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> Put forward by M.Sc. - Physics: Cristina Prados-Román Born in: Madrid, Spain

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# Aircraft-borne spectroscopic limb measurements of trace gases absorbing in the UV-A spectral range.

Investigations of bromine monoxide in the Arctic troposphere.



Referees: Prof. Dr. Klaus Pfeilsticker Prof. Dr. Ulrich Platt

### Aircraft-borne spectroscopic limb measurements of trace gases absorbing in the UV-A spectral range. Investigations of bromine monoxide in the Arctic troposphere.

Reactive halogen species (i.e., RHS=X, XO, X<sub>2</sub>, XY, OXO, HOX, XONO<sub>2</sub>, XNO<sub>2</sub>, with X,Y being I, Br and Cl) are known to be key compounds for the oxidation capacity of the troposphere, affecting the lifetime of relevant species such as  $O_3$ ,  $HO_x$ ,  $NO_x$ , hydrocarbons, dimethylsulfide and gaseous elementary mercury. Furthermore, recent observations link iodine species to the formation of new aerosol particles. This work aims at the characterization of the abundance of BrO in the Arctic troposphere during the spring season, when the auto-catalytic release of bromine species from sea ice related halides is known to cause tropospheric Ozone Depletion Events (ODEs).

A novel limb scanning mini-DOAS spectrometer for the detection of UV/vis absorbing radicals (e.g.,  $O_3$ , BrO, IO) was deployed on the DLR-Falcon (Deutsches Zentrum für Luft- und Raumfahrt) aircraft and tested during a field campaign that took place at Svalbard (78°N) in spring 2007. Herein, a new algorithm for inferring concentration vertical profiles of tropospheric trace gases from aircraft-borne DOAS limb observations is presented, characterized and validated through the profile retrieval of the UV-A absorber  $O_4$ . The method is then applied for retrieving tropospheric vertical profiles of BrO during the polar campaign.

For deployments during ODEs, the retrieved BrO vertical profiles consistently indicate high BrO mixing ratios (~ 15 pptv) within the boundary layer, low BrO mixing ratios ( $\leq 1.5$  pptv) in the free troposphere, occasionally enhanced BrO mixing ratios in the upper troposphere (~ 1.5 pptv), and increasing BrO mixing ratios with altitude in the lowermost stratosphere. These findings are well in agreement with satellite and balloon-borne soundings of total and partial BrO atmospheric column densities. Moreover, the capabilities of the aircraft-borne measurements are further exploited by analyzing the sources, photochemistry and transport processes of BrO in the boundary layer above the sea ice.

# Flugzeuggestützte Streulicht-Spektroskopie von UV-A absorbierenden Spurengasen. Erforschung von Brommonoxid in der arktischen Troposphäre.

Reaktive Halogenverbindungen (RHS=X, XO, X<sub>2</sub>, XY, OXO, HOX, XONO<sub>2</sub>, XNO<sub>2</sub>, mit X,Y entweder I, Br oder Cl) haben eine Schlüsselfunktion für die Oxidationskapazität der Troposphäre, insbesondere indem sie die Lebensdauer wichtiger Schadstoffe wie O<sub>3</sub>, HO<sub>x</sub>, NO<sub>x</sub>, Kohlenwasserstoffe, Dimethylsulfid and gasförmiges, elementares Quecksilber beeinflussen. Des weiteren, weisen neuere Beobachtungen auf eine wichtige Rolle von Iodverbindungen bei der Bildung von Aerosolpartikeln hin. Ziel dieser Arbeit ist es, die Verteilung von BrO in der arktischen Troposphäre zu charakterisieren, wenn im Frühling Bromverbindungen auto-katalytisch aus Haliden über dem Meereis freigesetzt werden und es dadurch zu troposphärischem Ozonabbau (Ozone Depletion Events - ODEs) kommt.

Ein neuartiger mini-DOAS Spektrometer wurde auf dem Falcon-Flugzeug des DLR (Deutsches Zentrum für Luft- und Raumfahrt) eingesetzt und während einer Messkampagne bei Svalbard (78°N) im Frühling 2007 getestet. Der Spektrometer ist auf den Nachweis von Radikalen ausgelegt, die im UV und sichtbaren Spektralbereich absorbieren, und kann Streulichtbeobachtungen in verschiedenen Sichtgeometrien durchführen. In dieser Arbeit wird ein neuer

Algorithmus zur Bestimmung von vertikalen Konzentrationsprofilen troposphärischer Spurengase aus flugzeuggestützte DOAS Streulichtbeobachtungen vorgeschlagen, charakterisiert und mittels der Profilbestimmung von  $O_4$  validiert. Anschließend wird die Methode zur Auswertung troposphärischer BrO-Profile während der Kampagne am Pol verwendet.

Bei Auftreten von ODEs, weisen die BrO Vertikalprofile durchgehend hohe BrO Konzentrationen (~ 15 pptv) in der planetaren Grenzschicht, niedrige BrO Konzentrationen ( $\leq$  1.5 pptv) in der freien Troposphäre, gelegentlich erhöhte BrO Konzentrationen in der oberen Troposphäre (~ 1.5 pptv) sowie mit der Höhe ansteigende BrO Konzentrationen in der unteren Stratosphäre auf. Diese Befunde werden von Satelliten- und Ballonmessungen der BrO Gesamt- and Teilsäulendichte bestätigt. Weiterhin werden die Möglichkeiten der flugzeuggestützten Messungen zur Erforschung von Brom-Quellen sowie der relevanten Photochemie und Transportprozesse über dem Meereis in der planetaren Grenzschicht erkundet.

# Contents

1	Intr	roduction						
<b>2</b>	Phy	sics of radiation and molecular absorption	5					
	2.1	Interaction of electromagnetic radiation with matter	5					
	2.2	Solar radiation and the Earth-atmosphere system	8					
	2.3	Radiative transfer in the Earth's atmosphere	10					
		2.3.1 Scattering of light	11					
		2.3.2 Absorption and emission of light	17					
		2.3.3 Radiative transfer equation	19					
3	Atn	Atmospheric structure and dynamics 2						
	3.1	Vertical structure	21					
	3.2	Atmospheric circulation	24					
		3.2.1 Tropospheric circulation	24					
		3.2.2 Stratospheric circulation	26					
		3.2.3 Stability and vertical transport	28					
4	Atmospheric chemistry 3							
	4.1	Ozone photochemistry	37					
	4.2	Hydrogen oxide radicals	41					
	4.3	Nitrogen oxide radicals	43					
	4.4	Halogen oxide radicals	47					
		4.4.1 Reactive halogen species in the troposphere	49					
		4.4.2 Reactive halogen species in the stratosphere	60					
	4.5	Aerosol particles and heterogeneous chemistry	65					
5	The	Arctic environment	71					
0	51	Defining the Arctic	71					
	0.1	5.1.1 Geographical extension	71					
		5.1.2 The Arctic Ocean	73					
		5.1.2 The filtene Ocean	73					
		5.1.5 Dealee	80					
	59	Helogen species in the Arctic etmosphere	81					
	0.4	5.2.1 Polar Stratognheric Clouds and the Ozona Hole	81					
		5.2.1 Forai Stratospheric Clouds and the Ozone Hole	84					
	59	Arotic and Climate Change	00					
	0.0		92					

CONTENTS
----------

6	<b>Ren</b> 6.1	ote sensing of the atmosphere Basics of the optical absorption spectroscopy	<b>97</b> 97							
	6.2	Differential Optical Absorption Spectroscopy in the UV/vis	99 99							
	6.3	6.2.2 Experimental DOAS measurements setups	.08 .10							
7	Airo	raft deployment of the mini-DOAS instrument	15							
	7.1	Description of the mini-DOAS instrument	15							
	7.2	Deployment on the DLR-Falcon aircraft	18							
	7.3	Aircraft-borne limb DOAS measurements in the Arctic	20							
		7.3.1 The ASTAR 2007 campaign	20							
		7.3.2 The GRACE 2008 campaign	.21							
8	Ret	ieval of tropospheric trace gas abundances 1	29							
	8.1	Spectral retrieval	.30							
		8.1.1 BrO spectral retrieval	32							
		8.1.2 OCIO spectral retrieval	37							
		8.1.3 $O_4$ spectral retrieval	38							
	8.2	Tropospheric vertical profile retrieval	40							
	0	8.2.1 Theory	40							
		8.2.2 Application 1	43							
		8.2.3       Validation       1	51							
9	Bromine monoxide in the Arctic troposphere									
0	9.1	Tropospheric vertical profile of BrO volume mixing ratios	56							
	0.1	9.1.1 BrO ymr vertical profile in context with other trace gases	62							
		9.1.2 Satellite validation	65							
	92	Sources photochemistry and transport processes	67							
	0.2	9.21 BrO and the dynamical tropopause 1	60							
		9.2.2 BrO in the polar marine boundary layer	.73							
10	Con	clusion 1	93							
Ρı	ublica	tions	99							
			00							
Li	st of	Figures 2	04							
List of Tables										
Bibliography										
Ac	Acknowledgements									

ii

# Chapter 1

# Introduction

A novel limb scanning mini-DOAS spectrometer measuring scattered skylight was deployed on the DLR-Falcon (Deutsches Zentrum für Luft- und Raumfahrt) aircraft for the detection of UV/vis absorbing radicals (e.g.,  $O_3$ , BrO, IO, HNO<sub>2</sub>). The instrument was tested during two campaigns based in the Arctic region within the framework of the International Polar Year 2007/08, and as part of the POLARCAT project ("Polar Study using Aircraft, Remote Sensing, Surface Measurements and Models, of Climate, Chemistry, Aerosols, and Transport"). Main objectives during these campaigns were to examine the capabilities of the mini-DOAS aircraft-borne instrument, and to perform spectral and vertical profile retrievals of tropospheric trace gases.

