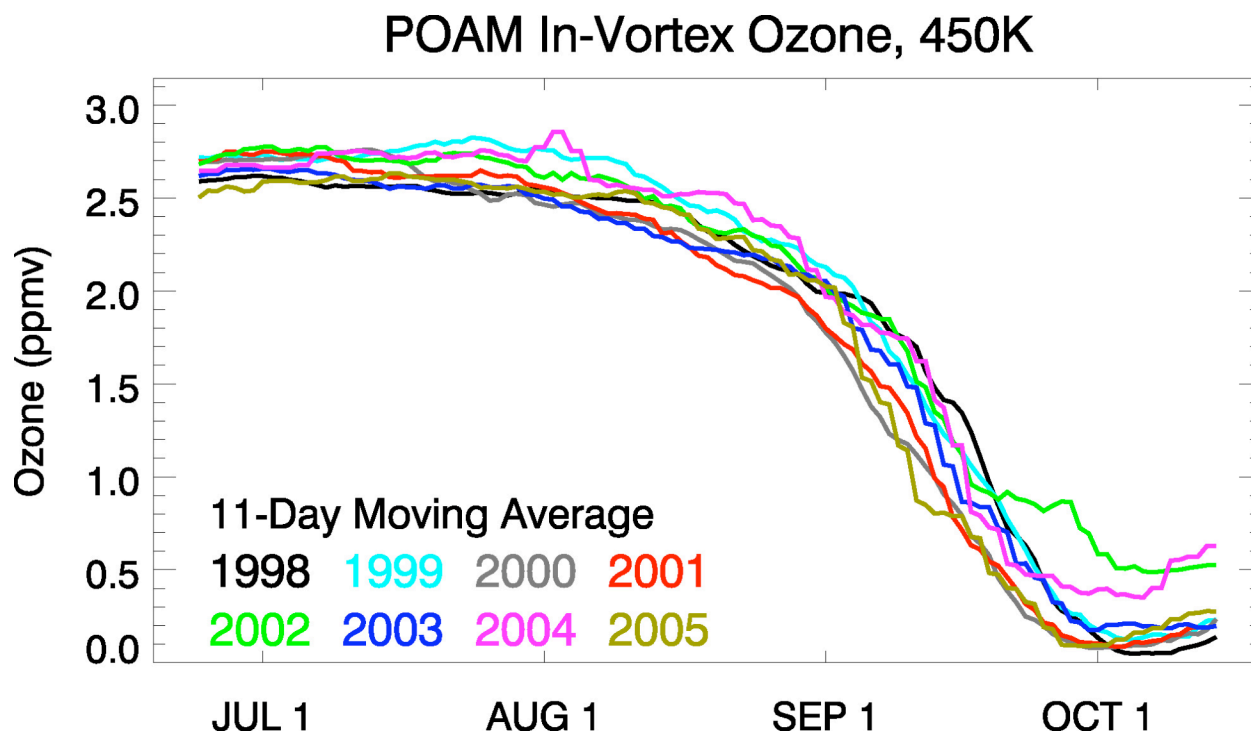


Figure 4.3. Time series of ozone through winter/spring averaged in the SH vortex as observed by POAM at 450 K potential temperature for multiple years.

In the Arctic, ozone loss rates have been regularly observed by Match campaigns since the early 1990s. To explain observed loss rates during a number of cold Arctic Januaries with a model based on standard chemistry, a contribution to stratospheric bromine from VLSL and J_{ClOOCl} at the upper end of available laboratory measurements have to be assumed (Rex *et al.* [2003]; Frieler *et al.* [2006]). The cold Arctic winter 1999/2000 provides a key test of our quantitative understanding of the observed ozone loss rates, since *in situ* measurements of ClO and ClOOCl are available from the SOLVE campaign at the same time as ozone loss rate measurements were being made. Figure 4.4 shows that observed loss rates best agree with a model based on standard chemistry (and high bromine) if $J_{\text{ClOOCl_Burkholder}}$ is used. $J_{\text{ClOOCl_JPL06}}$ is within the combined

uncertainties of the ClO_x observations and the ozone loss observations, while the agreement between the measurements and model results based on $J_{\text{ClOOC}_l\text{Huder\&DeMore}}$ is marginal. Figure 4.4 also shows that a model based on standard chemistry and $J_{\text{ClOOC}_l\text{Pope}}$ cannot be reconciled with the ozone loss observations, even if the highest estimates for stratospheric bromine are used. Hence, if $J_{\text{ClOOC}_l\text{Pope}}$ is correct, then currently unknown chemistry would be needed to explain the ozone loss observations. The observed Match ozone loss rates in the Antarctic and Arctic have been compared to results from the SLIMCAT 3D CTM [Feng *et al.*, 2007] with similar conclusions (Section 6 below).

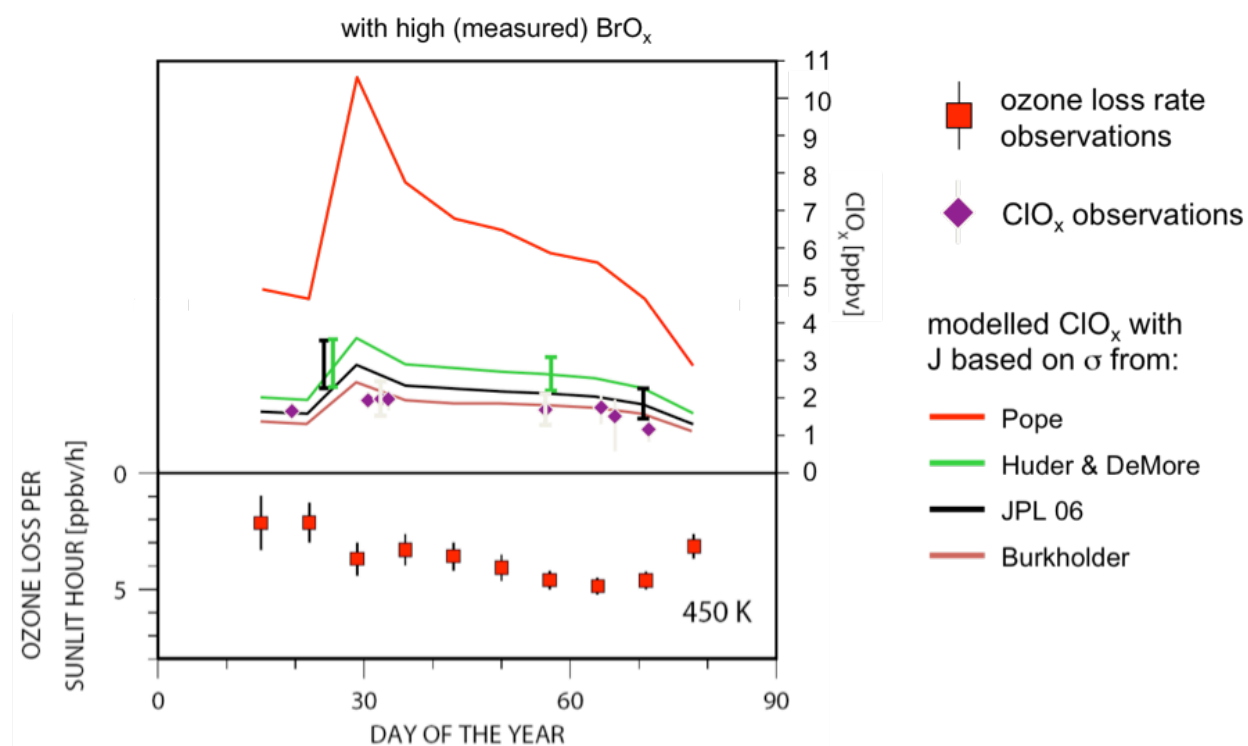


Figure 4.4. Ozone loss rates and reactive chlorine abundance from Match observations and photochemical model calculations (based on Frieler *et al.* [2006]; WMO 2007).

