The very short-lived ozone depleting substance, $CHBr_3$ (bromoform): Revised UV absorption spectrum, atmospheric lifetime and ozone depletion potential

Dimitrios K. Papanastasiou [a,b], Stuart A. McKeen [a,b], and James B. Burkholder [a]

[a] Earth System Research Laboratory, Chemical Sciences Division, NOAA, 325 Broadway, Boulder Colorado 80305, USA
[b] Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder Colorado 80309, USA

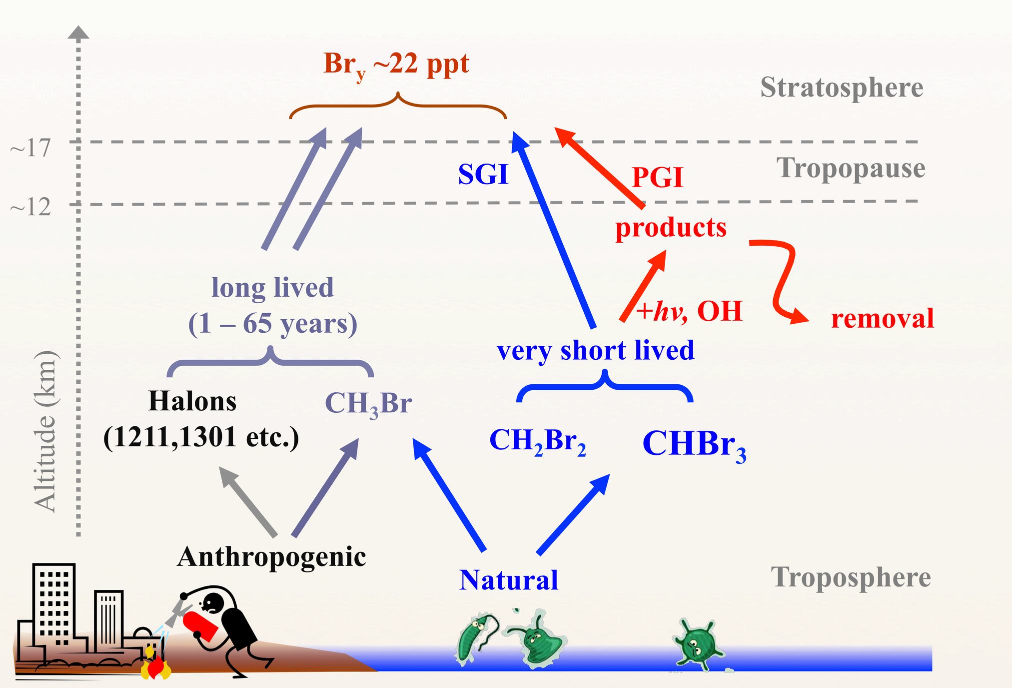
Email: dimitris.papanastasiou@noaa.gov
james.b.burkholder@noaa.gov