The Differential Optical Absorption Spectroscopy (DOAS) is a well known and established atmospheric measurement technique (Platt and Stutz, 2008). In many applications using scattered skylight, the main challenge of the remote sensing DOAS method consists in retrieving trace gas concentrations from the measured differential Slant Column Densities (dSCDs). Trace gas concentrations are inferred by consecutively probing the air masses at different viewing geometries, and a subsequent mathematical inversion of the whole set of observations (e.g., Rodgers, 2000). In the best case scenario, the sampling is arranged so that the amount of pieces of independent information on the multi-dimensional (spatial and temporal) distribution of the targeted species is maximized. In practice however, the degrees of freedom are often limited since the changing viewing geometries are predetermined by movements of the light source (e.g., by celestial light sources), by displacements of the instrument platform (ships, aircrafts, balloons, satellites, etc), by the change of the viewing direction of the light receiving telescope, or by a combination of all of the above. Gathering the information often requires sampling over a large spatial or temporal domain of the atmosphere, in which the radiative transfer (RT) may change considerably as well. The need of dealing with these observational limitations correctly, and of accounting for the atmospheric RT of each individual measurement properly, defines a rather complicated (and in general ill-posed) mathematical inversion problem. As solutions largely depend on the individual kind of observations, different strategies have been developed to solve these ill-posed inversion problems (e.g., *Rodgers*, 2000). This work reports on aircraftborne observations of important and rare trace gases absorbing in the UV-A spectral range (e.g., tropospheric BrO), monitored in a heterogeneously scattering atmosphere (the Arctic troposphere). Herein, a dedicated method for the profile retrieval of trace gases constrained by means of measured relative radiances is introduced and validated. In a similar way as in the recently published work of *Vlemmix et al.* (2010), the observed (relative) radiances are used to describe the scattering processes in the atmosphere during the time of the measurements. Unlike *Vlemmix et al.* (2010), here not just the total aerosol optical thickness is inferred, but vertical profiles of the extinction coefficient ( $\mathcal{E}_{\mathcal{M}}$ ) of aerosol and cloud particles (from now on referred to as 'aerosols'). The targeted trace gas profile inversion, constrained by the retrieved aerosol  $\mathcal{E}_{\mathcal{M}}$ , is then addressed with a regularization approach using no a priori knowledge of its vertical distribution (e.g., *Phillips*, 1962; *Rodgers*, 2000).

The validity of the novel algorithm and the capabilities of the instrument are demonstrated for deployments of the mini-DOAS instrument on the DLR-Falcon aircraft during the ASTAR 2007 campaign ("Arctic Study of Tropospheric Aerosol, Clouds and Radiation"). The campaign was based on Spitsbergen (78°N, 18°E) and took place during March and April 2007. During this field campaign, target trace gases to be detected from the boundary layer (BL) up to the upper troposphere/lowermost stratosphere (UT/LS) with the mini-DOAS instrument were  $O_3$ , NO<sub>2</sub>, BrO, OCIO, IO, OIO, HONO, C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>O, H<sub>2</sub>O and O<sub>4</sub>.

Since recent studies point out the relevance of halogens for the tropospheric photochemistry (e.g., Von Glasow and Crutzen, 2007), this work focuses on the detection and retrieval of bromine monoxide (BrO). Indeed, reactive halogen species (i.e., RHS=X, XO, X<sub>2</sub>, XY, OXO, HOX, XONO<sub>2</sub>, XNO<sub>2</sub>, with X,Y as I, Br and Cl) are known to be key species, e.g., for the oxidation capacity of the troposphere and for the lifetime limitation of other species such us  $O_3$ ,  $HO_x$ ,  $NO_x$ , hydrocarbons and dimethylsulfide. RHS are also known to be involved in new particle formation (by iodine compounds, e.g., O'Dowd et al., ). Moreover, RHS are related to atmospheric mercury depletion events that eventually yield scavenge of Hg by snow and particles, and deposition of toxic mercury to the polar ecosystems (e.g., Steffen et al., 2008). Also characteristic (but not unique) of polar regions are the ozone depletion events (ODEs) occurring in the low troposphere during springtime. These ODEs are linked to halogen activation in auto-catalytic cycles involving salt halides aerosols (e.g., Br<sup>-</sup>), and take place over areas covered by first-year sea ice, i.e., sea ice lasting less than one melting season (e.g., SciAMACHY, and references therein). While the horizontal extent of the BrO associated with this type of sea ice is fairly well captured by total column satellite measurements (e.g., SCIAMACHY,

GOME, OMI), a detailed tropospheric distribution profile of bromine monoxide volume mixing ratios (vmr) remains uncertain. This lack of tropospheric BrO vertical profile climatology during the polar spring triggered the development of a the profile retrieval method presented herein.

This work is structured in three main parts. Chapters 2 to 5 present the general concepts regarding the physics of radiation, the molecular absorption, and the radiative transfer in the Earth's atmosphere. Moreover, after describing its structure and dynamics, the atmospheric chemistry is addressed focusing on the ozone loss catalytic reactions involving the radicals  $HO_x$  $(H+OH+HO_2)$ ,  $NO_x$   $(NO+NO_2)$  and RHS in the stratosphere and in the troposphere. Since this work reports on BrO measurements gathered from the boundary layer up to the UT/LS, the tropospheric and stratospheric sources, pathways and sinks of the RHS are treated in detail. Furthermore, Chap. 5 introduces the Arctic environment in order to characterize the presence of RHS in that unique region.

Once the context of this work has been set in those chapters, the methodology of the atmospheric remote sensing technique used is given. Chapter 6 provides the theoretical background for the retrieval of trace gas differential Slant Column Densities (dSCDs) with the Differential Optical Absorption Spectroscopy (DOAS method), and the concept of the radiative transfer modeling needed for inferring trace gas volume mixing ratios from the measured dSCDs. In addition, Chap. 7 summarizes the technical details of the mini-DOAS instrument used in this work, and its deployment on the DLR-Falcon aircraft during the ASTAR 2007 campaign (main core of this work), and the GRACE 2008 campaign ("Greenland Aerosol and Chemistry Experiment", summer 2008). In Chap. 8, the DOAS method is applied for the spectral retrieval of BrO,  $O_4$ and OCIO in the UV-A spectral range. Moreover, in that chapter the novel method dedicated for the vmr vertical profile retrieval of trace gases constrained by means of measured relative radiances is introduced and validated. The method comprises the characterization of scattering events present in the atmosphere via a non-linear inversion of the vertical profile of the  $\mathcal{E}_{\mathcal{M}}$ , and the regularization of the targeted trace gas vertical profile. Hence, Sect. 8.2 addresses the rigor of the assumptions needed for the RT modeling, the validation and sensitivity of the method to retrieve  $\mathcal{E}_{\mathcal{M}}$  vertical profiles, and the robustness and sensitivity of the profile regularization of tropospheric trace gases, tested with the absorber of known vertical distribution in the troposphere  $O_4$  ( $O_2$ - $O_2$  collisional dimer, e.g., *Pfeilsticker et al.*, 2001).

The above described retrieval algorithm is applied in Chap. 9 for inferring BrO abundances in the Arctic troposphere. Section 9.1 presents the retrieved BrO vmr vertical profiles, and compares them to other measured trace gases ( $O_3$ , CO) and to total BrO column densities measured by satellite. Once an overview of the retrieved BrO abundances in the Arctic troposphere is given, the capabilities of the mini-DOAS measurements are further exploited by characterizing the

bromine monoxide sources, photochemistry and transport processes. Section 9.2.1 analyzes the measured BrO in the UT/LS region toward other traces gases (O<sub>3</sub>, CO), aiming at delimiting the vertical extent of the UT/LS exchange layer. Moreover, Sect. 9.2.2 provides a 2-D description of the BrO and O<sub>3</sub> abundances and lifetimes in the BL above the sea ice, addressing the role of heterogeneous chemistry and the sea ice properties in an ODE. Finally, Chap. 10 summarizes and concludes this work.

# Chapter 2

# Physics of radiation and molecular absorption

Until the 19<sup>th</sup> century aether was believed to be the omnipresent substance responsible for the transport of light in the form of wave vibrations. Only after Max Planck set the basis of the quantum theory and Albert Einstein explained the photoelectric effect in the early 1900's, scientists embraced the nature of light as a wave-particle duality. With that novel understanding, a new world opened for the study of the behavior of light (i.e., electromagnetic radiation). This section introduces basic concepts of molecular physics and the interaction of light with matter. Those concepts are then related to the interaction of solar radiation with the Earth's atmosphere, and to the processes involved in the propagation of electromagnetic radiation.

## 2.1 Interaction of electromagnetic radiation with matter

As a time independent quantum-mechanical system, any matter or physical substance is characterized by its *wave function*  $\Psi$ , and its behavior within an electromagnetic field is given by the Schrödinger's equation

$$E\Psi = H\Psi \tag{2.1}$$

where H is the Hamiltonian operator consisting of a kinetic energy operator and the potential energy V:

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V. \tag{2.2}$$

Equation (2.1) can only be solved numerically for certain values of energy E (*Eigenvalues*) and, thus, the interaction of electromagnetic radiation with atoms or molecules yields transitions at

Table 2.1: Electromagnetic spectral ranges and associated phenomena observed at a molecular level.

Region	Microwave	Far infrared	Infrared	Ultraviolet/visible
	MW	FIR	IR	UV/vis
Energy/eV	$4 \cdot 10^{-6} - 4 \cdot 10^{-4}$	$4 \cdot 10^{-4} - 4 \cdot 10^{-2}$	$4 \cdot 10^{-2} - 1.8$	1.8 - 6.2
Wavelength/m	$0.3 - 3 \cdot 10^{-3}$	$3 \cdot 10^{-3} - 3 \cdot 10^{-5}$	$3 \cdot 10^{-5} - 7 \cdot 10^{-7}$	$7 \cdot 10^{-7} - 2 \cdot 10^{-7}$
Observed	Rotation of	Rotation of	Vibration of	Electronic
phenomenon	polyatomic molecules	small molecules	bonds	transitions

different (allowed) energy levels  $E_n$ . In general, a molecule is an ensemble of several nuclei and electrons and, by means of the Born-Oppenheimer approximation, its Eigenfunction  $\Psi$  can be divided into an electronic and a nuclear component,  $\Psi_E$  and  $\Psi_N$  resp., where  $\Psi_N$  comprises rotational and vibrational movements (for details on molecular physics refer to e.g. *Herzberg*, 1950 and *McQuarrie and Simon*, 1997). Hence, as summarized in Table 2.1 and described below, depending on the energy of the incoming radiation, some of the phenomena observed when light interacts with molecules are (1) rotational, (2) vibrational and (3) electronic transitions.

