Chapter 1

Introduction

The discovery of the ozone hole by Farman et al. [1985] may have shown more clearly than ever before to what extent mankind can influence environmental conditions to the detriment of (human) live on this planet. At that time total atmospheric ozone above the Antarctic during spring was found to have decreased to below 200 Dobson Units[1], i.e. about 70 % of the values observed in the years before. In the following years springtime ozone columns fell even below 100 DU. This observation was very disturbing because the ozone layer protects life on Earth against harmful ultraviolet radiation of the sun.

A slight decrease in the stratospheric ozone concentration was expected after Molina and Rowland [1974] and Stolarski and Cicerone [1974] had shown that atmospheric chlorine compounds could engage catalytic ozone destruction cycles. They predicted a global ozone reduction of 10-20% during the next 50-100 years because of the anthropogenic emissions of halogen containing compounds like CFCs (chlorofluorocarbons) and halons (bromine containing fully halogenated organic compounds) into the atmosphere. With respect to these predictions the observations of Farman et al. were totally unexpected.

One year later, Solomon et al. [1986] suggested that chlorine compounds might react on the surfaces of polar stratospheric clouds (PSCs) which occur at the low temperatures during polar night. And McElroy et al. [1986] found additional ozone destruction cycles involving the active forms of both, chlorine <u>and</u> bromine. These theories were confirmed by many studies in the following years, thus in particular demonstrating the important role of halogen species for stratospheric chemistry.

In the late 1980s the puzzle of atmospheric halogen chemistry was extended to the troposphere: It turned out that also in the planetary boundary layer reactive halogen compounds are involved in catalytic ozone destruction during Arctic spring [Barrie et al., 1988]. And, very recently, indications for the presence of reactive bromine and probably chlorine compounds also in the free troposphere were found [Friess et al., 1999; McElroy et al., 1999].
Thus, halogen compounds can now be expected to have a large influence to the <u>whole</u> atmosphere.
Today, still many questions regarding atmospheric halogen chemistry remain open:

- What is the exact budget and partitioning of halogen compounds in the stratosphere and in the troposphere ?
- Will ozone destruction similar to the ozone hole occur also in the northern hemisphere?
- What is the cause of stratospheric ozone destruction at mid latitudes ?
- How does the possible presence of reactive halogen compounds in the free troposphere change the current picture of tropospheric chemistry?
- What are the release mechanisms for reactive halogen compounds in the troposphere?

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[1] One Dobson Unit (DU) corresponds to an O_3 column of 0.01 mm for normal conditions.

The active forms of chlorine and bromine, which take part in the ozone destruction cycles, are ClO (chlorine oxide) and BrO (bromine oxide). Chlorine dioxide (OClO) is (only) formed by the reaction of BrO and ClO and hence can serve as an indicator for BrO and ClO. Since 1986 many spectroscopic observations of BrO and OClO were performed from balloons, aircrafts and from the ground. These measurements contributed to much of our current understanding of halogen chemistry of the atmosphere. However they suffer from several important restrictions

• Ground based measurements can only provide time series of the OClO and BrO absorptions for specific locations which are often situated at the edge of the polar vortex (like e.g. Kiruna). Thus these time series can provide data related to 'ozone hole chemistry' only for days when the vortex is above the measuring site. For Kiruna (67.9°N, 21.1°E) this is the case for only about 50% of the observations.

• Comparisons for different locations are difficult. Since the atmospheric OClO and BrO absorptions are very weak (typical optical densities are only a few times 10^{-3}) relatively large statistic but also <u>systematic</u> errors result (see section 4.3.8). Thus it is difficult to perform a comparison of OClO and BrO data derived from different instruments at different locations, e.g. in both hemispheres.

• No true total column densities are measured. From spectroscopic measurements of atmospheric OClO and BrO usually the <u>difference</u> of the absorption between two spectra, one at low and one at high sun is determined. In particular during polar winter/spring when stratospheric ozone destruction takes place, observations of atmospheric OClO and BrO are in particular important. However, for measurements at high latitudes during winter the daily maximum elevation of the sun is rather low, leading to large uncertainties especially during this period.

In April 1995 the Global Ozone Monitoring Experiment (GOME) aboard the European research satellite ERS-2 was launched. Since then GOME has been continuously measuring the UV/vis radiation of the sun light which is reflected on the Earth's surface or scattered by the atmosphere. While the GOME instrument was first designed to measure the atmospheric ozone content, the spectra also contain the absorptions of other atmospheric trace species like NO_2, BrO, OClO, O_4, and HCHO. Since the GOME measurements cover (almost) the whole globe they are not restricted by the first two shortcomings mentioned above. In addition, GOME can measure spectra of the direct sun light (without the absorptions of the Earth's atmosphere); thus absolute atmospheric column densities can be retrieved from GOME observations.

In this PhD thesis algorithms for the analysis of BrO and OClO from GOME spectra were developed. Thus it was possible for the first time to measure the temporal and spatial evolution of these species which are very important with respect to ozone chemistry on a global scale. In particular for the BrO measurements it was possible to separate the contributions from the boundary layer, the free troposphere and the stratosphere.
The results for both species were compared to balloon and ground based measurements and a good agreement was found.

The outline of the work is as follows:

First an overview of the role of halogen species for the atmospheric ozone chemistry is given. The GOME instrument is described in chapter 3; chapter 4 introduces the DOAS method which was used for the analysis of the GOME spectra. The modelling of the radiative transport in the atmosphere necessary for the interpretation of the satellite data is described in chapter 5. In chapter 6 and 7 the results for BrO and OClO are presented, respectively. The last chapter summarises the results and gives an outlook.