

Potential for enhanced halogen-catalyzed ozone loss in conditions of high water vapor and low temperature

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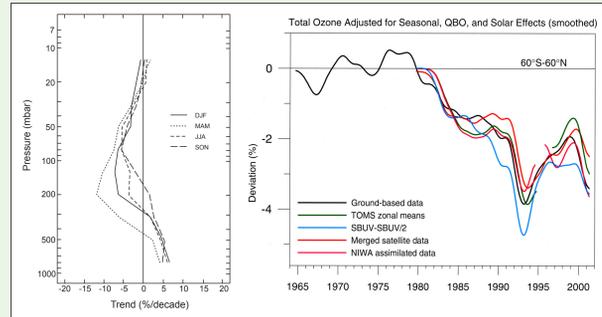
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Introduction

The impact that climate change will have on the processes that control mid-latitude ozone is a primary concern. Most notable is the realization that modest increases in water vapor concentration or small decreases in temperature can trigger extremely rapid conversion of HCl and ClONO₂ to ClO. Coupling with BrO amplifies the impact on ozone loss. Recent work in our laboratory has led to substantial improvements in the BrO detection sensitivity of our halogen flight instrument.

Mid-latitude Ozone Loss

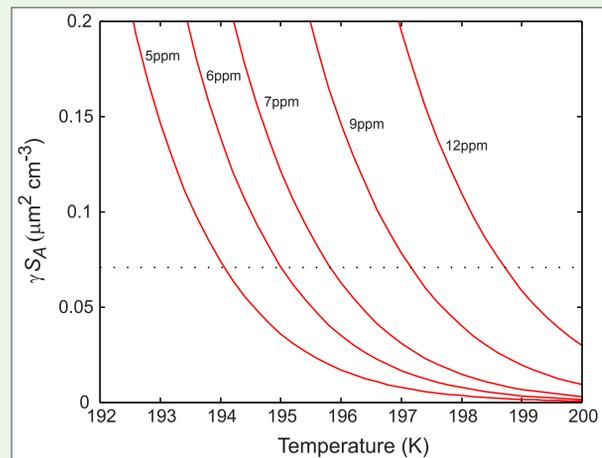
Accurately establishing the mechanism responsible for observed mid-latitude ozone losses is a dominant issue.



Left panel, seasonal mean ozone trend profiles for ozone sonde stations located 36°–53°N for data collected from 1980 to 1996 (Logan et al., 1999). Right panel, from WMO, 2003, deseasonalized, area-weighted total ozone deviations, adjusted for solar and QBO effects (Fioletov et al., 2002).

Linking Climate Change to Ozone Destruction

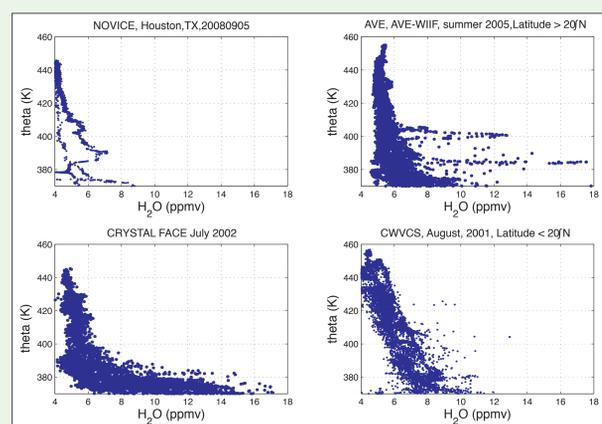
Forcing of climate by increases in CO₂ and H₂O that radiatively cool the lower stratosphere, along with increases in stratospheric water vapor, have the potential to significantly enhance chlorine activation through the catalytic conversion of inorganic halogens to free radical form on cold aerosols and ice particles.



The potential for raising the threshold temperature for halogen activation and thereby enhancing ClO concentrations in the lower stratosphere (Kirk-Davidoff et al., 1999). The ordinate displays the product of aerosol reactive surface area, S_a, and reaction probability per collision, γ, that determine the rate of inorganic chlorine conversion to free radical form. The horizontal dotted line marks the threshold above which the conversion is virtually instantaneous.