#### 1. Rotational transitions

Molecules exposed to an electromagnetic field of about  $10^{-3}-10^{-5}$  eV experience rotational transitions characterized by its angular momentum  $\vec{J}$  and quantum number J. In general, the thermal kinetic energy of most molecules at room temperature is enough to trigger these kind of transitions. The allowed rotational energy levels in a molecule under such an electromagnetic field are  $E_j = BJ(J+1)$ , where B is the rotational constant depending on the moment of inertia  $\Theta$  about the center of mass ( $B = \hbar^2/2\Theta$ ). These sort of transitions comprise different branches depending on the angular momentum difference between the initial and final state.  $\Delta J = -2, -1, 0, +1, +2$  are denoted as the O, P, Q, R and Sbranches, resp., where the Q-branch is associated with instantaneous electronic transitions (see below).

#### 2. Vibrational transitions

Under rather more energetic electromagnetic fields, molecular bonds suffer vibrations. These type of oscillations are described by their vibrational quantum number (v) and the zero-point energy  $(\frac{1}{2}\hbar\omega_0)$ . Hence, the vibrational energy levels of molecules under IR radiation are quantized as  $E_v = (v + \frac{1}{2})\hbar\omega_0$ . Often molecules experience both vibrational and rotational transitions (*ro-vibrational transitions*). Thus, each vibrational transition can comprise different rotational lines.

#### 3. Electronic transitions

Atoms (and molecules) in an electromagnetic field in the order of 1.8 - 6.2 eV undergo a redistribution of their electronic shell. The energy of a particular atomic electronic state ncan be approximated by the Rydberg's formula  $E_n = -R_{Ry}/n^2$ , where  $R_{Ry}$  is the atomic Rydberg's constant. Thus, if the incoming radiation has a wavelength  $\lambda$  within the UV/vis spectral range, the energy of the transition  $n_1 \cdot n_2$  is quantized as  $E_e = E_{n_1} - E_{n_2} = \frac{hc}{\lambda}$ . In a molecule, the electronic transitions are more complex since each electronic state is characterized by distinctive vibrational and rotational levels, which also depend on the internuclear distance R. Following Franck-Condon's principle, the electronic transitions in a molecule are faster than the vibrational period and, thus, the electronic transitions occur approximately at a constant R. In a potential well diagram, such in Fig. 2.1, this principle translates into assigning vertical lines to the electronic transitions.



Figure 2.1: Quantized transitions within a diatomic molecule. The fast electronic transitions (e) due to UV/vis radiation occur at a given internuclear distance of equilibrium  $R_e$ . Within a given electronic state, there are different vibrational levels (v), and transitions between them occur when molecules are exposed to IR radiation. For MW radiation, rotational transitions take place mostly between rotational levels (J).

After introducing the basis for a quantum-mechanical understanding of matter as a physical body comprising atoms and molecules, Fig. 2.2 shows a schematic description of the main radiometric quantities related to the matter-light interaction from a macroscopic point of view.

At the beginning of the  $20^{th}$  century, Planck introduced the idea of thermal emission with his theory of the black body radiation. Plank's law associates a spectral radiance at a given wavelength  $\lambda$  to a black (Lambertian) body of a given temperature T

$$I(\lambda,T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}.$$
(2.3)



Figure 2.2: Radiometric quantities (and units). The radiant flux  $\Phi_{\lambda}$  is defined as the energy radiated  $R_{\lambda}$  from a body A per time interval (W). Confined to a solid angle  $\Omega$ ,  $\Phi_{\lambda}$  leads to the radiant intensity (W/sr). Irradiance  $E_{\lambda}$  is the radiant flux received by a surface per unit area (W/m<sup>2</sup>). Radiance, also referred to as intensity  $I_{\lambda}$ , is the radiant flux (per  $\Omega$  and unit projected area) emitted (or reflected) from a surface (W/m<sup>2</sup> sr).

The integration of Eq. (2.3) over all wavelengths, also known as Stefan-Boltzmann's law, defines the radiant flux  $\Phi_{\lambda}$  emitted by an ideal black body. Hence, the Stefan-Boltzmann's law ( $I = \sigma \cdot T^4$ ) provides an upper limit for the radiant emission of a real body with a temperature T. According to Wien's law, the wavelength of maximum emission is anti-correlated to the temperature of the emitting source.

In general, planets and stars can be regarded as ideal black bodies and, therefore, their radiative emissions follow Plank's law and the related spectrum is centered at a wavelength given by Wien's law.

### 2.2 Solar radiation and the Earth-atmosphere system

With a surface temperature of about 5800 K and a diameter of about 1.4 million kilometers, the Sun can be approximated by a black body radiating around 64 MW/m<sup>2</sup>. The Solar continuous electromagnetic spectrum is centered at 500 nm (i.e., in the visible spectral range) and is referred to as *shortwave* radiation (*SW*). As a result of the solar absorption of certain elements of the cooler out part of the Sun, the Solar spectrum is characterized by dark (absorption) lines named after the German physicist Joseph von Fraunhofer. These *Fraunhofer lines*, initially labeled in 1814 with the letters A to H, provide a description of the chemical components of the the photosphere and chromosphere, but also include absorption lines related to Earth's atmospheric constituents such as molecular oxygen (see Fig. 2.3).



Figure 2.3: Fraunhofer lines as sketched by Fraunhofer in 1814. The letters A to H (added to the original picture for clarity) correspond to approx. 760 and 380 nm (resp.). Bands A and B correspond to absorption by the molecular oxygen contained in the Earth's atmosphere, while the hydrogen absorptions  $H_{\alpha}$  and  $H_{\beta}$  (Balmer lines) yield the C and F bands (resp.). Sodium and iron absorption result in the lines D and E, while calcium absorption produces the H and K bands. Figure adapted from Mappes (2010).

According to the inverse-square law  $(I = \frac{1}{d^2})$ , and considering a Sun-Earth distance of around 150 million kilometers, roughly 1368 W/m<sup>2</sup> of that SW radiation reach the Earth's top of the atmosphere TOA (see Fig. 2.4). This total incoming energy at the TOA is referred to as Solar constant (S<sub>0</sub>).



Figure 2.4: Solar flux spectrum centered at 500 nm (SW radiation). Atmospheric constituents such as molecular oxygen, water vapor and ozone absorb part of the SW radiation. Thus, as a consequence of the Earth's atmosphere, the solar irradiance spectrum reaching the TOA is reshaped on its way to the Earth's surface. Adopted from Finlayson-Pitts and J. N. Pitts (2000).

Since the solar energy received by a planet depends not only on its surface area<sup>1</sup>, but also on the illuminated surface, the average incoming solar radiation on Earth is  $\frac{S_0}{4} = 342W/m^2$ . As shown in Fig. 2.5, roughly 40% of that shortwave radiation reaching the TOA is reflected and absorbed by atmospheric constituents (e.g., O<sub>3</sub>, refer to Chap. 4). From the 198 W/m<sup>2</sup> reaching the Earth's surface from the Sun, an average of 15% is reflected and 85% is absorbed by the ground. Thus, nearly 50% of the total solar incoming radiation is absorbed by our planet.



Figure 2.5: Earth-atmosphere global radiation and energy balance. Left side: Solar (short-wave) radiation. Right side: Earth's (longwave) radiation. Adopted from the IPCC 2007 report (Solomon et al., 2007).

With a surface temperature of about 290 K, the Earth can also be approximated by an ideal black body radiating around 390 W/m<sup>2</sup>. After Wien's law, the Earth flux spectrum is centered at around 10  $\mu$ m (see Fig. 2.6) and, in contrast to the solar flux spectrum, is referred to as *longwave* radiation (*LW*). Roughly 80% of that radiation is absorbed by the atmospheric greenhouse gases (e.g., H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, see Chap. 4) and re-emitted back to the Earth's surface. As a result of these atmosphere-Earth energy exchanges, our planet is 30 degrees warmer than if the Earth's radiative equilibrium was considered without atmosphere. Hence, the atmosphere is a relevant factor controlling the type and amount of radiation reaching the surface, making life as we understand possible.

## 2.3 Radiative transfer in the Earth's atmosphere

The propagation of electromagnetic radiation, also called *radiative transfer* (RT), is driven by a combination of extinction (i.e., absorption and scattering) and emission processes which

<sup>&</sup>lt;sup>1</sup>Earth's surface area =  $510 \text{ Mkm}^2$ 



Figure 2.6: Spectrum of the terrestrial radiation (for clear sky conditions), centered at 10  $\mu$ m (LW radiation). Adopted from G. P. Brasseur (1999).

affect the incoming radiation budget. Following the molecular perspective of the matter-light interaction introduced in Sect. 2.1, the RT is here addressed considering the interaction of electromagnetic radiation and the constituents of the Earth's atmosphere (for details on those constituents, refer to Chap. 4).

#### 2.3.1 Scattering of light

Most of the extinction of the electromagnetic radiation in the Earth's atmosphere is due to scattering processes involving air molecules and suspended particles (referred both from now on as *scattering centers*, *SCs*). In general, when the unpolarized solar radiation interacts with a SC, a dipole moment is induced. Hence, the light becomes polarized and the direction of the incident radiation is changed. As depicted in Fig. 2.7, after a scattering process and as a result of the dipole oscillation, the energy of the incoming radiation can either remain constant (*elastic scattering*), or change its quantum-mechanical state (*inelastic scattering*).