Sensitivity to Temperature and Sunlight

A critical test of our theoretical understanding of the ozone loss process is to compare the expected sensitivities of the ozone loss rate to solar illumination and temperature history with observations. The currently expected theory of polar ozone loss predicts that ozone loss is only possible in an individual air mass in the presence of sunlight and after that air mass has been exposed to temperatures below $\sim 195\text{K}$. In the Match approach, ozone loss rates are derived from ensembles of individual air masses and conditions in these air masses are very well characterized. In a bivariate statistical approach [Rex *et al.*, 2003], ozone loss rates can be

Section 4. Diagnostic Ozone Loss in Polar Regions

derived for dark portions and sunlit portions of the individual air mass trajectories individually. Figure 4.5A shows that significant ozone loss only occurs while the air masses are exposed to sunlight. In Figure 4.5B, the ozone loss rate in thousands of individual match events from many years of Match observations is shown as a function of temperature in the history of the individual air masses. As expected, significant ozone loss occurs only in air masses that have been exposed to temperatures below 195K, where heterogeneous processes occur that produce the reactive ClO_x required for rapid catalytic loss [Webster *et al.*, 1993; Kawa *et al.*, 1997]. These results strongly support the canonical view of the polar ozone loss process.

The critical point for this report is that any new species must to lead to an ozone loss with a similar dark/light dependence to ClOOCl , which implies an equilibrium with (or at least easy formation from) the dimer. This is discussed in more detail in Section 5.

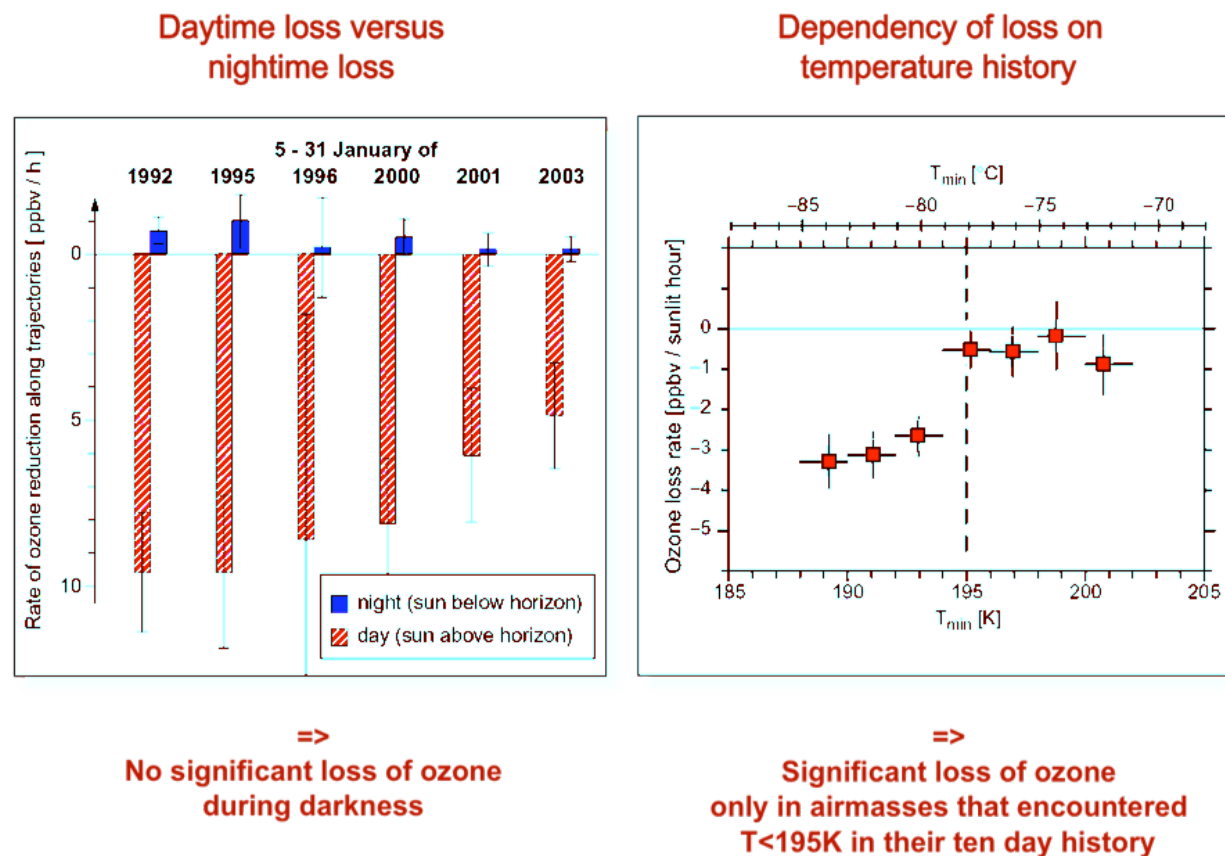


Figure 4.5. Match ozone loss rate separating daytime from nighttime loss and as a function of recent back trajectory minimum temperature.

Sensitivity to Other Reactions

The impact and significance of uncertainties in photolysis cross sections on calculated ozone loss in photochemical models must be evaluated with respect to the overall uncertainty in these calculations based on the combined uncertainty of the kinetic parameters. The overall uncertainty in modeled ozone loss has been derived from Monte Carlo scenario simulations varying the kinetic (reaction and photolysis rates) parameters randomly within their estimated uncertainty bounds given by the rate evaluation tables (JPL 06). Simulations of Match scenarios in the Arctic and a typical winter/spring Antarctic vortex scenario (Figure 4.6) show significant uncertainty in ozone loss diagnostics (20-300% in Arctic loss rate or ± 12 d in Antarctic ozone disappearance). Note that these simulations only test rate uncertainties, and their fidelity depends on the accuracy and completeness of the underlying chemical reaction set. Transport uncertainty is not included. However, the scenarios are chosen to minimize sensitivity to transport errors. The simulations clearly indicate that the largest single source of model uncertainty in polar ozone loss is uncertainty in the Cl_2O_2 photolysis reaction. Other reactions producing large sensitivity include $\text{BrO} + \text{ClO}$ and its branching ratios. Comparisons to Match, South Pole ozonesonde, and MLS data all show that nominal JPL rate simulations agree with data within uncertainties, although in both Arctic and Antarctic tests a faster rate of model ozone loss (e.g., Burkholder *et al.* Cl_2O_2 cross sections) is favored. Comparisons to simulations using Pope *et al.* cross sections are outside the error bounds in each case.

5. Missing Chemistry

From the previous two sections it is clear that using $J_{\text{ClOOCl_Pope}}$ in a model based on standard chemistry leads to:

1. buildup of larger concentrations of ClOOCl than in observations,
2. lower concentrations of ClO than in observations, and
3. smaller ozone loss rates than in observations.

In all three points, the discrepancies are larger than the combined uncertainties of the model results and the measurements. Particularly for ClO a wide range of observations exists from widely different techniques (*in situ* fluorescence based measurements and remote sensing results based on observations in the microwave and infrared spectral regions), making it extremely unlikely that unknown instrumental issues can account for the discrepancies that appear between observations and models, when $J_{\text{ClOOCl_Pope}}$ is used in the model calculations.

Hence, if J_{ClOOCl} is anywhere close to $J_{\text{ClOOCl_Pope}}$, there must be a mechanism that prevents the buildup of ClOOCl by either limiting the loss of ClO to the dimer or by rapid conversion of ClOOCl back to ClO . In principle, to prevent the buildup of unrealistic amounts of ClOOCl , either the production rate of ClOOCl could be slower than in the standard chemistry or a currently unknown additional breakdown mechanism could exist. A wealth of stratospheric observations spanning over two decades places tight constraints on any unknown chemical mechanism. Additional constraints come from numerous laboratory studies of the species and reactions in question. During the workshop, potential unknown chemistry was discussed in the light of these constraints.