Evidence for High Water Vapor

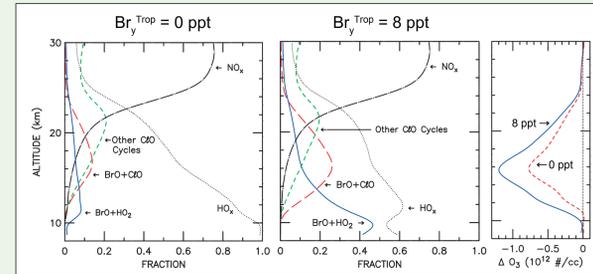
Observations of highly elevated water vapor convected into the cold lower stratosphere are now recognized to be ubiquitous, and they raise the potential for amplifying the destruction of ozone by catalytic loss. Examples of the mounting series of water vapor observations from recent NASA airborne missions are seen in NOVICE, AVE-WIFF, CRYSTAL-FACE, and CWVCS.



Water vapor profiles observed by the Harvard Lyman-α instrument on the NASA WB-57.

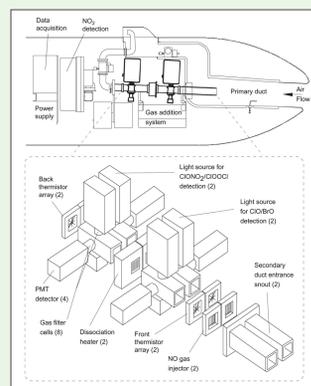
The Role of Bromine

In addition to the mechanism involving ClO alone, the link with BrO significantly amplifies potential ozone losses through the ClO + BrO → Cl + Br + O₂ rate-limiting step.



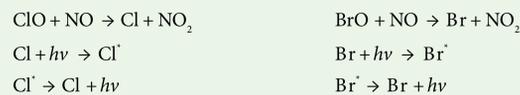
Dominant rate-limiting reactions controlling the photochemical loss of ozone in the lower stratosphere (Salawitch et al., 2005). An increase in BrO of only 8 ppt substantially elevates the role of the bromine/chlorine catalytic step in lower stratospheric ozone loss.

Resonance Fluorescence Detection of BrO, ClO, ClONO₂, and ClOOCl



In addition to the need to measure BrO in the context of understanding the link between halogen radicals and column ozone, there is, as well, a more focused need to understand what the atmospheric burden of BrO in the atmosphere is presently and what are its sources and sinks. The Harvard Halogen instrument measures BrO, ClO, ClONO₂, and ClOOCl in flight.

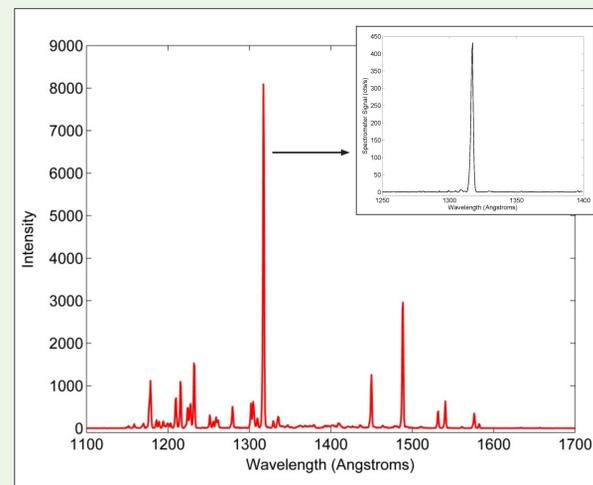
Detection Method:



Improved Bromine Sensitivity

Why is measuring BrO more difficult than ClO?

- Low atmospheric BrO abundances
- Br emission lines more heavily absorbed in air



Typical bromine lamp spectrum in nitrogen. There are approximately 30 lines present in the emission spectrum of a bromine RF lamp from 115 to 158 nm. Oxygen absorbs all signal from the bromine lines above ~132 nm and significantly reduces the signal of all other bromine lines below 132 nm.

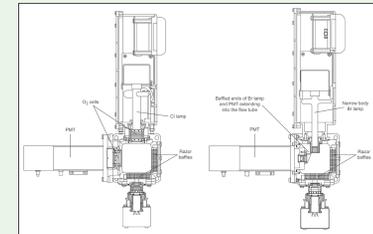
Significant progress has been made recently in our laboratory effort aimed at improving the detection sensitivity for bromine. The laboratory work has centered on three avenues of improving signal-to-noise.

Conclusions

- The quantitative role played by the combination of low temperature and amplified water vapor in the bromine/chlorine radical catalytic destruction of ozone in the lower stratosphere is potentially extremely important, particularly as climate is increasingly forced by carbon release.
- There is currently no quantitative information on the catalytic response of ozone loss to high water and low temperatures at mid-latitudes.
- A number of instrument changes have resulted in a BrO instrument that is capable of up to a factor of ten improvement in the detection limit for BrO in the lower stratosphere and troposphere relative to what has flown before. Work is ongoing to incorporate these demonstrated improvements in the laboratory into the flight instrument.