#### Elastic scattering

In elastic scattering, the incoming beam  $I(\lambda)$  can be either attenuated if photons are scattered out of the direction of propagation  $(dI(\lambda)_{-})$ , or enhanced if photons are scattered into the direction of propagation  $(dI(\lambda)_{+})$ . Thus, the change of the radiation budget  $dI(\lambda)$  is defined by the angular distribution of the scattered radiation with respect to the direction of the incident beam (referred to as *phase function*,  $\wp(\vartheta)$ ), and by the scattering efficiency  $Q_s$  of the SC.  $Q_s$  is



Figure 2.7: Energy level diagram for elastic and inelastic scattering processes.

defined as

$$Q_s = \frac{\sigma_s}{A_s} \tag{2.4}$$

and describes the efficiency with which a SC (with scattering cross-section  $\sigma_s$ ) is able to scatter light as compared to the ability of that SC to scatter light based on its geometrical cross-section  $A_s$ . Thus,  $Q_s$  relates the optical properties of a SC, to its microphysical properties. A relevant parameter characterizing the scattering of light by a SC, is the *size parameter*  $\alpha_s = \frac{2\pi r}{\lambda}$ , where r is the radius of the scattering center. Also important is the *refractive index* of a SC, given as  $m = n - i\kappa$ , where n comes from the refraction of light<sup>2</sup>, and  $\kappa$  derives from the absorbing properties of the SC.

Depending on the size of a SC compared to the wavelength of the incoming radiation, there are two types of elastic scattering processes:

### 1. Rayleigh scattering

If the size of the SC is smaller than the wavelength of the incoming photons ( $\alpha_S \ll 1$  and  $|m| \alpha_S \ll 1$ ), Rayleigh scattering takes place (*Rayleigh*, 1871). In an infinitesimal volume of length dl with n defining the number density of scattering centers, Rayleigh scattering (denoted with R as subscript) yields a decrease of the radiation budget

$$dI_{R-}(\lambda) = -n \cdot \sigma_R(\lambda) \cdot I(\lambda) dl = -\mathcal{E}_R(\lambda) \cdot I(\lambda) \cdot dl$$
(2.5)

where  $\sigma_R$  is the Rayleigh cross-section, and  $\mathcal{E}_R$  is the Rayleigh scattering coefficient ( $\mathcal{E}_R = n \cdot \sigma_R(\lambda)$ ).

 $<sup>^{2}</sup>n = \frac{\text{speed light}^{\text{vacuum}}}{\text{speed light}^{\text{medium}}}$ 

#### 2.3. RADIATIVE TRANSFER IN THE EARTH'S ATMOSPHERE

This type of scattering is the result of the interaction of light with very small particles ( $r < 0.1 \mu m$ ) and air molecules (trace gas scattering is considered negligible). If the polarizability of a SC is given by  $\alpha$ , and  $\epsilon_0$  is the vacuum permittivity, then the Rayleigh scattering is defined by its cross-section

$$\sigma_R(\lambda) = \frac{8\pi^3 \alpha^2}{3\epsilon_0^2 \lambda^4} \tag{2.6}$$

and by its phase function

$$\wp_R(\vartheta) = \frac{3}{4} (1 + \cos^2 \vartheta). \tag{2.7}$$

Under atmospheric conditions, Eq. (2.6) and (2.7) are given in *Chance and Spurr* (1997) and *Goody and Yung* (1989) (resp.) as

$$\sigma_R(\lambda) = \frac{3.9993 \cdot 10^{-56} m^6 \alpha^{-4}}{1 - 1.069 \cdot 10^{-14} m^2 \lambda^{-2} - 6.681 \cdot 10^{-29} m^4 \lambda^{-4}}$$
(2.8)

$$\varphi_R(\vartheta) = 0.76 \cdot (1 + 0.93 \cos^2 \vartheta). \tag{2.9}$$

Rayleigh scattering is characterized by a weak angular dependency of the scattered light (see the polar diagram of Fig. 2.8). However, Rayleigh scattering depends strongly on the wavelength of the incoming photon ( $\sim \lambda^{-4}$ ). As a consequence, this scattering yields diffusive skylight. Its preference of scattering short wavelengths is the reason of the blue color of the sky during the day, and also for the red sunrises and sunsets<sup>3</sup>.

In addition to light attenuated as a consequence of Rayleigh scattering  $(dI_{R-}(\lambda))$ , photons can also get scattered into the direction of propagation of the beam and, hence, an increase of radiation may take place  $(dI_{R+}(\lambda))$ . Thus, the overall change of the radiation budget due to Rayleigh scattering is given by  $dI_R(\lambda) = dI_{R-}(\lambda) + dI_{R+}(\lambda)$ . The increase  $dI_{R+}(\lambda)$ depends on the probability with which radiation propagating in the direction  $(\vartheta', \varphi')$ , gets scattered into the incoming beam with propagating direction  $(\vartheta, \varphi)$ , i.e.,  $\wp_R(\vartheta, \varphi, \vartheta', \varphi')$ . The enhancement of radiation due to Rayleigh scattering (over all directions of propagation) then reads as

$$dI_{R+}(\lambda) = \frac{\mathcal{E}_R(\lambda)}{4\pi} \int_0^{2\pi} \int_0^{\pi} \varphi_R(\vartheta, \varphi, \vartheta', \varphi') \cdot I(\lambda)(\vartheta', \varphi') \cdot \sin\vartheta' d\vartheta' d\varphi' dl$$
(2.10)

#### 2. Mie scattering

If the dimension of the SC is bigger than the wavelength of the incident beam ( $\alpha_s \ge 1$ ),

<sup>&</sup>lt;sup>3</sup>Since most of the blue light is deflected away due to a longer light path through the atmosphere



Figure 2.8: Rayleigh phase function for unpolarized light, which yields an uniform instantaneous electromagnetic field of the incident light over the scattering center. Adopted from Hönninger (2002).

the so-called Mie scattering takes place. Compared to Rayleigh scattering, Mie scattering has a rather weak wavelength dependency (~  $\lambda^{-1...-1.5}$ ), and a complex angular scattering pattern characterized by a forward peaked phase function (see Fig. 2.9). As a result of the interaction of radiation of a given wavelength  $\lambda$  with a SC of similar size (e.g., aerosol and cloud particles), complicated interferences occur and the dipole approximation is not longer valid. In general, the cross-section related to these sort of scattering processes is not straight forward to calculate. Formally Mie scattering is often simplified by means of the Mie theory for spherical particles (*Mie*, 1908). Through this theory, Mie phase functions and extinction coefficients can be estimated. Further simplifications are frequently done with analytical formula for the Mie scattering phase function  $\wp_M(\vartheta)$ . An often used expression is the Henyey-Greenstein approximation (*HG approx., Henyey and Greenstein*, 1941):

$$\wp_M(\vartheta) = \frac{1 - g^2}{4\pi (1 + g^2 - 2g\cos(\vartheta))^{3/2}}$$
(2.11)

where g is the asymmetry parameter (-1 < g < 1) that depends on  $\langle \cos(\vartheta) \rangle := \langle \mu \rangle$ , which defines the anisotropy of the phase function:

$$g = \langle \mu \rangle = \frac{1}{2} \int_{-1}^{1} \mu P(\mu) d\mu$$
 (2.12)

#### 2.3. RADIATIVE TRANSFER IN THE EARTH'S ATMOSPHERE

Thus, g>0 indicates a dominating forward scattering  $\wp_M$ , g=0 an isotropic scattering phase function, and g>0 a backward one (e.g., *Van de Hulst*, 1981).

A property commonly used to describe the absorbing character of a particle is the *single* scattering albedo which reads as:

$$\varpi_0 = \frac{\mathcal{E}_{\mathcal{M}}}{\mathcal{E}_{ext}} = \frac{\mathcal{E}_{\mathcal{M}}}{\mathcal{E}_a + \mathcal{E}_{\mathcal{M}}}$$
(2.13)

where  $\mathcal{E}_{ext}$  is the extinction coefficient which comprises the absorption and the (Mie) scattering coefficients ( $\mathcal{E}_a$  and  $\mathcal{E}_{\mathcal{M}}$ , resp.). If  $\varpi_0 \sim 100\%$  (non-absorbing particles), the scattering coefficient due to particles is often referred to as the "particle extinction coefficient". For the definition of  $\mathcal{E}_a$  refer to Sect. 2.3.2.

In case of a medium containing N particles with a *particle size distribution* given by  $n = \frac{dN}{d\hat{r}}$ ( $\hat{r}$  is a normalized radius), the scattering coefficient can be calculated as

$$\mathcal{E}_{\mathcal{M}} = \int_0^\infty \sigma_M(\alpha_s) \cdot n(\hat{r}) \cdot d\hat{r}$$
(2.14)

where  $\alpha_s$  is the size parameter. Thus, Eq. (2.14) relates the optical properties of particles to microphysical properties and will become again relevant later in this work (Chap. 6).

In a similar way as for the Rayleigh scattering, the total change on the radiation budget due to Mie scattering  $dI_M(\lambda)$  is given by the decrease  $dI_{M-}(\lambda)$  and increase of radiation  $dI_{M+}(\lambda)$  after accounting for the former describe optical properties of the Mie scattering centers.

In addition to the Mie theory, if  $\alpha_s >> 1$  and regarding radiation as a set of rays interacting with a SC, scattering by particles can also be approximated by e.g. geometric optics, or the anomalous diffraction theory (*Van Hulst*, 1957).

#### Inelastic scattering

Inelastic scattering takes place when the interaction of radiation with a SC results not only in a change of the direction of propagation of the radiation, but also in an exchange of energy between the photons and the SC (i.e,  $\lambda_{\text{in coming rad.}} \neq \lambda_{\text{outgoing rad.}}$ , Fig. 2.7). If the SC are air molecules, this scattering is referred to as *Raman scattering*. As a consequence, molecules may change their rotational and vibrational states. If there is no change on the vibrational state ( $\Delta v = 0$ ), the scattering is called *rotational Raman scattering* (RRS). Other wise ( $\Delta v = \pm 1$ ), it is referred to as *rotational-vibrational Raman scattering* (VRS). If the energy is transferred from the photon to the SC as a result of an inelastic scattering, Stokes scattering is said to take place (S-branch). If, on the other hand, the transfer of energy occurs from the SC to the



Figure 2.9: Mie scattering phase functions for water droplets of different size parameters  $\alpha_s \equiv \alpha$  (550 nm). Left panels: logarithmic representation. Right panels: polar diagrams. As depicted by the diagrams, the forward direction of the Mie scattering clearly dominates with increasing particle size. Adapted from Shangavi (2003).

photons (O-branch), the scattering produces anti-Stokes lines.