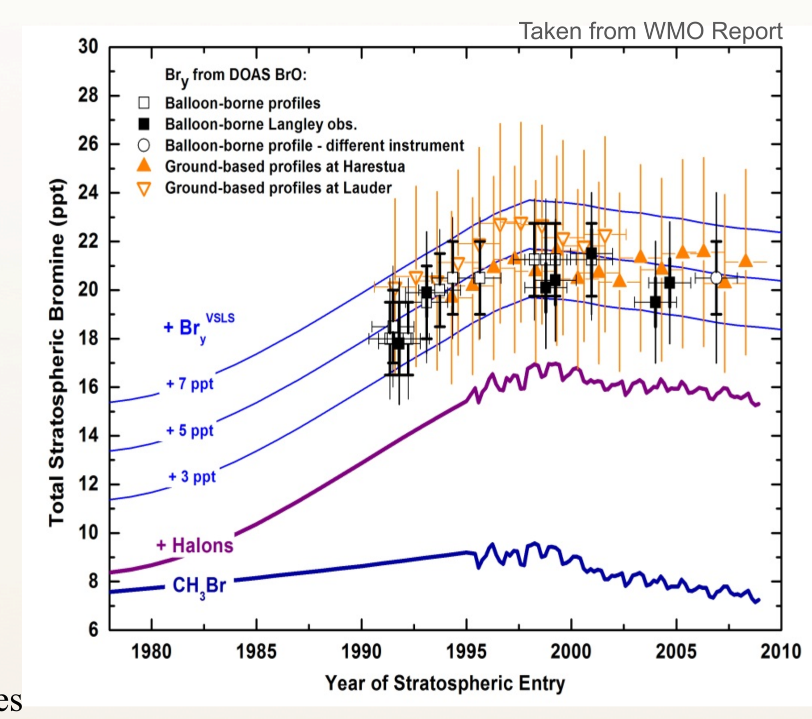
I. Introduction

Reactive Bromine (Br_y) in the Stratosphere

Bromine has a significant impact on stratospheric ozone through its participation in various catalytic ozone destruction cycles

Bromine is ~60 times more efficient in depleting ozone than chlorine



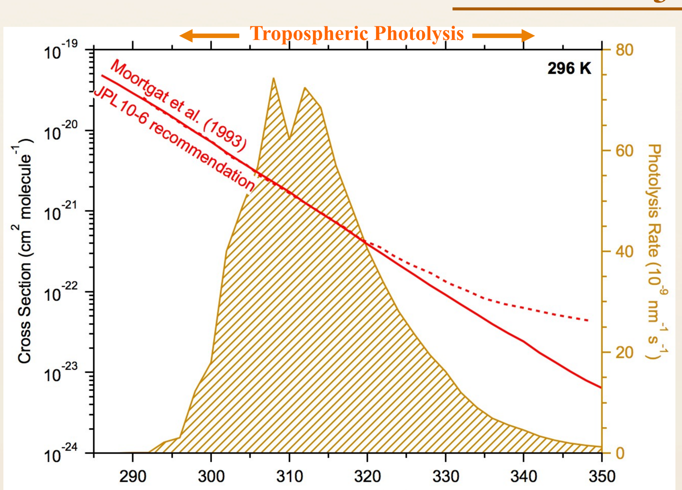


Bromine is transported to the stratosphere as either stable source gases (**source gas injection, SGI**) or product gases (**product gas injection, PGI**)

Fast convective transport in the tropics allows transfer of short-lived substances (e.g. CH_2Br_2 and $CHBr_3$) to the stratosphere

Very short-lived substances (VSLS), such as $CHBr_3$, make a significant, but currently poorly quantified, contribution to total stratospheric bromine.

$CHBr_3$, a very short lived substance



$CHBr_3$ info (*WMO; Hossaini et al.; Aschmann et al.*):
* Biogenic emissions
* one of the major VSLS
* Lifetime is short (~10s of days)
  - *UV photolysis is the primary loss process*

JPL 10-6 recommendation on $CHBr_3$ UV absorption spectrum:
* Based on the only available study of Moortgat et al. for λ>310 nm (*solid line*)
* Possible systematic errors associated with optical artifacts and impurities (*dashed line*)

Modeling the impact of $CHBr_3$ on stratospheric ozone requires an accurate knowledge of its atmospheric loss rates (e.g. photolysis)

Uncertainty in $CHBr_3$ absorption cross section data impacts calculated atmospheric photolysis rate, lifetime, and transport to the stratosphere

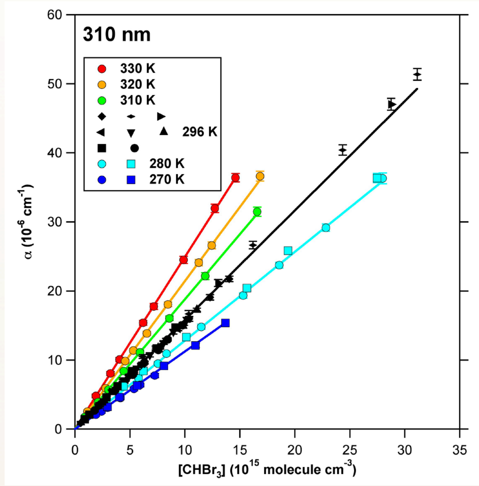
Objectives of this work

* Accurately quantify the $CHBr_3$ atmospheric photolysis rate
  - *via improved absolute UV cross sections measurements of $CHBr_3$*
  - *identify and account for sources of systematic errors*
* Estimate the total $CHBr_3$ gas-phase lifetime
  - *photolysis + OH reactive loss*
* Estimate the Ozone Depletion Potential (ODP) for $CHBr_3$
  - *using a semi-empirical method (Brioude et al.)*