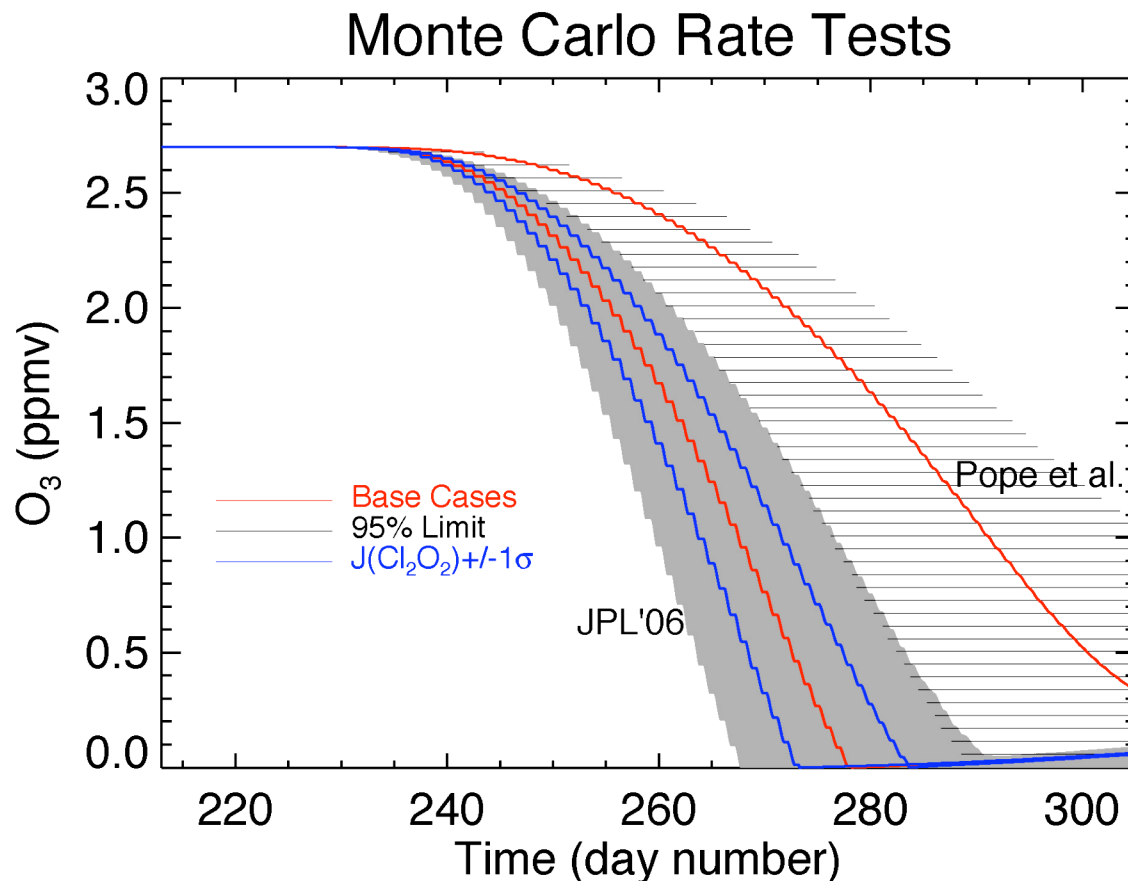


Figure 4.6. Time series of winter/spring ozone abundance from a box model simulation for a typical Antarctic vortex scenario (80°S , 50 hPa) with varying kinetic rate parameters. A 1000-member ensemble is run for each of two base cases: nominal JPL-06 and JPL-06 with Pope *et al.* photolysis cross sections substituted in for Cl_2O_2 (red curves). For each ensemble member the kinetic and photolysis rates are allowed to vary randomly within a distribution given by their JPL-06 uncertainty. The shaded and horizontal lines give the 95% confidence limits on the calculated O_3 abundance. The case with $J_{\text{Cl}_2\text{O}_2}$ set at its JPL-06 uncertainty limits is shown by the blue curves.

Basic Constraints for Unknown Mechanisms Based on Stratospheric Observations

From the previous sections, and in particular from Figure 3.3, it follows that atmospheric *in situ* measurements of ClO and ClOOCl suggest that:

- The diurnal variation of ClO and $\text{Cl}_{\text{Harvard}}$ (the sum of all species that are measured as ClOOCl in “Harvard-type” *in situ* instruments; i.e., all species that decompose into ClO at about 370K without also releasing Cl-atoms) is reproduced in a model that uses standard chemistry along with $J_{\text{ClOOCl}_{\text{Burkholder}}} \times [\text{Cl}_{\text{Harvard}}]$ as the daytime production rate of ClO (termed here $P_{\text{day}}(\text{ClO})$); assuming $k_{\text{ClO}+\text{ClO}_{\text{JPL06}}}$ for $\text{ClO} + \text{ClO}$; Stimpfle *et al.*, 2004):

$$P_{\text{day}}(\text{ClO}) = J_{\text{ClOOCl}}_{\text{Burkholder}} \times [\text{Cl}_{\text{Harvard}}] \quad (\text{I})$$

- The nighttime observations of ClO and $\text{Cl}_{\text{Harvard}}$ suggest that the nighttime production rate of ClO is about two to four times faster than that based on $k_{\text{EQ_JPL06}}$ (if $k_{\text{ClO+ClO_JPL06}}$ is used; e.g., Stimpfle *et al.*, 2004, von Hobe *et al.*, 2005, Schofield *et al.*, 2008).

$$P_{\text{night}}(\text{ClO}) = 3 \times k_{\text{ClO+ClO_JPL06}} / k_{\text{EQ_JPL06}} \quad (\text{II})$$

ClOOCl Production

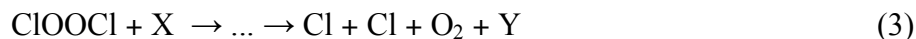
The reaction rate of ClO + ClO is fairly well known, with uncertainties small enough to rule out any role this reaction could have in reconciling models based on $J_{\text{ClOOCl_Pope}}$ with observations (e.g., Bloss *et al.* [2001], JPL 2006). This indicates that the production rate of ClOOCl would have to be much smaller than the rate of ClO + ClO (i.e., at stratospheric pressures the termolecular production rate of ClOOCl by this reaction would be much slower than the other bimolecular mechanisms for ClO + ClO). This has been ruled out by extensive lab studies (e.g., Nickolaison *et al.* [1994], Bloss *et al.* [2001]).

Alternative Mechanisms for ClOOCl Breakdown

Potential alternative breakdown mechanisms of ClOOCl fall into two basic categories. In category (1) Cl atoms are directly recycled by the breakdown of ClOOCl without requiring a photolytic step. In category (2) another nighttime reservoir (here termed Cl~) is formed by a reaction involving ClOOCl.

1. Direct Breakdown Mechanism

ClOOCl breaks down by the reaction with some species, X, directly producing Cl radicals or producing products that rapidly release two Cl radicals without involving a photolytic step:



In this case, ClOOCl is the only nighttime reservoir and $\text{Cl}_{\text{Harvard}}$ equals ClOOCl. Hence, the rate of ClOOCl + X must vary with solar zenith angle (sza) in a manner similar to the variation of the photolysis rate of ClOOCl based on Burkholder cross sections. This means that the concentration of X has an sza dependence similar to that of $J_{\text{ClOOCl_Burkholder}}$. Since this reaction has to compete with $J_{\text{ClOOCl_Burkholder}} \times [\text{ClOOCl}]$ and it cannot occur faster than collision frequency, the mixing ratio of X must be at least a few pptv. BrO (and ClO) are species that could be consistent with these two conditions. However, ClO appears to be unlikely because Bloss *et al.* [2001] would have seen it. This leaves BrO as the remaining potential candidate for X.