For atmospheric conditions, the RRS cross-section is more relevant than the VRS one, but still weaker than the Rayleigh scattering cross-section yielding the Cabannes lines ( $\Delta v = 0, \Delta J = 0$ ). Therefore, for radiative transfer studies, the total scattering of light due to air molecules may be approximated by its elastic component (Rayleight scattering). However, in spectroscopic measurements of scattered sunlight, Raman scattering may be observed as a "filling in" of the Fraunhofer lines. This effect, often referred to as the *Ring effect*, is considered to be due to the RRS and may affect the spectral retrieval of atmospheric trace gases (e.g., *Grainger and Ring*, 1962; *Vountas et al.*, 1998).

#### 2.3.2 Absorption and emission of light

Given two different energy levels (i, j), their equilibrium distribution may be modified by absorption, and by stimulated or spontaneous emission through transitions taking place at a quantum-mechanical level (see also Sect. 2.1).



Figure 2.10: Energy diagram for absorption and emission processes.

For a system with n molecules with two stationary wave functions  $(\Psi_i, \Psi_j)$  and energies  $(E_i, E_j)$ , the number of different states at an energy level (i, j) is given by their particular degeneracies  $(g_i, g_j)$ . If  $E_i < E_j$ , then the relative population of the excited state at thermal equilibrium follows the Boltzmann's distribution

$$\frac{n_j}{n_i} = \frac{g_j}{g_i} e^{-\frac{E_j - E_i}{kT}},$$
(2.15)

where T is the absolute temperature, and  $k = 8.617 \cdot 10^{-5} \text{ eV/K}$  is the Boltzmann's constant. The rate at which the population of the lower state *i* changes when interacting with a radiation density  $\rho_{\lambda}$  (see Fig. 2.10) reads as

$$\frac{dn_i}{dt} = -n_i \rho_\lambda B_{ij} + n_j \rho_\lambda B_{ji} + n_j A_{ji}, \qquad (2.16)$$

where  $B_{ij}$ ,  $B_{ji}$  and  $A_{ji}$  are the *Einstein coefficients* for stimulated absorption, stimulated emission and spontaneous emission (decay), resp. Thus, the change of radiation intensity through a small volume of length dl with  $n_i + n_j$  molecules due to absorption (subindex a), induced or stimulated emission (subindex ie), and spontaneous emission (subindex se), is given by the equation

$$dI(\lambda) = dI_a(\lambda) + dI_{ie}(\lambda) + dI_{se}(\lambda) =$$
  
=  $-n_i \frac{B_{ij}h}{\lambda} I(\lambda) dl + n_j \frac{B_{ij}h}{\lambda} I(\lambda) dl + n_j \frac{A_{ji}hc}{4\pi\lambda} dl,$  (2.17)

where the  $\frac{1}{4\pi}$  factor in the last term of the equation is due to the isotropic character of the spontaneous emission, while the induced one only take places in the direction of propagation.

In the case of the Earth's atmosphere and considering thermodynamical equilibrium, the density of electromagnetic radiation  $\rho_{\lambda}$  is given by Eq. (2.3). Thus, considering Eq. (2.15), the *Einstein coefficients* are

$$g_i B_{ij} = g_j B_{ji}, A_{ji} = \frac{8\pi hc}{\lambda^5} B_{ji}.$$
 (2.18)

Hence, considering the above equations, in the atmosphere these processes render a change of the radiation budget given by

$$dI(\lambda) = dI_a(\lambda) + dI_{ie}(\lambda) + dI_{se}(\lambda) =$$
  
=  $-n_i \frac{B_{ij}h}{\lambda} I(\lambda) dl + n_j \frac{B_{ij}h}{\lambda} e^{-\frac{E_j - E_i}{kT}} I(\lambda) dl + n_j \frac{B_{ij}h}{\lambda} e^{-\frac{E_j - E_i}{kT}} dl$  (2.19)

so that

$$dI(\lambda) = -n_i \frac{B_{ij}h}{\lambda} I(\lambda) dl + n_j \frac{B_{ij}h}{\lambda} e^{-\frac{E_j - E_i}{kT}} I(\lambda) dl + n_j \frac{B_{ij}h}{\lambda} \frac{8\pi hc^2}{4\pi\lambda^5} e^{-\frac{E_j - E_i}{kT}} dl$$
(2.20)

Considering the absorption cross-section  $\sigma_a = \frac{B_{ij}h}{\lambda}$ , and the absorption coefficient  $\mathcal{E}_a(\lambda) =$ 

 $n_i \sigma_a(\lambda) \left(1 - e^{-\frac{\Delta E}{kT}}\right)$ , then Eq. (2.20) results as

$$dI(\lambda) = -\mathcal{E}_a(\lambda) \left[ I(\lambda) - \frac{1}{4\pi} P(\lambda) \right] dl, \qquad (2.21)$$

where P is the Plank's distribution of thermal radiation.

In general, for temperatures encountered in the first 80 km of the Earth's atmosphere,  $n_i \gg n_j$ . Hence, the probability of absorption of light is higher than the probability of either of the emissions. As a result, Eq. (2.21) gets simplified as

$$dI(\lambda) \sim dI_a(\lambda) = -\mathcal{E}_a(\lambda) \cdot I(\lambda) \cdot dl, \qquad (2.22)$$

and, if n is the number density of absorbers present in the studied volume (i.e.,  $n_i$ ), the coefficient of absorption reads

$$\mathcal{E}_a(\lambda) = n \cdot \sigma_a(\lambda). \tag{2.23}$$

#### 2.3.3 Radiative transfer equation

Bearing in mind all the processes above described, the overall change of radiation when photons transfer from the source to the observer yields the *radiative transfer equation (RTE)*, that comprises scattering and absorption processes decreasing the light, and scattering processes that increase the radiation budget. Thus, in the atmosphere, this renders the following simplified RTE:

$$dI(\lambda) = dI_{R-}(\lambda) + dI_{M-}(\lambda) + dI_a(\lambda) + dI_{R+}(\lambda) + dI_{M+}(\lambda)$$
(2.24)

If both (Mie and Rayleigh) scattering coefficients are added as  $\mathcal{E}_s$ , then the extinction coefficient  $\mathcal{E} = \mathcal{E}_s + \mathcal{E}_a$  and, accounting for the equations of  $dI_{R+}(\lambda)$  and  $dI_{M+}(\lambda)$ , the RTE results in

$$dI(\lambda) = -\mathcal{E}(\lambda) \cdot dI(\lambda) \cdot dl + \frac{\mathcal{E}_s(\lambda)}{4\pi} \int_0^{2\pi} \int_0^{\pi} \varphi_s(\vartheta, \varphi, \vartheta', \varphi') \cdot I(\lambda)(\vartheta', \varphi') \cdot \sin\vartheta' d\vartheta' d\varphi' dl$$
(2.25)

where  $\varphi_s = \varphi_R + \varphi_M$  is the *total scattering function*, which gives the probability with which radiation propagating in the direction  $(\vartheta', \varphi')$ , gets scattered into the incoming beam with propagating direction  $(\vartheta, \varphi)$ .

When referring to the radiation transfer from the Sun (SW), and considering an infinitesimal volume dl, the second term on the right side of the RTE (2.25) may be neglected. Thus, the

transport of a beam  $I_0(\lambda)$  entering an infinitesimal volume of air dl following a light path L, results on a RTE which simplified form stands as the *Beer-Lambert's law* 

$$I(\lambda, L) = I_0(\lambda) \cdot e^{-\int_L \mathcal{E}(\lambda, L) \cdot dl} = I_0(\lambda) \cdot e^{-\tau(\lambda, L)}, \qquad (2.26)$$

where the *optical density* is

$$\tau(\lambda, L) = \ln \frac{I_0(\lambda)}{I(\lambda, L)} = \int_L \mathcal{E}(\lambda, L) \cdot dl.$$
(2.27)

In general, the light path L is the standard targeted output when addressing radiative transfer studies as detailed later in Chap. 6.

## Chapter 3

# Atmospheric structure and dynamics

With a size that represents only 1% of the Earth's radius, the terrestrial atmosphere is a shield layer controlling the type and amount of radiation reaching and leaving the Earth and, thus, making the life as we know, possible. Depending on its physical properties, the Earth's atmosphere can be understood as a combination of different spherical layers (sphere or *sphaira*). This chapter focusses on the vertical stratification of the atmosphere. In addition, and based on thermodynamics and fluid dynamics, the circulation of the atmosphere is also addressed.

### **3.1** Vertical structure

The vertical structure of the atmosphere can be related to the motion mechanism, the degree of ionization, and the thermal structure.

Depending on the dominant motion mechanism (mixing or diffusion), the atmosphere can be divided in *homosphere* and *heterosphere* (see Fig. 3.1). In the heterosphere the effectivity of diffusion increases with the velocity of the molecular motion and with the mean free path between collisions (which increases with altitude). In the homosphere, on the other hand, the free path length is so short that the atmospheric constituents are mixed by turbulent fluid motions rather than diffused. The region where the diffused and turbulent motions are balanced is called *turbopause*, which is located at 100 km above sea level. This region is also known as the *Kármán line*, and is often regarded as the boundary between the Earth's atmosphere and the outer space.

Considering its degree of ionization, the atmosphere can also be understood as *ionosphere* and *neutrosphere* (see Fig. 3.1), and the transition between both layers is located at roughly 65 km of altitude. Above that height, solar X-rays and extreme UV radiation excite atmospheric constituents and ionize them. The ionosphere, as the inner part of the magnetosphere, is highly affected by solar wind and space weather. Direct effect of the outer space in this layer are e.g.