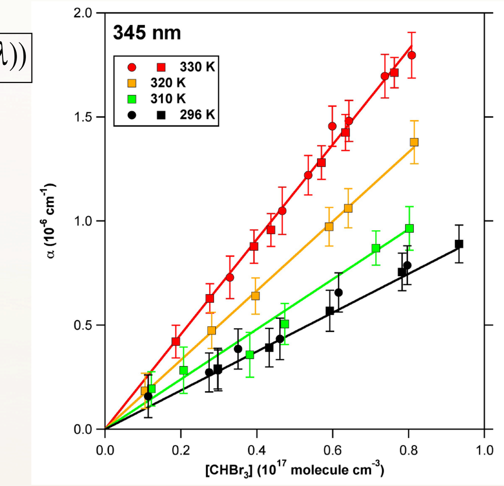
III. $CHBr_3$ UV Absorption Spectrum

Representative Data and Quality

Beer's law fits to experimental data at selected wavelengths and temperatures
Different symbols for each temperature represents variation of experimental conditions
(different samples, Br_2 scavenger, various flow and pressure conditions)

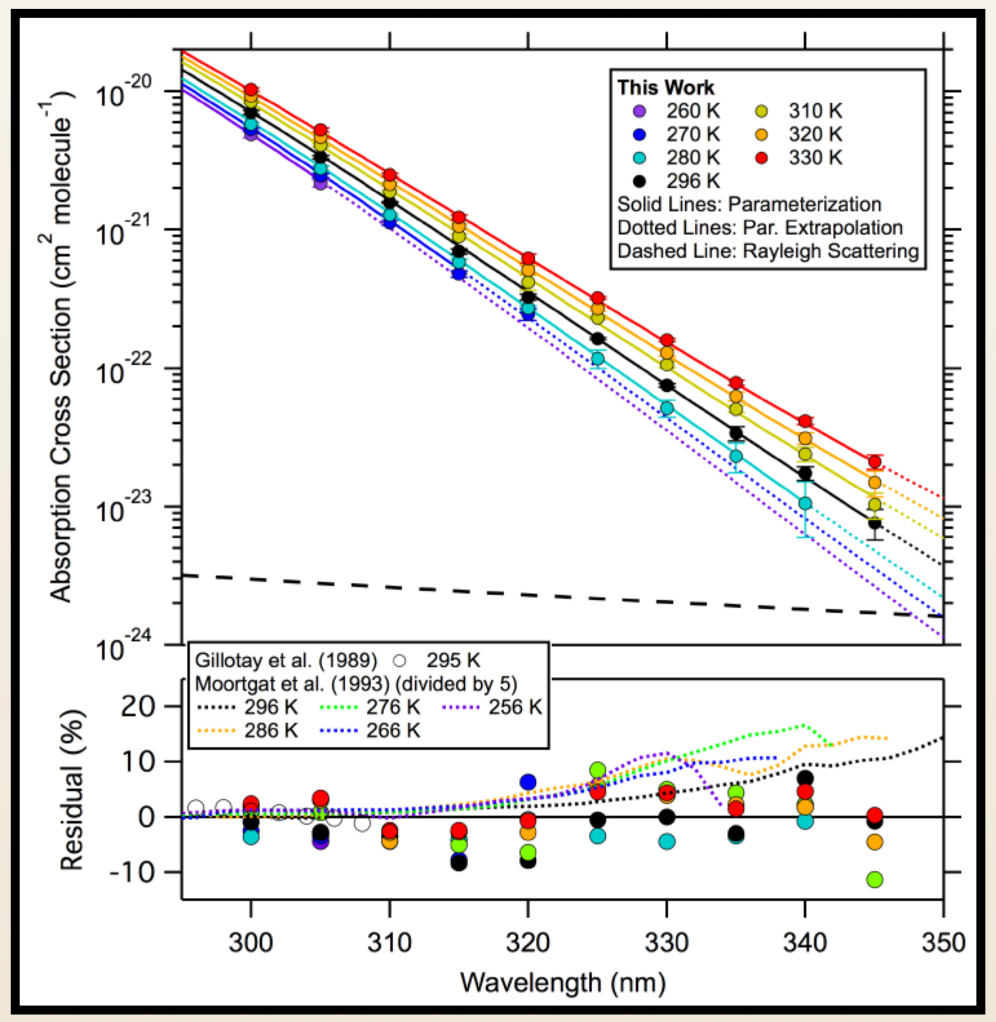


$$\alpha(\lambda) = [CHBr_3](\sigma(\lambda,T) + \sigma_R(\lambda))$$



* High reproducibility among experiments with different conditions
  - 2σ uncertainty (precision): ~3% at 300 nm and ~15% at 345 nm
  - uncertainty increases at lower temperatures

$CHBr_3$ Cross Sections and Comparison with Previous Studies