Potential products of the reaction are:



with only reaction (4a) being exothermic. The endothermic reactions (4b) and (4c) can be ruled out because they would be much slower than the collision rate and therefore cannot compete with the rate of $J_{\text{ClOOCl_Burkholder}} \times [\text{ClOOCl}]$. A model that includes reaction (4) does not reproduce the diurnal variation of ClO because the diurnal variation of [BrO] does not mimic that of $J_{\text{ClOOCl_Burkholder}}$. [BrO] is produced much too rapidly at sunrise from the photolysis of BrCl in the visible, i.e., the ratio $\text{BrO}(sza=90)/\text{BrO}(sza=80)$ is much larger than ratio $J_{\text{ClOOCl_Burkholder}}(sza=90)/J_{\text{ClOOCl_Burkholder}}(sza=80)$ and the direct breakdown mechanism appears to be unlikely. Furthermore, modelled BrOCl is not created in sufficient enough quantities to reconcile measured and modelled ClO_x .

2. Existence of an Unknown Nighttime Reservoir

In an indirect mechanism the breakdown of ClOOCl by reaction with X produces another nighttime reservoir of ClO_x , which we will denote Cl~.



The sum of ClOOCl and Cl~ is denoted Cl_{night} :

$$[\text{Cl}_{\text{night}}] = [\text{ClOOCl}] + [\text{Cl~}] \quad (\text{III})$$

or:

$$[\text{Cl~}] = a \times [\text{Cl}_{\text{night}}] \quad (\text{IV})$$

$$[\text{ClOOCl}] = (1-a) \times [\text{Cl}_{\text{night}}] \quad (\text{V})$$

where a denotes the fraction of Cl_{night} that is in the form of Cl~.

If the Pope *et al.* [2007] ClOOCl cross sections are correct, the source of ClO from photolysis of Cl_{night} is:

$$P_{\text{day}}(\text{ClO}) = J_{\text{ClOOCl_Pope}} \times [\text{ClOOCl}] + J_{\text{Cl~}} \times [\text{Cl~}] \quad (\text{VI})$$

or, using Equations (IV) and (V),

$$P_{\text{day}}(\text{ClO}) = J_{\text{ClOOCl_Pope}} \times (1-a) \times [\text{Cl}_{\text{night}}] + J_{\text{Cl~}} \times a \times [\text{Cl}_{\text{night}}] \quad (\text{VII})$$

$$P_{\text{day}}(\text{ClO}) = J_{\text{Cl}_{\text{night}}} \times [\text{Cl}_{\text{night}}] \quad (\text{VIII})$$

with $J_{\text{Cl}_{\text{night}}}$ defined as:

$$J_{\text{Cl}_{\text{night}}}(sza) = (1-a) \times J_{\text{ClOOCl_Pope}}(sza) + a \times J_{\text{Cl~}}(sza) \quad (\text{IX})$$

In principle, Cl~ could be OClO, ClOO, Cl₂, Cl₂O, ClOClO, ClClO₂, Cl₂O₃, Cl₂O₄, Cl₂O₅, Cl₂O₆, Cl₂O₇. However:

- OClO can be ruled out because atmospheric measurements show that only about 40 pptv of OClO is present during night.
- Cl₂O₆ and Cl₂O₇ can be ruled out because there is no single reaction partner that has enough O atoms to make these (a multi-step process should be unlikely).
- At stratospheric temperatures, thermal decomposition of Cl₂O₃ is so rapid that it cannot form a significant reservoir (formation cannot be faster than ClO + ClO). Of course its short lifetime also rules out ClOO.
- From equations (I) and (VII) it follows that J_{Cl~} cannot be smaller than about 0.5 × J_{ClOOCl_Burkholder} for all sza, since J_{ClOOCl_Pope} is very small and can nearly be neglected and [Cl_{night}] cannot be larger than 2 × [Cl_{Harvard}], because [Cl_{night}] cannot be larger than [Cl_y]. This rules out Cl₂O₄ because J_{Cl₂O₄}(sza) << 0.5 × J_{ClOOCl_Burkholder}(sza)

Hence, Cl~ can only be Cl₂, Cl₂O, ClOClO, ClClO₂, or Cl₂O₅.

In the following, three scenarios are discussed. In the first scenario it is assumed that reaction (5) is slow, such that significant amounts of ClOOCl and Cl~ co-exist in the atmosphere. In the second scenario it is assumed that reaction (5) is sufficiently fast that it prevents the buildup of significant amounts of ClOOCl at any time and Cl~ is the only nighttime reservoir of ClO_x. In the third scenario reaction (3) is assumed to be rapid but a path back from Cl~ to ClOOCl also exists, such that ClOOCl and Cl~ co-exist close to an instantaneous equilibrium.

Slow transformation of ClOOCl into an unknown nighttime reservoir

If reaction (5) is slow, significant amounts of ClOOCl would form during sunset. During the night ClOOCl would be slowly transformed into Cl~. Hence, the sunset evolution of ClO would follow a curve defined by the photolysis of a mixture of ClOOCl and Cl~ while the sunrise evolution would follow a curve based on the photolysis of much purer Cl~. This is not consistent with the *in situ* observations that show identical assumptions on the efficiency of J for AM and PM conditions result in good agreement with models (cf. Figure 3.3). Hence, a slow transition from ClOOCl into Cl~ can be ruled out.

Fast transformation of ClOOCl into unknown nighttime reservoir

If reaction (5) is fast, Cl~ is the only nighttime reservoir:

$$Cl_{\text{night}} = Cl_{\sim} = Cl_{\text{Harvard}} \quad (\text{X})$$

Hence, J_{Cl_{night}} = J_{Cl~} and J_{Cl~} has to be similar to J_{ClOOCl_Burkholder}. This rules out ClClO₂ because J_{ClClO₂} >> J_{ClOOCl_Burkholder}. Further, based on nighttime observations of ClO abundances it is known that a nighttime source of ClO exists. If Cl~ is the only nighttime reservoir, it has to

decompose thermally (or react with something that exists during night) to release some ClO during cold conditions (SOLVE) and a lot during warm conditions (EUPLEX). This rules out Cl₂. Hence, Cl~ can only be the odd oxygen species Cl₂O or Cl₂O₅ or the isomer ClOClO.

The isomer is further discussed below. If Cl~ is odd oxygen, X also needs to be an odd oxygen species, otherwise reaction (5) produces odd oxygen and the mechanism is a null cycle that does not destroy ozone. Also, during night, reaction (5) has to proceed at a rate comparable to the nighttime rate of ClO + ClO. Otherwise significant amounts of ClOOCl would build up, leading to AM/PM differences in J_{Cl night} that are not consistent with *in situ* observations. Hence, at least some X has to be around during night. X = ClO is unlikely since such a reaction would have been seen in laboratory studies. X = O₃, N₂O, CO and H₂O are possibilities worth pursuing. Sufficiently fast reactions of ClOOCl with N₂O, CO and H₂O have recently been ruled out by new laboratory work reported by Bayes *et al.* at the workshop (cf. Section 2).

If X is ozone, the rate constant for (5) has to be larger than about 10⁻¹⁵ cm³ s⁻¹ to make the reaction sufficiently fast. This has been ruled out by Tschuikow-Roux *et al.* [1992]. A potential heterogeneous mechanism for any reaction that breaks down ClOOCl cannot be faster than the collision rate between ClOOCl and surfaces. Since the EUPLEX observations were in PSC free air, the mechanism would have to work on sulfate aerosol. Collision rate theory shows that a surface area density of about 10 μm²/cm³ would be required to make the reaction fast enough – about an order of magnitude greater than available in the polar lower stratosphere.