Figure 3.1: Vertical structure of the Earth's atmosphere. Adopted from Brasseur and Solomon (1986).

the shooting starts and the polar lights or aurorae (see Fig. 3.2).

Based on its thermal structure, the atmosphere can be also regarded as four different layers: the troposphere, the stratosphere, the mesosphere and the thermosphere. The boundary of each of these layers is regarded with the suffix *-pause* (e.g., tropo*pause*).

#### • The thermosphere

Being closer to the Sun, the thermosphere is highly influenced by the incoming solar radiation and its altitude range responds to the 11 year solar cycle and varies also with the solar weather (e.g., *Emmert et al.*, 2010). Extending from roughly 90 km above sea level, in the first kilometers of the thermosphere the temperature increases strongly with height, while this gradient relax above. As indicated in Fig. 3.1, this layer is partly ionized by high solar energy radiation, and diffusion directs the distribution of the atmospheric constituents based on their mass (including also the space shuttles that it harbors).

#### • The mesosphere

The mesosphere lays below the mesopause, which is located at around 85 km and is the



Figure 3.2: Aurora australis as seen from space (illuminated by the moon). Adopted from NASA (2010b).

coldest point of the atmosphere (-90° C). Extending from 50 km above sea level, the mesosphere presents a temperature lapse rate (i.e.,  $\frac{dT}{dz} < 0$ ) as shown in Fig. 3.1. This is the layer where, normally in polar regions, the noctilucent clouds can be seen in twilight.

#### • The stratosphere

From the Latin stratus ("spread out") and the Greek sphaira ("sphere"), the stratosphere extends from above 17 km in the tropics (10 km in the poles) until the stratopause, at roughly 50 km. Among its strong vertical stratification and horizontal mixing, this layer is characterized by a maximum ozone concentration at around 22 km, which is commonly known as the ozone layer (see also Chap. 4). The thermal emission by water vapor and  $CO_2$ , together with the strong absorption of UV-C radiation (and partly UV-B) by the ozone layer, define the stratospheric temperature gradient with a steady increase with altitude (see Fig. 3.1).

#### • The troposphere

From the Greek tropos ("turning"), the troposphere is the lowest layer of the atmosphere and extends from sea level, up to the tropopause (see Fig. 3.1). Comprising most of the mass of the atmosphere (50% in its first 5 km), the troposphere is often subdivided in three sections: the boundary layer (BL), the free troposphere (FT), and the upper troposphere (UT). Warmed mostly from below, the troposphere is characterized by a temperature lapse rate of about 10 degrees/km, and is strongly affected by latent heat transport (from phase changes of water), by sensible heat (convection), and also by turbulent mixing. In fact, in order to avoid these sort of tropospheric turbulence and also to decrease fuel consumption, most aircrafts usually cruise in the lower stratosphere (LS).

## **3.2** Atmospheric circulation

The solar energy reaching the TOA (see Chap. 2) is unevenly distributed in the different latitudes and, thus, the Earth-atmosphere system presents zonal and meridional (longitudinal and latitudinal) irregular radiative properties. Figure 3.3 shows the annual average distribution of short and long-wave radiation at the TOA, as well as of the net radiation budget. Also, Fig. 3.3 shows the zonal mean profiles of the dispersion of the radiation. As shown in the figure, there is a strong radiation gradient between the tropical regions and the poles. This gradient yields a re-distribution of energy via atmospheric and, in smaller scale, oceanic circulation. This sections focuses on the tropospheric and stratospheric dynamics, while in Chap. 5 the oceanic circulation is addressed.

#### 3.2.1 Tropospheric circulation

At the poles and at the tropics the temperature of the low atmosphere is rather stable. However the energy gradient at the TOA triggers a meridional poleward transfer of energy. This re-distribution of energy in the rotating Earth sets the pattern of the atmospheric circulation. As firstly suggested by Edmund Halley, and later corrected by George Hadley and William Ferrel, the large scale tropospheric circulation is defined by three different cells: the Hadley, the Ferrel, and the Polar cell (see Fig. 3.4). In addition, and as a direct consequence of the horizontal temperature gradient between the poles and the Equator, strong winds (*jet streams*) are located in the tropopause at meridional and subtropical latitudes (e.g., Fig. 3.4(b)). The location and shape of these westerly jet streams are linked to large-scale planetary waves originated in the troposphere by vorticity and shear stress, that transfer energy and momentum to upper layers (i.e., the *Rossby waves*).

In the low troposphere, there are also superficial winds. These winds are directed by pressure gradients from high to low pressure systems (i.e., from anticyclones to cyclones), by the Coriolis force, by centrifugal force, and by friction. The boundary between the Northeasterly and Southeasterly trade winds in equatorial regions (denoted as NE and SE in Fig. 3.4) is called the *Inter-Tropical Convergence Zone (ITCZ)*, which location directs the monsoon season in the tropical regions.

In the upper troposphere, where the Coriolis force is balanced with the pressure gradient force, the wind is referred to as *geostrophic*, and flows without friction parallel to the isobars with a speed proportional to the pressure gradient. In a fluid, the transition between the geostrophic and the surface flow is known as the *Ekman layer*. The same concept is applied



Figure 3.3: Annual mean TOA energy for shortwave, longwave and net radiation. Zonal mean profile panels are given at right. Adopted from Trenberth and Stepaniak (2003).



Figure 3.4: Tropospheric circulation. (a) Cells and trade winds (adopted from Short, 2010). (b) Cross-section of the tropospheric circulation in the northern hemisphere (adopted from NOAA, 2010).

for the atmosphere. Below the Ekman layer the flow moves across the isobars toward low pressure, at an angle that is a maximum at the surface ( $\leq 45^{\circ}$ ). Since the wind vector decreases exponentially from the geostrophic level to the ground, this low part of the troposphere is often regarded as the *Ekman spiral*, concept initially proposed for flows in the upper layers of the ocean.

As shown in Fig. 3.5, the horizontal transport in the troposphere in the longitudinal direction is fastest than in the meridional one. Due to the lack of thermal thermal forcing through the Equator, interhemispheric transport involves the seasonal drift of the ITCZ and convective systems developing at the edge of the ITCZ.

### 3.2.2 Stratospheric circulation

Unlike in the turbulent troposphere, the circulation in the stratosphere tends to be zonally symmetric. The meridional stratospheric circulation is described by the overturning *Brewer-Dobson circulation*. In general, as depicted in Fig. 3.6, air masses are injected to the stratosphere in the tropics and, directed by planetary waves, undergoes downward transport in the extratropics (surf zone in the figure).

In addition, driven by gravity waves, the wind regime in the equatorial LS alternates between



Figure 3.5: Horizontal transport times. Adopted from Jacob (1999).

easterlies and westerlies with a periodicity of roughly 28 months. This is the so called *Quasi-Biennial Oscillation* (*QBO*, Fig. 3.7). This tropical QBO propagates to the poles and penetrates the mesosphere and, therefore, affects the middle atmosphere circulation in a global scale (for a detail description refer to, e.g., *Baldwin et al.* (2001) and references therein).



Figure 3.6: Atmospheric circulation. Adopted from WMO (1999).



Figure 3.7: Quasi-Biennial Oscillation. Top: Altude-time cross-section of the monthly-mean zonal wind component (m/s), with the seasonal cycle removed. Bottom: Top panel band-pass filtered to retain periods between 9 and 48 months. Adopted from Baldwin et al. (2001).

#### 3.2.3 Stability and vertical transport

The atmospheric circulation detailed in Sect. 3.2.1 and Sect. 3.2.2 redistributes the atmospheric energy budget by movement of air masses aiming to gain an overall stability. However, consequences of the atmospheric circulation are not only dynamical but also chemical due to the constituents contained in those of air masses, which timescale depends mainly on the directing force. As illustrated in Fig. 3.8, turbulences mix the troposphere within a few months, while the interhemispheric transport of air masses in the stratosphere takes four to six years.



Figure 3.8: Vertical transport times. Adopted from Jacob (1999).

As a consequence of the low thermal and radiative conductivity of air, the vertical stability in the atmosphere is often addressed via the *potential temperature* lapse rate of a dry air parcel in adiabatic motion (i.e., without heat sources or sinks). The potential temperature ( $\theta$ ) of a dry air parcel is defined as the temperature (T) that an air parcel would have if (adiabatically) brought
to a standard pressure  $p_0$  (i.e., 1023 hPa or mbar):

$$\theta = T\left(\frac{p_0}{p}\right)^{\frac{\kappa-1}{\kappa}} \tag{3.1}$$

where  $\kappa$  is the ratio of the specific heat capacity at constant pressure and at constant volume ( $\kappa = c_p/c_v$ ). The hydrostatic stability of a stratified atmosphere to small air parcel displacements is then defined on basis of the  $\theta$  lapse rate  $(\frac{d\theta}{dz})$ . While air parcels in a stable environment tend to convey horizontally (advect) along constant  $\theta$  layers (isentropic surfaces), an atmospheric layer where  $\frac{d\theta}{dz} < 0$  is in unsteady state, which generally will be compensated by vertical motion of air (e.g., convection). On the other hand, if both  $\theta$  and T increase with altitude, the layer is referred to as an *inversion layer*, which is highly stable. Thus, as shown for instance in Fig. 3.1, the troposphere is an unstable layer with a *Dry-Adiabatic Lapse Rate* (*DALR*,  $\Gamma_d$ ) of roughly 10 K/km, drooping to  $\Gamma_d \leq 2K/km$  in the tropopause (*WMO*, 2003). On the other hand, the stratosphere can be regarded as an inversion layer where vertical motion of air masses is very limited. In the case of saturated air, the stability of the atmosphere is regarded with the *equivalent potential temperature* and, due to the release of latent heat as water condensates, the *Moist-Adiabatic Lapse Rate* (*MALR*,  $\Gamma_m$ ) is slower than the DALR (e.g., at sea level  $\Gamma_m \sim 7K/km$  at 0°C).