Negligible contribution (<0.5%) from impurities (Br_2, halocarbons etc.) in this wavelength range

Small corrections due to $CHBr_3$ Rayleigh scattering

Parameterization for use in atmospheric modeling reproduces experimental data points within ~5%

Excellent agreement (within 3%) with Gillotay et al. and Moortgat et al. for λ< 310 nm

Systematic deviation with Moortgat et al. at longer wavelengths and lower temperatures

The present work reduces the uncertainty in the $CHBr_3$ spectrum in the wavelength range most critical for atmospheric photolysis rate calculations

IV. $CHBr_3$ Photolysis Rates, Lifetimes and ODPs

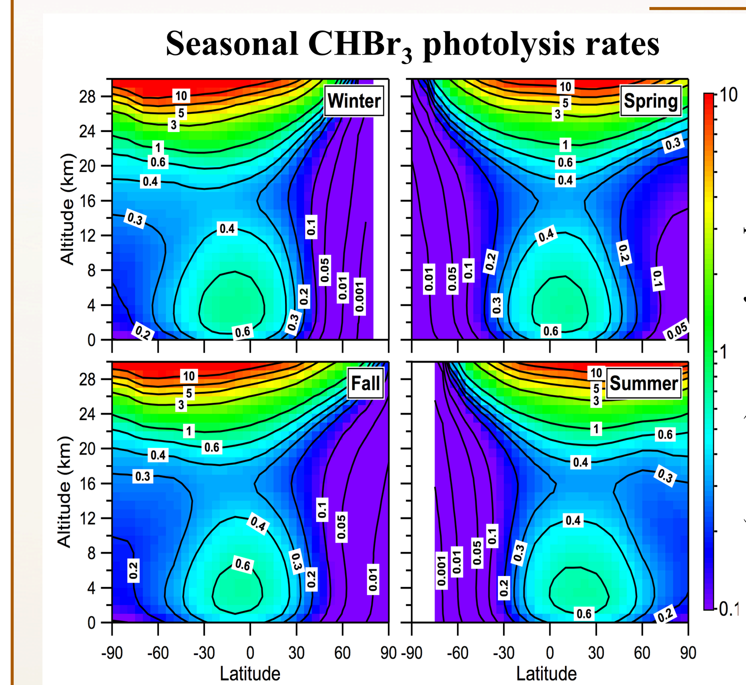
Atmospheric Photolysis Rate Calculation Details

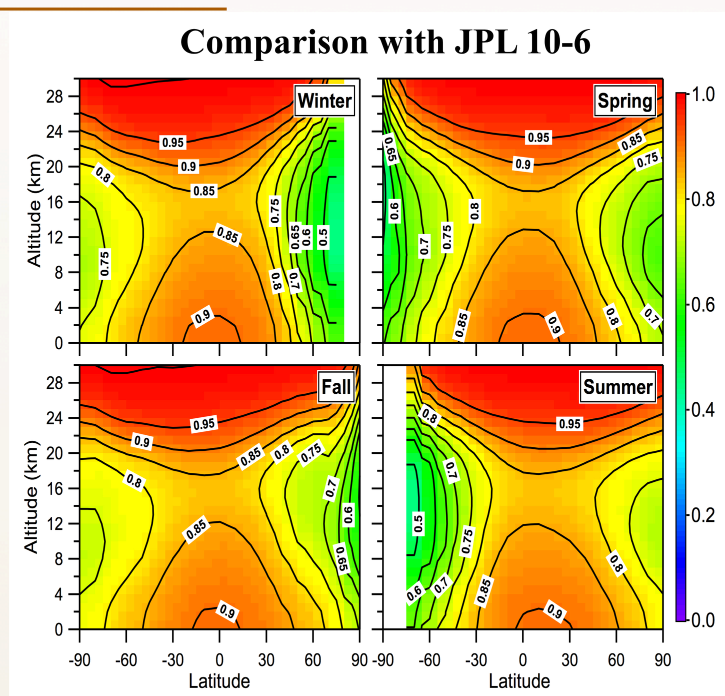
Photolysis Rate (s^{-1}):