Rapid equilibrium between ClOOCl and an unknown nighttime reservoir

If reaction (5) is rapid but a corresponding back reaction



also exists, Cl~ and ClOOCl could co-exist at a concentration ratio that is similar for AM and PM conditions. Therefore, J_{Cl night}(sza) would be similar for AM and PM, in agreement with observations. From equation (XI) it follows that J_{Cl~}(sza) has to be at least as large as J_{ClOOCl_Burkholder}. Cl₂ can be ruled out, because J_{Cl₂} is similar to J_{ClOOCl_Burkholder}. Accordingly, *a* in equation (IX) would have to be close to unity (i.e., Cl₂ would have to be the only nighttime reservoir). Since Cl₂ would not be confused with ClOOCl in Harvard type instruments, this is not consistent with the observation of high nighttime ClOOCl. Potential formation of Cl₂O₅ by reaction of ClOOCl with O₃ is much too slow (cf. last section). That leaves the two isomers ClClO₂ and ClOClO as potential candidates for Cl~. The absorption cross sections of ClOClO are not known but those of ClClO₂ are very favorable for such a mechanism. If the measured cross sections are log linearly extrapolated to 450nm, the shape of J_{ClClO₂}(sza) is very similar to J_{ClOOCl_Burkholder}, but the absolute values are about a factor of ten larger. Hence, J_{Cl night} for a mixture of 90% ClOOCl and 10% ClClO₂ is very similar to J_{ClOOCl_Burkholder}, even if J_{ClOOCl} = J_{ClOOCl_Pope}. Essentially, from its absorption and photolysis properties, such a mixture behaves identically to pure ClOOCl that photolyzes with Burkholder *et al.* [1990] cross sections, even if ClOOCl photolysis occurs according to the Pope *et al.* [2007] study.

According to *ab initio* calculations presented at the workshop by Dickson *et al.*, the barrier between ClOOCl and ClClO₂ is much too high to allow spontaneous transition between the isomers. However, chemical reactions between both species and ClO (or ClOOCl) could produce ClClO₂ and maintain equilibrium between the isomers. In principle such a mechanism could reconcile the *in situ* observations of ClO and ClOOCl with Pope *et al.* [2007] cross sections for the symmetric dimer and a chemical model that includes such a mechanism is able to reproduce the observations of chlorine species, including some SOLVE/EUPLEX differences that are hard to explain otherwise.

However, such a mechanism appears to be unlikely for two reasons. First, the photolysis of ClClO₂ would need to reestablish the O-O bond; otherwise the mechanism is a null cycle in terms of ozone loss. While such a photolysis pathway might not be ruled out completely, it is highly unlikely that it could be the dominant pathway. Second, Stimpfle *et al.* [2004] give an upper limit of 10 pptv for any species that releases chlorine atoms by thermal decomposition at temperatures of about 370K. They concluded that this upper limit applies to ClClO₂. Discussions at the workshop confirmed that this remains the case even for updated bond strength of ClClO₂, which was presented by Dixon *et al.* (cf. Section 2). To completely reconcile atmospheric observations with Pope *et al.* [2007] cross sections with the “isomer-mechanism,” about 10% of nighttime ClO_x would have to be in the form of ClClO₂, i.e., up to about 200 pptv, a factor of 20 more than the upper limit by Stimpfle *et al.* At the workshop, Jucks *et al.* presented another analysis of ClClO₂ in the atmosphere based on the analysis of IR-spectra from the MkIV instrument. They find an upper limit of 14-25 pptv for the twilight conditions close to 90° sza when these measurements were carried out.

These upper limits do not apply to ClOClO, which could breakdown into ClO without releasing Cl on thermal decomposition. The existence of this species, or the existence of trace amounts of ClClO₂ below the upper limits given above, could help to narrow the gap between observations and model calculations of ClO and ClOOCl if the cross sections of ClOOCl are indeed significantly smaller than $\sigma_{\text{ClOOCl}}_{\text{Burkholder}}$. A temperature dependent equilibrium between ClOOCl and one of its isomers could also help to explain some unresolved issues with different equilibrium constants derived from stratospheric observations for different temperatures. However, it is highly unlikely that such a mechanism could fully reconcile Pope *et al.* [2007] cross sections with atmospheric observations, particularly with those of high ozone loss rates.

Summary of Missing Chemistry Considerations

Many years of active polar ozone research have provided a wealth of information about the observable properties of the ozone loss mechanism. These include measurements of the detailed diurnal variation of key species under a range of stratospheric temperatures, observations in individual air masses before and after sunset, thousands of detailed observations of ozone loss rates in individual air masses for different air mass histories and under different solar illumination, and measurements of the seasonal evolution of ozone and key species from ground based stations and satellite instruments. All these observations together provide tight constraints on potential “missing chemistry.” It seems to be unlikely that any major chemical mechanism could remain undetected so far. If any relevant unknown chemistry plays a role for the ozone loss mechanism, it can only be a minor modification of the known mechanisms, like adding an

alternate breakdown mechanism for ClOOCl that has an overall effect very similar to the currently assumed rapid photolysis. Observational constraints for even such a minor modification of the chemical system are tight and it appears to be very difficult to reconcile cross sections of ClOOCl much smaller than current JPL recommendations with atmospheric observations.

6. Modeling of Chlorine Species and Ozone Loss

The photolysis of the ClO dimer is clearly one of the key processes controlling O₃ loss in the springtime polar regions. As shown in Section 4, using the Pope *et al.* ClO dimer cross sections has a large impact on calculated ozone loss rates. It is important to understand how the incorporation of the Pope *et al.* cross sections will affect ozone and other species in global 3D model calculations such as those used for assessment studies (e.g., WMO 2007).

Calculations of polar ozone loss with 3D models depend on many more parameters than the dimer photolysis. In order for a 3D model to simulate realistic polar ozone loss it will need to reproduce: (i) transport and degradation of chlorine source gases through the stratosphere; (ii) polar meteorology (i.e., polar vortex and temperatures); (iii) activation of chlorine species on polar stratospheric clouds; (iv) polar denitrification/dehydration processes and (v) deactivation. For these reasons comparison of 3D model O₃ loss with observations is not a critical test of a single photochemical parameter. However, given the large impact of the Pope *et al.* cross sections on ClO_x partitioning (e.g., Section 4) it is useful to explore the impact on 3D model runs.

Three-dimensional models can be categorized as either “off-line” chemical transport models (CTMs) or coupled chemistry-climate models (CCMs). CTMs are forced by analyzed winds and temperatures and thus are constrained by “real” meteorology. They will therefore have realistic polar temperatures but can still be subject to transport problems originating either from the analyzed winds or numerical transport scheme. CCMs calculate their own winds and temperatures and they are needed for predictions of the future.

Figure 6.1 compares Match observed O₃ loss rates in the Antarctic and Arctic (see Section 4) with results from the SLIMCAT 3D CTM (see Feng *et al.* [2007]). The model runs used different values for the dimer cross sections, and were sampled to mimic the Match analysis. The runs also assumed a 6 pptv contribution of Br_y from VLSL. In the Antarctic the observed loss rates peak at around 6 ppbv/hr in September, while in the Arctic they peak at just over 4 ppbv/hr in January. The model run with the fastest J_{ClOOCl} (i.e., Burkholder) produces the fastest O₃ loss rates, which agree with the observations (except for an underestimation of observed loss rates in early January). Ozone loss rates using JPL cross sections are slower, but still largely agree within the observed uncertainties. The Huder and DeMore cross sections give O₃ loss rates which generally lie close to observations in the Arctic but show a clear underestimation of the Antarctic loss rates (e.g., a peak loss of only 4 ppbv/hr in late September). Finally, the Pope *et al.* cross sections produce the slowest O₃ loss rate, which is significantly lower than the observations (e.g., the model loss rate in the Antarctic is ~30% of that observed in September).

Figure 6.2 shows the impact of changing ClO dimer photolysis on modeled O₃ loss. With the Burkholder *et al.* cross sections, which gave the best agreement with 2002/3 Match loss rates (Figure 6.1), the model produces a maximum vortex-averaged loss of 55% in mid March. However, with the Pope *et al.* cross sections the maximum loss is around 35%. Note that the peak loss is shifted later in the season due to the slower deactivation (see Figure 4.2). For the partial column ($\theta=380$ to 550K) the maximum vortex average loss decreases from ~140 DU to ~85 DU, again with a shift to later in the season. Although the change in modeled ozone loss is large, it is much smaller than the relative change in the dimer photolysis rate. The repartitioning of ClO_x within the model (i.e., shift of ClO_x to Cl₂O₂) offsets the smaller J_{ClOCl}.