Accordingly, in a stably stratified atmosphere, the oscillation frequency N of an air parcel when displaced adiabatically may be described by the *Brunt-Väisälä buoyancy frequency*, and a characterization of the *static stability of the environment* by  $N^2$  (e.g., *Holton*, 2004):

$$N^{2} = \frac{g}{\theta} \frac{d\theta}{dz} = \frac{g}{T} \left( \frac{dT}{dz} + \Gamma_{d} \right)$$
(3.2)

Therefore, the stratification of an environment with  $N^2 < 0$  is statically unstable and the displacement of the air parcel takes place  $(N^2 \propto \frac{d\theta}{dz})$ .  $N^2 = 0$  indicates lack of acceleration force and hence the air parcel lays in an environment in neutral equilibrium.  $N^2 > 0$  suggests statically stratification and, hence, the air parcel oscillates over the initial position. Thus, a well mixed troposphere is often characterized by very low static stability (small  $N^2$ ). The largest gradient in  $N^2$  takes place usually nearby the thermal tropopause, and the static stability of the stratified lower stratosphere is higher than the stability of the troposphere. Recent studies report on the correlation of regions with enhanced stability just above the thermal tropopause with a sharp inversion layer, so called *Tropopause Inversion Layer (TIL)*, that extends from the subtropics to the poles (e.g., *Birner et al.*, 2002; *Birner et al.*, 2006; *Kunz*, 2010; *Randel and Wu*, 2010). The *TIL* and its relation to stratospheric trace gases will be addressed later in Sect. 9.2.

Moreover, the combination of isentropic flow and stability leads to the concept of *Potential Vorticity* (PV). The trajectory followed by an air mass in a stratified atmosphere is usually defined by its PV, given by

$$Q = \eta \cdot \frac{\nabla \theta}{\rho} \tag{3.3}$$

where  $\theta$  is the potential temperature,  $\rho$  is the density of the fluid, and  $\eta$  is the absolute vorticity. The later can be calculated as

$$\eta = \xi + f = \nabla_h \times \mathbf{v} + 2\mathbf{\Omega}\sin\varphi \tag{3.4}$$

where f is the the Coriolis parameter  $f = 2\Omega \sin \varphi$  ( $\Omega$  is the angular velocity of the Earth,  $\varphi$  is the latitude), and  $\xi$  is the vorticity of a horizontal air flow **v** (i.e., the vertical component of the vector *rot* **v**) given by

$$\xi = rot_z \mathbf{v} = \frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y} = \nabla_h \times \mathbf{v}$$
(3.5)

In an adiabatic and geostrophic flow, the potential vorticity is conserved and transport of air masses only takes place along lines of constant PV. Thus, PV is a standard parameter regarded for the analysis of air masses trajectories. From a temperature perspective, the tropopause is defined by e.g. WMO (2003) as the lowest altitude at which the DALR  $\leq 2$  K/km for at least 2 km. However, if defined from a PV point of view, the tropopause is the region of constant potential vorticity of 2 PVU<sup>1</sup>. In the tropics this usually coincides with the isentropic surfaces at 380 K which, as shown in Fig. 3.9, decreases crossing diverse isentropic layers in the extratropics until the isentropic surfaces of roughly 300 K in the poles (e.g. Holton et al., 1995). In general, mass and chemical Stratosphere-Troposphere Exchange (STE) can take place by different processes. In the tropics air masses are injected into the LS through the Tropical Transition Layer (TTL). Those air masses are then distributed meridionally through the the Brewer-Dobson circulation. In the extratropics, air masses are transported down into the LS via large-scale subsidence. Exchange of air masses also occur via isentropic transport by eddy motions across the jet streams.

Also, nearby isentropic surfaces, regions of sudden gradients of PV may occur and, as a a result of eddy phenomena and weather related disturbances, mass and chemical STE may take place. These events are the so-called *tropopause folds* (e.g., *Danielsen*, 1968; *Bamber et al.*, 1984 *Holton et al.*, 1995; *Stohl et al.*, 2003; *Holton*, 2004; *James and Legras*, 2008). Tropopause folds

<sup>&</sup>lt;sup>1</sup>1 Potential Vorticity Unit  $\equiv 1 \text{ PVU} = 10^{-6} Km^2 kg^{-1}s^{-1}$ 



Figure 3.9: Dynamical stratosphere-troposphere exchange. The tropopause defined with PV is indicated by a red line. In the extratopics the LS ranges from the tropopause up to the 380 K isentropic surface. The yellow curved arrow indicate the Brewer-Dobson circulation. Exchange of air masses via isentropic transport is given by the horizontal yellow double-end arrows, and the jet streams are given by the blue contours. Tropopause deformations occur in the vicinity of the polar front and via diabatic processes (thin vertical yellow double-end arrows). Adopted from Kunz (2010).

usually occurs in mid-latitudes and polar regions, in areas with large vertical shear and strong meridional thermal gradients (i.e., under baroclinic instability). As schematized in Fig. 3.10, tropopause folds are frequently preceded by a low pressure system. Under these circumstances up to 50% of the mass within the fold may be exchanged (*Shapiro*, 1980). Thus, although the air mixing takes place in the low stratosphere, the tropopause folds represent a non negigible transport of gases and into the troposphere that affects the atmospheric chemistry not only at a local scale in the UT/LS (e.g., *Hocking et al.*, 2007).

Thus, the tropopause may be understood from a thermal point of view, from a static stability perspective (Eq. 3.2), and by PV analysis. Additionally, the tropopause may be defined from a chemical perspective (referred to as *chemopause* in *Pan et al.*, 2004). In this case, as depicted in Fig. 3.11, the relation between the abundance of tropospheric long lived trace gases (e.g., CO, H<sub>2</sub>O), and that from stratospheric tracers (e.g., O<sub>3</sub>) may serve also an indicator of the chemical STE (e.g., *Bamber et al.*, 1984; *Pan et al.*, 2004; *James and Legras*, 2008; *Kunz*, 2010). Although details on the stratospheric and tropospheric chemistry are given in the next chapter,



Figure 3.10: Classic view of the tropopause fold. The indirect cell comprises cold air masses (wet, cloudy, cyclonic conditions). The right hand direct cell contains warm air masses (dry, clear conditions). The trough is the mixing layer. Adopted from Danielsen (1968).

the idea of this *chemopause* principle relies on the fact that the abundance of the traces decreases with the distance form the source region across the tropopause. Thus, the representation of a stratospheric trace abundance *vs.* a tropospheric one is characterized by a *L-shape* profile, that may be divided in three layers from a chemical point of view: the stratosphere, the mixing layer, and the troposphere. This trace gas approach will be applied later in Chap. 9.



Figure 3.11: The "chemopause" concept. (a) Stratospheric and tropospheric tracer in altitude (b) their relations in tracer-tracer space. Adopted from Pan et al. (2004).

## CHAPTER 3. ATMOSPHERIC STRUCTURE AND DYNAMICS

## Chapter 4

# Atmospheric chemistry

The most abundant gases in dry unpolluted air are molecular nitrogen (N<sub>2</sub>, 78.08 %) and molecular oxygen (O<sub>2</sub>, 20.95 %). The remaining components are *trace gases* and *aerosols*, accounting for roughly 1% of the atmosphere. For atmospheric chemical and radiative studies the units describing the abundance of those trace gases are *concentration* or *number density* (molecules per cm<sup>3</sup>). If, on the other hand, atmospheric transport investigations are needed, their abundance is regarded based on their temperature and pressure independent units of *molar mixing ratios* (moles of trace species per mole of air) which, under ambient conditions, are equivalent to *volume mixing ratios* (*vmr*, i.e., the amount of a trace species per volume of air).

Most abundant trace species in the Earth's atmosphere are argon (Ar,  $9 \cdot 10^3 \ \mu \text{mol/mol}$  or ppmv), carbon dioxide (CO<sub>2</sub>, 380 ppmv), neon (Ne, 18.18 ppmv), helium (He, 5.24 ppmv), methane (CH<sub>4</sub>, 1.7 ppmv), krypton (Kr, 1.14 ppmv), molecular hydrogen (H<sub>2</sub>, 0.55 ppmv) and dinitrogen oxyde (N<sub>2</sub>O, 0.3 ppmv). In addition, the atmosphere contains the three states of water (H<sub>2</sub>O, 0.40% of the total volume, 1-4% near the ground), and many other substances that, despite their relatively low abundance (in the order or nmol/mol or ppbv), can have a large impact in the atmosphere's chemistry. Such is the case for, e.g., ozone (O<sub>3</sub>), sulfuric dioxide (SO<sub>2</sub>), nitrogen oxyde and dioxyde (NO, NO<sub>2</sub>), and carbon monoxide (CO). This work focuses in some of these trace substances present at a nmol/mol and pmol/mol level (ppbv and pptv).

Besides the energy and momentum addressed in the previous chapters, mass is a quantity also conserved in the atmosphere. In general, for a given volume, the accumulation rate of a substance in that volume is defined by the change in time of its concentration c, so that

$$\frac{dc}{dt} = (F_{in} - F_{out}) + (P - L),$$
(4.1)

where F stands for the flux of the species in and out of the volume  $(F_{in}, F_{out})$ , and P and

L are the production and the removal or loss rates, respectively. In equilibrium,  $\frac{dc}{dt} = 0$ . Also the fluxes in and out of the volume are null and, hence, the production rate equals the removal rates. Therefore, regarding the complete atmosphere as a reservoir,

$$\frac{c}{P} = \frac{c}{L} = \tau, \tag{4.2}$$

where  $\tau$  is the *residence time* or *lifetime* of the substance in the atmosphere, and addresses the possibility of that substance to undergo chemical reactions and to be transported in the atmosphere. Figure 4.1 summarizes the lifetime of relevant atmospheric constituents, their associated transport within the atmosphere and, thus, their potential influence in the atmospheric chemistry at a micro, local, regional or global scale.



Figure 4.1: Atmospheric lifetimes of trace substances. Adapted from Seinfeld and Pandis (1998).