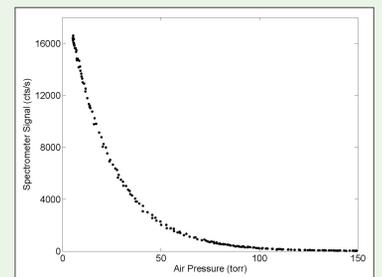
I. Reduce Impact of Oxygen

One way to reduce the deleterious effects of oxygen on bromine sensitivity is to decrease the O₂ absorption pathlength by bringing the lamp and PMT close together. This was the primary method employed in a preliminary attempt to improve bromine detection capability during the SOLVE mission.



Cross section of the complete RF detection axis of chlorine (left) and bromine (right) as used during the SOLVE mission.

An alternate, and more promising, method to minimize the deleterious impact of oxygen involves a pump-down technique. Decreasing the pressure in the flight instrument duct significantly reduces both oxygen absorption and quenching.



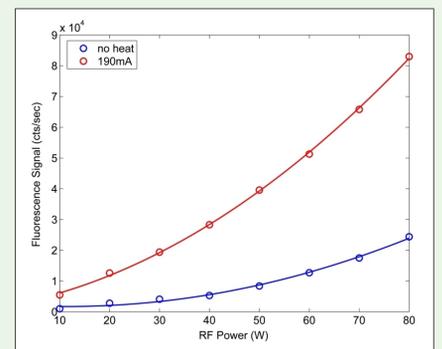
Lamp output at the 131.7 nm ground state Br line as a function of air pressure in the flow tube. The bromine signal at the 131.7 nm line is a factor of 10 greater at 50 torr than 100 torr and a factor of 30 greater at 30 torr than 100 torr.

II. More Light on Detector

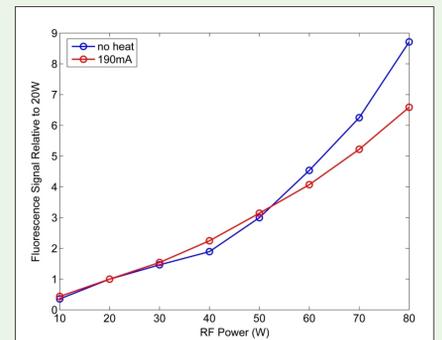
Increasing the amount of light from the bromine lamps can most effectively be achieved by increasing the RF power, but a complete redesign of the lamp-module system is required, and there are notable challenges:

- Electronics capable of generating high RF power for extended periods of time
- Prevention of RF interference with surrounding electronics at high power
- Sufficient dissipation of the large heat generation in the lamp housing

Br fluorescence signal as a function of RF power. System was previously only capable of ~30 W maximum.



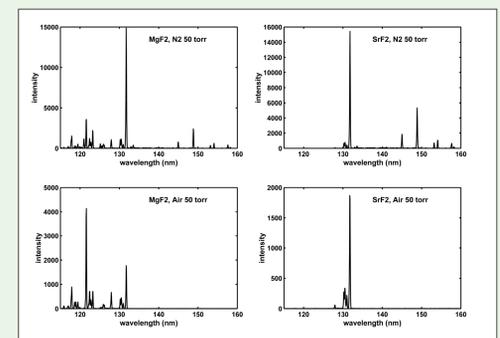
Br fluorescence signal at each power level relative to the fluorescence signal at 20 W, the approximate power historically used in flight. The relative gain in fluorescence signal is nearly a factor of 9 at 80 W with the lamp sidearm heat off and about 6.5 with the lamp sidearm heat on.



III. Filter Bromine Lamp Output

In an attempt to isolate only ground state bromine lines from other bromine lines and the 121.6 nm Lyman-α impurity, we have pursued several avenues of filtering our lamp output.

- No suitable commercial filters exist for this wavelength region.
- Of the 100+ gas filter options researched, none are suitable.
- Alkali halide windows are effective – have very sharp transmission cutoffs – from 100% to 0% in 2-3 nm.



The combined effects of filtering a Br lamp with MgF₂ or SrF₂ windows and a N₂ or air gas fill in the detection volume, as labeled. Using a SrF₂ window or CaF₂ window (not shown) is useful in eliminating the H atom impurity line at 121.6 nm.