$$J = \int \sigma(\lambda,T) \times \Phi(\lambda) \times F(\lambda,Z,SZA)\,d\lambda$$

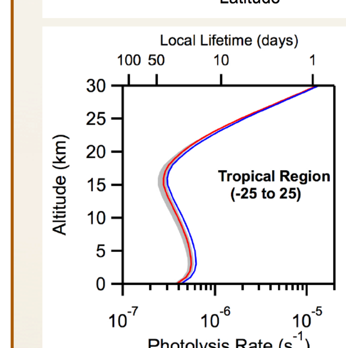
* Photolysis Flux (*F*) calculated using NCAR TUV (*Madronich and Floke*)
* Quantum Yield (*Φ*) assumed to be 1 (*Bayes et al.*)
* Ozone, temperature, and pressure climatology taken from FAST-J model (*Wild et al.*)

$CHBr_3$ Photolysis Rates





The present $CHBr_3$ spectrum lead to smaller photolysis rates (longer lifetimes)



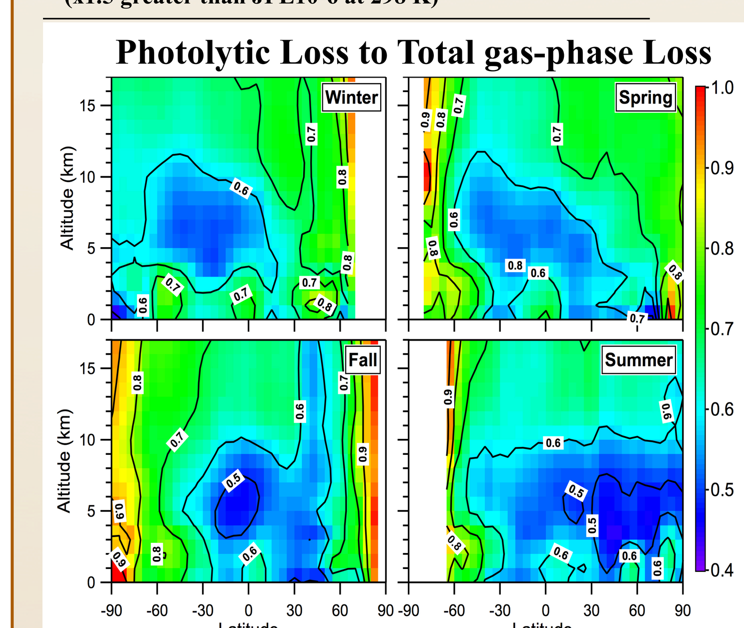
Tropical Region

* Critical wavelength range for photolysis in the Tropics: 95% of photolysis at λ < 335 nm
* Local tropospheric lifetimes: 17-38 days
* Weak local lifetime dependence on season (Summer and Winter shown)

In the lower altitude tropics, the photolysis rate is ~10 to 15% lower compare to JPL10-6 recommendation.

Relative Contribution of Atmospheric Loss Processes of $CHBr_3$

* OH radical climatology was taken from *Spivakovsky et al.*
* OH + $CHBr_3$ rate coefficient data was taken from *Orkin et al.* **(x1.5 greater than JPL10-6 at 298 K)**



*** Increased importance (by 15-20%) of OH loss compared to JPL10-6 recommendation**
*** Shift in product distribution from $CHBr_3$ loss processes**

$CHBr_3$ Lifetimes and ODPs

Calculated Tropical Total Lifetime (days)

Winter	13.6
Spring	13.4
Summer	14.3
Fall	13.0

* Short-lifetime
* Weak seasonal dependence
* Lifetimes ~10% greater than with JPL10-6