Simulations with the Chemical Lagrangian Model of the Stratosphere (CLaMS) for different Arctic winters [Groß *et al.*, 2005; 2007] have also been used to investigate the sensitivity with respect to the Cl₂O₂ absorption cross sections. Figure 6.3 shows the CLaMS simulated vortex partial column ($\theta=380$ K to 550 K) ozone loss sensitivity for 2002/03 and 2004/05. According to these simulations, the partial column ozone loss for the Pope *et al.* cross sections is 12-24 DU (28-34%) smaller than for the Burkholder *et al.* cross sections. The timing of ozone loss is also somewhat different. From early March onwards the Pope *et al.* case even shows a slightly larger ozone loss rate than the Burkholder case due to less efficient chlorine deactivation (see above). Comparisons of the CLaMS results with ACE-FTS ozone observations in March show somewhat larger deviations for the Pope case (average difference 0.21±0.26 ppmv) than for the Burkholder case (-0.03±0.26 ppmv).

While the SLIMCAT and CLaMS models show similar qualitative sensitivity to the Cl₂O₂ cross sections, they predict very different overall polar ozone loss for Arctic winter 2004/5. The SLIMCAT modeled partial column loss for 2004/5 almost twice that of CLaMS. This illustrates how modeled O₃ loss can be sensitive to other factors such as Cl_y and Br_y loading, chlorine activation etc., and shows why the impact on model ozone is not a critical test for the evaluation of dimer kinetics.

Figure 6.4 shows results for the Antarctic using the MOZART-3 chemical-transport model (see Kinnison *et al.* [2007]) driven with chemistry-climate model winds (WACCM). This approach decouples the feedback between chemistry and dynamics and allows a straightforward comparison of chemical sensitivity for a given choice of the ClO dimer cross section. MOZART-3 was run 4 times with different assumptions for the ClO dimer absorption cross sections. As a sensitivity test, the Pope *et al.* [2007] ClO dimer cross-section case was simulated with three different choices for total inorganic bromine (0, 16, and 22 pptv). In addition, one simulation assumed that the ClO dimer photolysis rate is zero. In Figure 6.4, column ozone evolution, along with local ozone, HCl, and ClO_x (ClO + 2Cl₂O₂) is shown. As the ClO dimer photolysis becomes slower (ranging from Burkholder *et al.* [1990] to J_{ClOCl}=0), the partitioning of ClO_x into Cl₂O₂ increases, the deactivation of ClO_x and recovery of HCl is delayed, and the O₃ loss rate decreases. Again, this shows the large impact of the slower ClO dimer photolysis rate on the calculation of polar ozone loss. While the simulation using Pope *et al.* [2007] cross sections and high bromine still shows an Antarctic “ozone hole,” it is not as deep as observed, consistent with the other CTM results mentioned above.

CCMs are increasingly being incorporated as the atmospheric component of Earth System Models (ESMs). These models attempt to couple surface, ocean and atmospheric processes in order to predict the overall evolution of the Earth system. Many of the processes in these models are poorly constrained and rely on fairly crude parameterizations. Despite the uncertainties in J_{ClOOC1} highlighted in this report, our understanding of polar stratospheric ozone depletion is still an example of a process that is comparatively well understood.

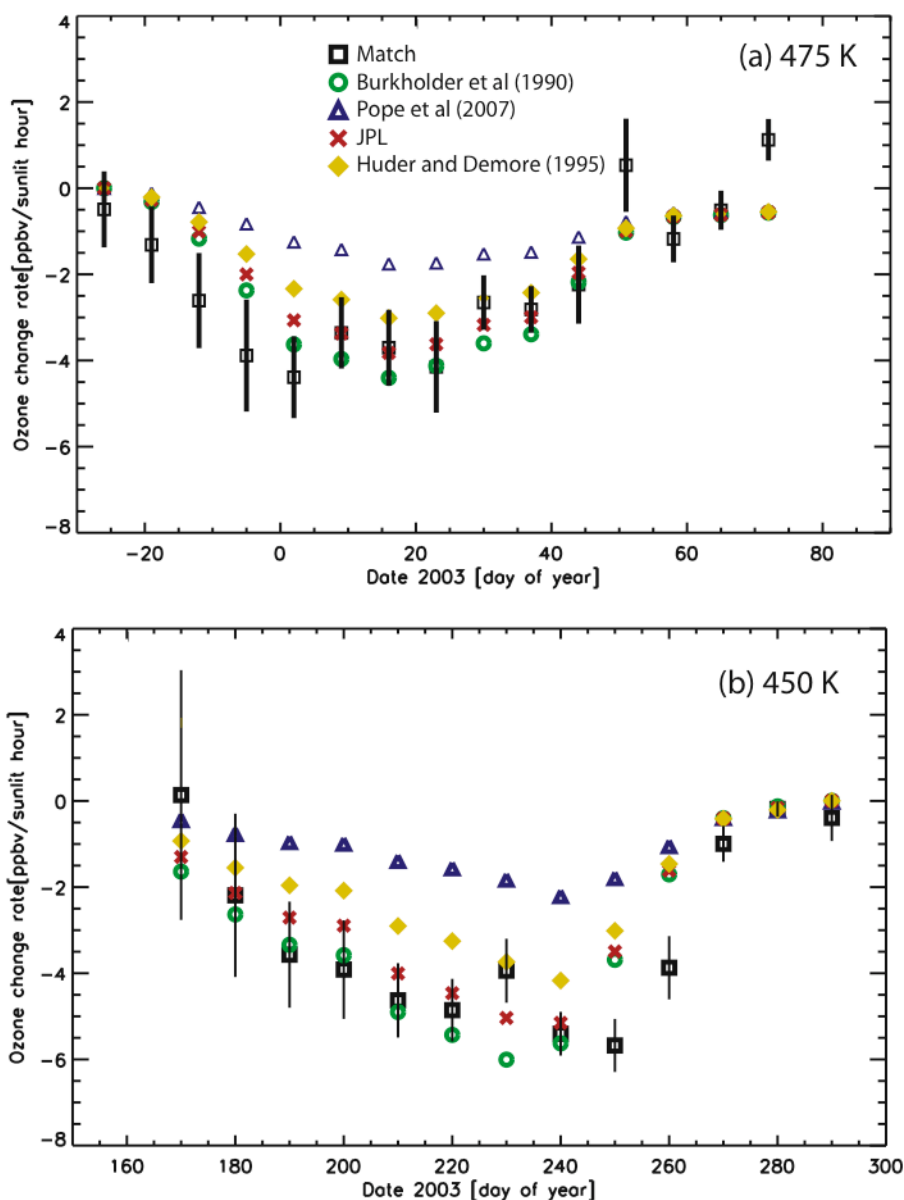


Figure 6.1. Comparison of the Match observed O_3 loss rates (ppbv/sunlit hour) with results from four simulations of the SLIMCAT 3D CTM using different Cl_2O_2 cross sections for (a) the Arctic in 2002/3 at 475 K potential temperature altitude and (b) the Antarctic in 2002 at 450 K. Figure courtesy of W. Feng.

