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

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$CHBr_3$ (bromoform) is a short-lived atmospheric trace gas primarily of natural origin that represents a source of reactive bromine (Br_y; Br + BrO) in the troposphere as well as the stratosphere. The transport of short-lived brominated species, and their brominated degradation products, to the stratosphere is known to be particularly impactful to stratospheric ozone due to the high efficiency of ozone destruction cycles involving bromine. Evaluating the impact of $CHBr_3$ on stratospheric ozone requires not only a thorough understanding of its emissions, but also its atmospheric loss processes, which are primarily UV photolysis and reaction with the OH radical. The total global lifetime of $CHBr_3$ is $\sim$24 days and is mostly governed by its photolytic loss. Therefore, accurate $CHBr_3$ UV absorption cross section data for wavelengths (λ) in the actinic region, greater than 290 nm, are needed to calculate its photolysis loss rate.

Currently, there is a single study (*Moortgat et al., Springer-Verlag Berlin Heidelberg, 1993; Vol. 17*) that reports $CHBr_3$ UV absorption cross sections and their temperature dependence in a wavelength and temperature range applicable for atmospheric photolysis rate calculations. However, there are indications that the reported longer wavelength cross section data, in the Moortgrat et al. study, might be subject to systematic errors which possibly lead to erroneous $CHBr_3$ atmospheric photolysis rate calculations and a misleading picture of its impact on stratospheric ozone.

In this study, UV absorption cross sections, $\sigma(\lambda$,T), for $CHBr_3$ were measured at wavelengths between 300 and 345 nm at temperatures between 260 and 330 K using cavity ring-down spectroscopy. A thorough investigation of possible sources of systematic error in the measurements is presented. The present UV absorption cross sections at longer wavelength (>310 nm) are systematically lower compared to currently recommended values for use in atmospheric models, with the deviation being more pronounced as wavelength increases and temperature decreases. The source of this discrepancy is further discussed. A parameterization of the $CHBr_3$ UV spectrum for use in atmospheric models is developed and illustrative photolysis rate calculations are presented to highlight the impact of the revised $\sigma(\lambda$,T) values on its calculated local lifetimes. For instance, $CHBr_3$ atmospheric photolysis rate in the tropical region obtained with the present spectral data was found to be 10-15% lower (longer lifetime) than that obtained using the currently recommended values. Moreover, seasonally dependent ozone depletion potentials (ODPs) for $CHBr_3$ emitted in the Indian sub-continent were calculated using the semi-empirical relationship of Brioude et al. (*Brioude et al., Geophys. Res. Lett., 37, L19804, doi: 10.1029/2010GL044856, 2010*) to evaluate the impact of the present results on stratospheric ozone.

In conclusion, the present study reports improved UV absorption cross section data for the short-lived ozone depleting substance $CHBr_3$, which are a result of high quality measurements and a thorough investigation of possible sources of systematic error. The $CHBr_3$ UV cross section data, from this study, combined with OH kinetic data enables more accurate model predictions of stratospheric bromine loading and its impact on stratospheric ozone.