1. INTRODUCTION

Free tropospheric BrO and the occurrence of ‘bromine explosion’ events that lead to the total depletion of surface ozone are intriguing, though not well understood, tropospheric BrO phenomena (see Kreher et al. this proceedings 16.2). Obtaining vertical resolution from ground-based total column measurements allows quantification of tropospheric BrO.

Differential Optical Absorption Spectroscopy (DOAS) UV-Vis measurements have been made for BrO at Arrival Heights, Antarctica (77S, 166E). Observations are made using three different viewing geometries and the measurement ensemble is used in this study to improve our understanding of the vertical distribution of BrO in the southern polar atmosphere. Direct-sun and off-axis measuring modes provide sensitivity to tropospheric absorbers while the complementary zenith-sky mode is sensitive to stratospheric absorbers.

Long term zenith-sky and off-axis observations of BrO have been made (since 1995 and 1999 respectively) and these combined with a short campaign of direct-sun measurements in spring 2002 provide a comprehensive measurement study of BrO at this southern hemispheric polar site. A radiative transfer model is coupled with an optimal estimation retrieval algorithm to retrieve stratospheric and tropospheric columns for BrO. An investigative study of the measurements is performed to evaluate their information content and errors.

All three measuring modes are investigated for evidence of BrO explosion events. The following description outlines the retrieval method designed for direct-sun and zenith-sky observations. This retrieval method allows the vertical separation of BrO into its tropospheric and stratospheric components.

2. RADIATIVE TRANSFER AND RETRIEVAL ALGORITHM DETAILS

The direct-sun observing geometry is the simplest case in terms of understanding and modelling of the measurements. Light is assumed to have travelled a single path from the sun to the detector. Light scattered in the forward direction is indistinguishable from unscattered light. Only at high solar zenith angles (SZA) (>89°) where the signal intensity is low, does multiply scattered light become an issue.

The detector for the zenith-sky viewing geometry observes light that has been scattered from the zenith. The radiative transfer model used here assumes zenith observations are a result of a single scattering event. Due to Rayleigh and Mie scattering most of the light sampled by a zenith-viewing detector has been scattered down from the stratosphere (~15 km) and multiple scattering is not an important consideration (Perliski and Solomon, 1993).

The off-axis viewing geometry is always observing light that has traversed a long, diffuse, tropospheric path. The effects of multiple scattering must be taken into account to accurately model these measurements.

2.1 Differential Optical Absorption Spectroscopy (DOAS)

DOAS is used for all three observing modes giving a differential slant column density (DSCD) for some SZA:

\[ y_i = DSCD_i = -\frac{1}{\sigma(\lambda)} \ln \left( \frac{I_i(\lambda)}{I_{o_i}(\lambda)} \right) \]  

where \( I_i \) is the intensity that reaches the detector and \( I_{o_i} \) is the intensity at some reference time (or SZA). By taking the ratio of these two spectra, complications due to Fraunhofer, Rayleigh and Mie features are eliminated. Absorption cross-sections of species with sharp absorption features are fitted, and a DSCD for the species of interest is determined.

DSCDs are calculated using equation (1) in a radiative transfer model. The intensity is determined at the measurement SZA with all absorbers present \( (I_i) \) and excluding the absorber of interest \( (I_{o_i}) \) thus avoiding intensity-weighting approximations (Sarkissian et al., 1995).

2.2 Characterization of the measurements and profile retrieval

To evaluate the altitude information that measurements contain both individually and collectively concerning the atmospheric distribution of BrO, weighting functions (K) are determined. Weighting functions or the sensitivity of the measurements to changes in the atmospheric profile of BrO are given.
\[
K = \frac{\partial y}{\partial x} \quad (2)
\]

where \( x \) is the true profile. Once \( K \) is evaluated, an appropriate error covariance for the measurements \( (S_x) \), combined with an estimate of the initial \( \text{BrO} \) profile (the \textit{a priori} \( x_a \)) and its associated covariance \( (S_{x_a}) \) allows inversion of the measurements to provide altitude information about \( \text{BrO} \) (\( \hat{x} \) - the retrieved state). Inversion of the measurements is performed using optimal estimation (Rodgers, 2000) for a linear case (such is the case with \( \text{BrO} \) being a weak absorber and \( K \) being independent of \( x \)):

\[
\hat{x} = x_a + S_xK^T(KS_xK^T + S_{x_a})^{-1}(y - Kx_a) \quad (3)
\]

The weighting functions for the direct-sun viewing geometry show these measurements to be most sensitive to tropospheric changes in the \( \text{BrO} \) profile. In contrast zenith-viewing observations show sensitivity to the stratosphere. Combining these two sets of complementary measurements in a formal retrieval allows tropospheric and stratospheric absorber separation.

The measurements can be characterized by the degrees of freedom and information content in the retrieval. The degrees of freedom describe the number of useful independent quantities that can be determined from a set of measurements and are evaluated from the trace of the averaging kernel matrix (\( A \)):

\[
A = \frac{dx}{dx} = G_yK = (K^T S_e^{-1}K + S_{x_a}^{-1})^{-1}K^T S_e^{-1}K \quad (4)
\]

Information content (\( H \)) of the measurements is qualitatively the factor by which knowledge is improved by making the measurement and is given

\[
H = \frac{1}{2} \ln |I_n - A| \quad (5)
\]

2.3 Diurnally varying species

A radical species such as \( \text{BrO} \) has a further complicating issue in retrieving profile information. The profile of \( \text{BrO} \) changes over the measurement period as displayed in figure 1. To treat this accurately, a profile set describing the diurnal variation is retrieved, instead of just a single profile.

3. SUMMARY

The retrieval technique described here is used to interpret the DSCD measurements made at Arrival Heights in terms of their altitude information. By taking advantage of the complementary sensitivities of the different sampling geometries, stratospheric and tropospheric absorber separation is possible. This is essential for the understanding and quantification of the unusual tropospheric \( \text{BrO} \) phenomena typical of springtime polar atmospheres.

The DSCD measurement ensemble of direct-sun, zenith-sky and off-axis viewing geometries are further investigated using ancillary data such as ozone measurements and meteorological data. Such a complete data record for Arrival Heights enables us to perform a comprehensive investigation.

4. REFERENCES