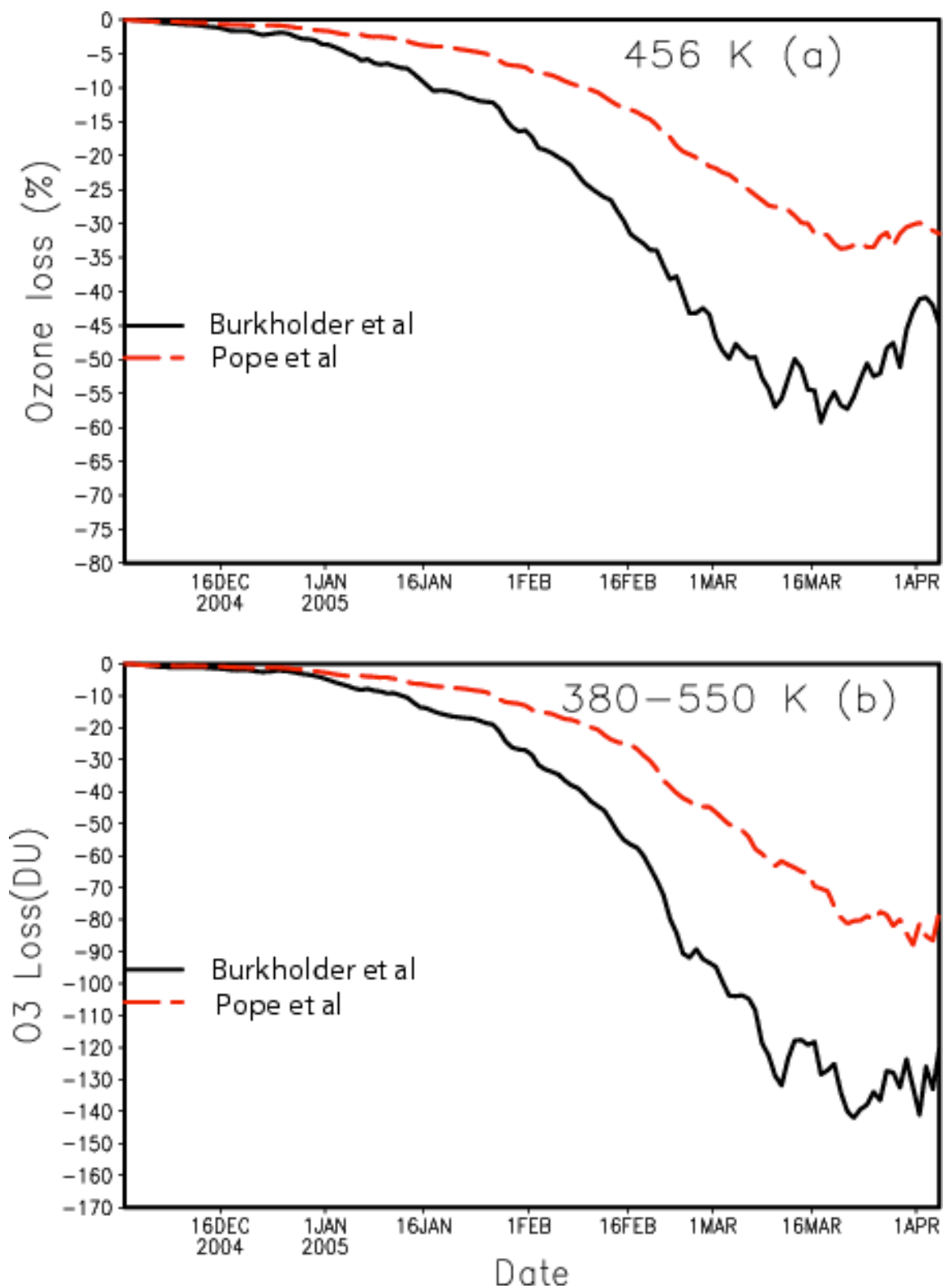


Figure 6.2. Vortex-average ozone loss from SLIMCAT 3D model for Arctic winter 2004/5 using different values of the ClO-dimer cross sections for (a) 456 K (%) and (b) partial column 380-550 K (DU). Figure courtesy of W. Feng.

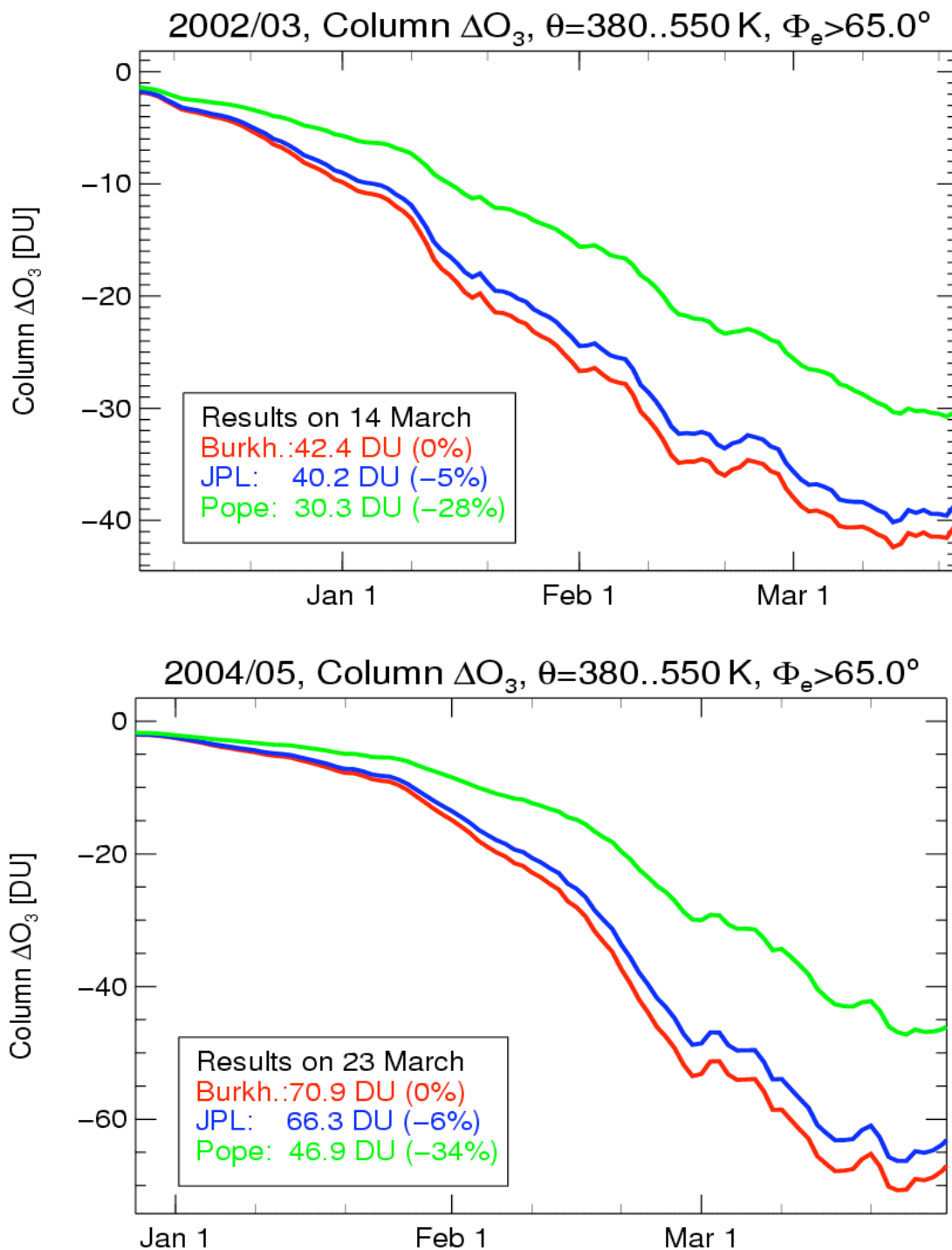


Figure 6.3. Simulated partial column ozone loss ($\theta=380$ to 550 K) in the polar vortex (equivalent latitude $> 65^\circ$) from CLaMS simulations for (a) 2002/03 and (b) 2004/05. Colors correspond to Cl_2O_2 absorption cross sections, as indicated in the plot legend. The percentage difference to ozone loss calculated for the Burkholder is also indicated. Figure courtesy of J.-U. Grooß.