Ozone Depletion Potentials (ODPs)
Semi-empirical method of *Brioude et al.*

$CHBr_3$ Originating from the Indian sub-continent

Winter	0.08
Spring	0.26
Summer	0.54
Fall	0.17

* $CHBr_3$ is a potent ozone depleting substance *Particularly in the Spring and Summer seasons*
* Other regions of origin lead to much smaller ODPs

II. Experimental Details

Approach and Conditions

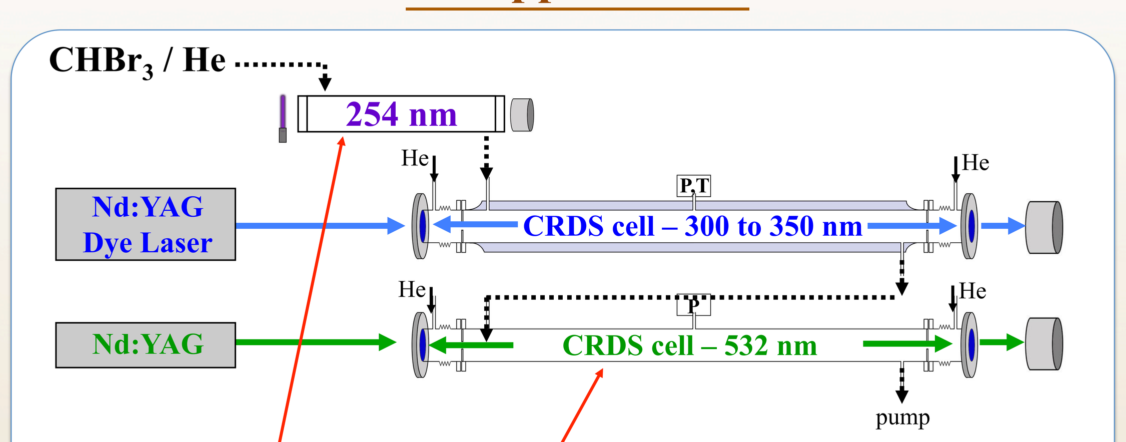
Measure the $CHBr_3$ weak absorption cross sections using the sensitive cavity ring-down spectroscopy (CRDS) technique

Identify and account for possible systematic errors (Rayleigh scattering, impurities) using CRDS (532 nm) and Fourier Transform Infrared Spectroscopy (FT-IR)

*** Atmospherically important wavelength range: 300 – 345 nm**

*** Temperature range: 260 – 330 K**
- limited by $CHBr_3$ vapor pressure and CRDS sensitivity
- high T included for more precise extrapolation of the dataset fit to lower temperature

Apparatus



$$\alpha(\lambda) = \frac{1}{c}\frac{d}{L_{abs}}\left(\frac{1}{\tau(\lambda)} - \frac{1}{\tau_0(\lambda)}\right) = [CHBr_3](\sigma(\lambda,\mathrm{T}) + \sigma_R(\lambda))$$

* τ(λ) and $\tau_0(\lambda)$ are the ring-down times with and without $CHBr_3$, respectively
* c = speed of light, d = cavity pathlength, L_{abs} = sample pathlength
* σ(λ,T) = absorption cross section
* $\sigma_R(\lambda)$ = Rayleigh scattering cross section

Methods and Materials

* **Online measurement of [$CHBr_3$] with 254 nm absorption** (cross section taken from *JPL10-6*)
* **$CHBr_3$ sample purity checks:**
  - Several samples used
  - Br_2 scavenger used (Cu turnings)
  - Br_2 impurity upper level measured with CRDS at 532 nm
  - Upper limits for commonly used stabilizers and halocarbons was established with FTIR
* **$CHBr_3$ Rayleigh scattering cross section measured at 532 nm. Scattering between 300 and 345 nm determined by $1/\lambda^4$ dependence**
* **Negligible loss of $CHBr_3$ through the flow system determined using different flow configurations**

V. Concluding Statement

$CHBr_3$ is a potent ozone-depleting substance, and the improved UV cross section data provided in this work combined with the recent OH kinetic data enable an improved estimate of its impact on stratospheric ozone – particularly in a changing climate.

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