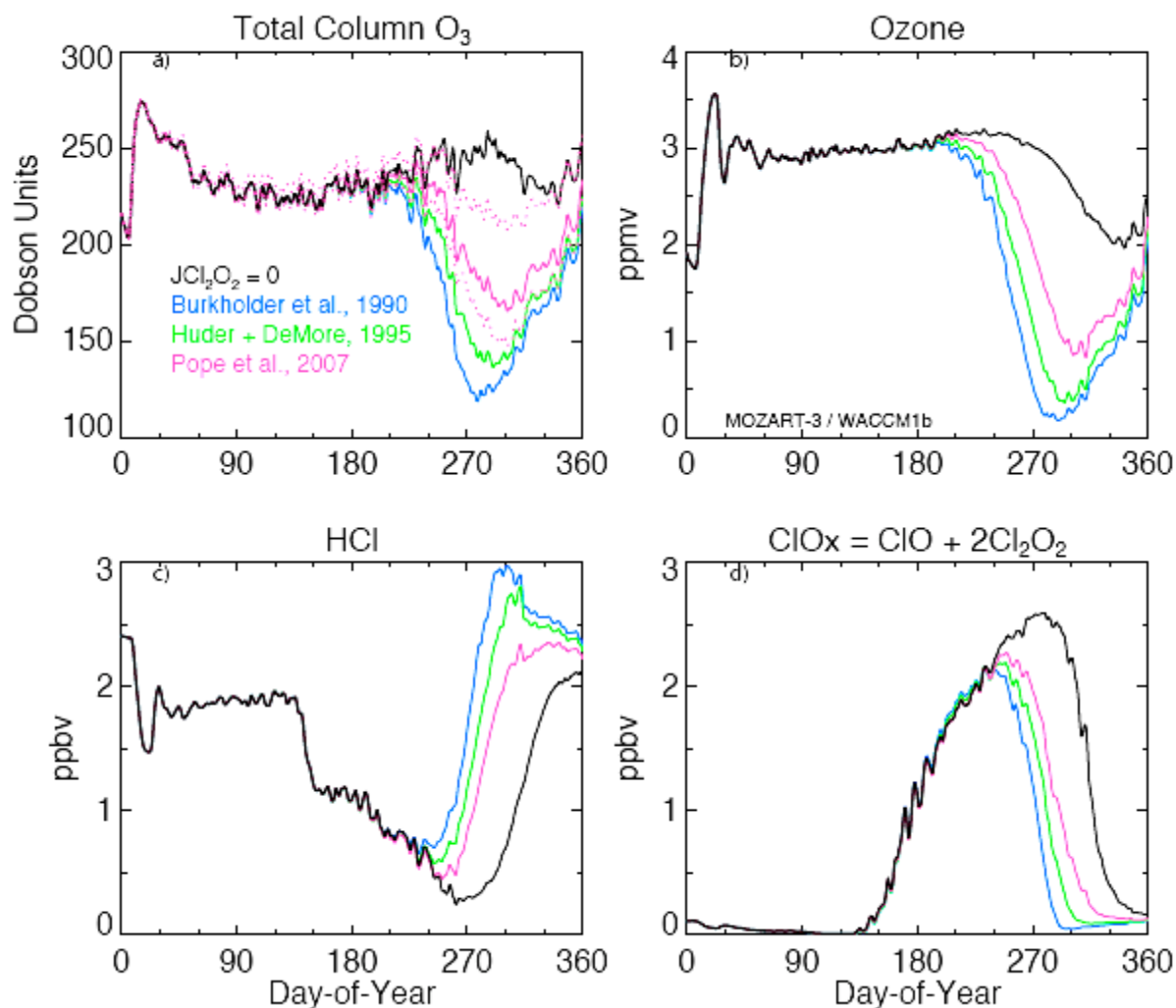


Figure 6.4. The zonal-mean annual cycle at 82°S is shown for select species from the MOZART-3 CTM driven with WACCM meteorological fields assuming different ClO dimer cross sections and total inorganic bromine abundances (0, 16, 22 pptv). Panel (a) shows the evolution of total column ozone. For the Pope *et al.* [2007] simulation (solid magenta line), the sensitivity of total inorganic bromine (Bry) is also shown (dotted lines). The case with zero Bry shows only a small decrease in total column ozone during Antarctic spring conditions. The case with 22 pptv has approximately 20% more column ozone depletion relative to the reference case (16 pptv Bry). Panels (b)-(d) show the volume mixing ratio evolution at 82°S, 43 hPa for O₃, HCl, and ClO_x respectively. Figure courtesy of D. Kinnison.

7. Summary

It was clear from the presentations and discussions at the Cambridge Workshop that this SPARC Initiative is succeeding in encouraging the research necessary to draw this issue to closure. It is particularly important that as many of the new scientific investigations as possible are published in the peer reviewed literature on a time frame suitable for use by the authors of chapters that will be written for the WMO / UNEP 2010 Scientific Assessment of Ozone Depletion. In this regard, the Initiative Co-Chairs, together with the Steering Group, are gathering publication topics from the participants to foster collaborative studies and to arrange for publication in a special journal issue.

8. References

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9. Acknowledgements

The organization of the workshop was supported through SPARC, the EC Integrated Project SCOUT-O3, and NASA's Atmospheric Composition Focus Area in Earth Science.

10. Authorship and Review Process

Authorship of this report resides with all of the scientists that have actively participated in this SPARC Initiative. However, specific groups of individuals should be acknowledged for their roles in drafting the individual sections of this report. They are:

- Section 1. J. G. Anderson, M. J. Kurylo, R. J. Salawitch, M. L. Santee, and B.-M. Sinnhuber
- Section 2. N. R. P. Harris and M. von Hobe
- Section 3. R. J. Salawitch, T. P. Canty, R. Müller, M. L. Santee, R. Schofield, R. M. Stimpfle, F. Stroh, D. W. Toohey, and J. Urban
- Section 4. S. R. Kawa, M. P. Chipperfield, N. R. P. Harris, D. J. Hofmann, K. W. Hoppel, M. L. Santee, and M. Rex

Section 5. M. Rex, K. D. Bayes, T. P. Canty, D. A. Dixon, K. W. Jucks, S. P. Sander, and R. M. Stimpfle

Section 6. M. P. Chipperfield, J.-U. Grooß, and D. E. Kinnison

The sections underwent a first round of review by the Initiative Co-Chairs and the Steering Group. Following revision, they were made available to the entire group of participants for further review and subsequent revision. The Co-Chairs then integrated the report, and the Initiative Organization and workshop attendees reviewed the complete document.

11. Appendix

Initiative Organization:

Co-Chairs

M. J. Kurylo and B.-M. Sinnhuber

Steering Group

Laboratory/Theory: N. R. P. Harris and M. von Hobe

Atmospheric Measurements: P. A. Newman, D. W. Fahey, and R.-S. Gao

Modeling/Analysis: R. J. Salawitch and M. P. Chipperfield

Executive Secretary

K. A. Thompson

Workshop and Documentation Support:

R. M. Kendall R. Penkett

Workshop Attendees (* indicates presenter):

J. G. Anderson	K. D. Bayes *	W. Bloss	G. E. Bodeker
J. B. Burkholder *	T. P. Canty *	M. P. Chipperfield *	B. J. Connor *
D. A. Dixon *	S. Dobe	W. Feng	J. S. Francisco
R.-S. Gao *	N. Glatthor	J. C. Gomez-Martin	J.-U. Grooß *
T. F. Hanisco *	N. R. P. Harris *	D. J. Hofmann *	K. W. Hoppel *
T. Imamura	K. W. Jucks *	S. R. Kawa *	D. E. Kinnison *
K. Kreher	M. J. Kurylo *	G. Le Bras	G. K. Moortgat
O. Morgenstern	R. Mueller	P. A. Newman *	J. J. Orlando
R. Penkett	F. D. Pope *	R. W. Portman	G. Poulet
J. A. Pyle *	M. Rex *	P. Ricaud *	D. M. Rowley *
R. Ruhnke *	R. J. Salawitch *	S. P. Sander *	M. L. Santee *
R. Schofield *	B.-M. Sinnhuber *	I. Smith	R. M. Stimpfle *
F. Stroh *	K. A. Thompson	D. W. Toohey *	J. Urban *
T. von Clarmann *	M. von Hobe *	D. M. Wilmouth *	P. H. Wine