By natural and by anthropogenic means, many trace gases are continuously emitted into the atmosphere, usually in a reduced (oxidising) state. Since the Earth's atmosphere is rich in e.g.  $O_2$ , these species are often broken down by oxidation in the troposphere and in the stratosphere (e.g., *Wayne*, 2009). These redox mechanisms prevent the atmospheric accumulation of harmful species such as e.g. methane (CH<sub>4</sub>, greenhouse gas), or carbon monoxide (CO, toxic gas deriving from combustion). As a result, the *oxidising capacity* of the atmosphere is often referred to as the *self-cleaning capacity* of the atmosphere. Most of these oxidising processes involve chemical species with high free energies due to their free electron (i.e., highly reactive), called *radicals*.

Relevant atmospheric oxidants are  $O_2$ ,  $O_3$ , oxygen atoms in the excited state (O(<sup>1</sup>D)), the hydroxyl radical (OH), as well as nitrogen and halogen oxide radicals. The later are mainly relevant in marine environments, over salt lakes and in polar regions. The core of this work reports on measurements of a particular halogen oxide, bromine monoxide (BrO), in the Arctic atmosphere from the boundary layer up to the low stratosphere. Therefore, in order to understand the chemistry behind this particular radical, and its effect on the oxidising capacity of the atmosphere, an overview of the atmospheric chemistry is given in the following, focusing on the photochemistry related to ozone and to the main sources and sinks of the ozone loss catalysts.

Here, Sect. 4.1 to 4.3 provide an overview of the photochemistry of the ozone, and of the hydrogen and nitrogen oxide radicals in the stratosphere, and also in the troposphere. Section 4.4 focuses on the main chemical compounds in this work: the reactive halogen species. Therein, the sources, pathways, sinks and impacts of these compounds are detailed first for the troposphere, and then for the stratosphere. Finally, this chapter finishes providing main features of the aerosol particles and heterogeneous reactions in Sect. 4.5.

## 4.1 Ozone photochemistry

Besides its oxidising properties, the absorption of UV light by ozone makes it a trace gas of vital importance. Depending on the photon energy, UV radiation is classified in three branches: UV-A (315 to 400 nm), UV-B (280 to 315 nm) and UV-C radiation (100 to 280 nm). The Sun emits UV radiation in the three branches, all of them considered as carcinogens. As introduced in Chap. 3 and shown in Fig. 4.2, the stratospheric ozone layer located at 20–30 km above sea level, absorbs the UV-C radiation and most of the UV-B, and only the UV-A radiation (and  $\sim$ 5-10% UV-B) reaches the ground. Therefore, O<sub>3</sub> shields plants, animals, humans and materials at sea level from the most harmful UV radiation. However, ozone is also considered a greenhouse gas and a polluting trace gas in the troposphere. Here the O<sub>3</sub> photochemistry is discussed in these two atmospheric layers.

In the first half of the  $20^{th}$  century the production and loss of the shielding stratospheric ozone layer was described based on an oxygen chain of reactions referred to as the Chapman cycle (*Chapman*, 1930):

Production :

$$\begin{array}{cccc} O_2 & \xrightarrow{h\nu} & O+O & (\lambda \le 242 \, \mathrm{nm}) & (4.3) \\ O+O_2 & \xrightarrow{M} & O_3 & (4.4) \end{array}$$



Figure 4.2: Solar actinic flux (UV) at different altitudes (SZA=30°). Available UV light decreases with altitude as a result of  $O_2$  and  $O_3$  absorption. Adopted from DeMore et al. (1997).

Loss :

$$O_3 \xrightarrow{h\nu} O(^1D) + O_2 \qquad (\lambda \le 320 \text{ nm})$$

$$(4.5)$$

$$\xrightarrow{h\nu} O + O_2 \qquad (\lambda \le 1180 \,\mathrm{nm}) \tag{4.6}$$

$$O(^{1}D) \xrightarrow{M} O$$
 (4.7)

$$O + O \xrightarrow{M} O_2 \tag{4.8}$$

$$O + O_3 \longrightarrow 2 O_2 \tag{4.9}$$

where  $O(^{1}D)$  are the oxygen atoms in the excited state which are the most active oxidants in the stratosphere. Since reaction (4.3) takes place for wavelengths smaller than 242 nm (UV-C), the photodissociation of molecular oxygen (and thus the ozone production) occurs mainly in the upper stratosphere. The photochemical lifetime of ozone is in the order of 30 minutes, while the residence time of  $O(^{1}D)$  is roughly  $10^{-8}$  s, and  $\tau_{O} \sim 0.04$  s. Generally, the ensemble of  $O+O(^{1}D)+O_{3}$  is called *the odd-ozone family*,  $O_{x}$ . The lifetime of this chemical family ranges from several months to years in the lower stratosphere, weeks at 30 km, and less than a day in the upper stratosphere. In general, the concentration of  $O_{x}$  gives an indication of the balance between the production and loss of ozone (e.g. *Dessler*, 2000).

Although the Chapman cycle involving only oxygen could describe the ozone distribution in the stratosphere qualitatively, the cycle overestimated the stratospheric  $O_3$  concentration. The

#### 4.1. OZONE PHOTOCHEMISTRY

discrepancy between theory and observations indicated either an overestimated source of  $O_x$ , or a missing channel for the removal of ozone. Since sources of  $O_x$  were well established, a sink of  $O_3$ was argued as the reason of the difference between the Chapman mechanism, and measurements. In the second half of the 20<sup>th</sup> century, that sink was established to be related to catalytic reactions involving radicals such as OH (HO<sub>x</sub>-cycle, *Bates and Nicolet*, 1950), NO (NO<sub>x</sub>-cycle, *Crutzen*, 1970; *Johnston*, 1971), Cl (ClO<sub>x</sub>-cycle, *Molina and Rowland*, 1974), Br (BrO<sub>x</sub>-cycle, *Wofsy et al.*, 1975), and possibly I (IO<sub>x</sub>-cycle, *Solomon et al.*, 1994). These catalytic reactions proceed as

$$X + O_3 \longrightarrow XO + O_2$$
 (4.10)

$$XO + O \longrightarrow X + O_2$$
 (4.11)

net: 
$$O_3 + O \longrightarrow 2O_2$$

where X is the catalyst (OH, NO, Cl, Br, or I). These cycles result in a loss of  $O_x$  (see Fig. 4.3), while the catalyst is recycled. Thus, the relevance of the catalytic cycle toward the ozone depletion depends on the number of cycles completed before X is lost by some sink mechanism. The catalysts involved in these cycles are addressed in detail in Sect. 4.2 to 4.4.



Figure 4.3: Calculated fractional contribution  $O_x$  loss by catalytic cycles:  $HO_x$ ,  $NO_x$ ,  $ClO_x$ ,  $BrO_x$ and  $IO_x$  (negligible). In general, the removal of  $O_x$  in the stratosphere is directed by  $BrO_x$  and  $HO_x$  reactions in the low stratosphere, by  $NO_x$  reactions between 25-40 km, and by the  $ClO_x$ catalytic cycle for higher altitudes. Adopted from WMO (2007).

Stratospheric ozone is mostly produced at equatorial regions where the quantum yield is higher. Also because of the high irradiation, the photochemical destruction of  $O_3$  is also higher in the tropics. Thus, ozone does not accumulate over the Equator. On the contrary, through the Brewer-Dobson circulation (Chap. 3),  $O_3$  gets transported toward the cold subpolar regions. During winter, ozone concentrations over the poles do not increase due to the lack of sunlight. But after the polar sunrise, photolytic reactions can take place and ozone shows maximum concentrations over the poles as shown e.g. in Fig. 4.4. However, this springtime maximum is perturbed in case of *stratospheric ozone hole* situation, an event that will be addressed in Chap. 5.



Figure 4.4: Enhanced  $O_3$  total column density during the polar sunrise (01.04.2010). The color code provides the ozone column density, in Dobson units. Image from the Ozone Monitoring Instrument (OMI, Nasa).  $O_3$  total column retrieved by DOAS method (TEMIS/BIRA). Note: 1 Dobson Unit  $\equiv$  1 DU = 0.01 mm film thickness of pure ozone at the ground (2.69·10<sup>20</sup> molecules/m<sup>2</sup>). Adopted from Veefkind et al. (2006).

Main sources of tropospheric ozone are downward transport from the stratosphere (accounting for 50% of the total tropospheric  $O_3$ , *Fishman and Crutzen*, 1978), and reactions comprising nitrogen oxides (see also Sect. 4.3):

$$NO_2 \xrightarrow{h\nu} NO + O$$
  $(\lambda \le 420 \text{ nm})$  (4.12)

$$O + O_2 \xrightarrow{M} O_3 \tag{4.13}$$

In case of a polluted troposphere, reactions of organic compounds involving the degradation of

methane or higher hydrocarbons, also yield ozone, in addition to water and carbon monoxide. The later can undergo further reactions yielding  $CO_2$  and hydrogen :

$$CO + OH \longrightarrow CO_2 + H$$
 (4.14)

$$H + O_2 \xrightarrow{M} HO_2.$$
 (4.15)

According to *Fishman and Crutzen* (1978), HO<sub>2</sub> can produce ozone in case of high NO<sub>x</sub> (> 10 pptv) by the reaction

$$HO_2 + NO \longrightarrow OH + NO_2$$
 (4.16)

followed by reactions (4.12) and (4.13). However, in case of low  $NO_x$ ,  $HO_2$  acts as an ozone sink:

$$HO_2 + O_3 \longrightarrow CO_2 + O_2$$

$$(4.17)$$

Further tropospheric ozone sinks are photolysis, as well as catalytic reactions with  $NO_x$ ,  $HO_x$  and halogen oxides as detailed below.

## 4.2 Hydrogen oxide radicals

Transported from the troposphere, and also resulting from the oxidation of methane and molecular hydrogen, water vapor is present in the stratosphere, and represents the main source of the hydroxyl radical:

$$H_2O + O(^1D) \longrightarrow 2OH$$
 (4.18)

$$CH_4 + O(^1D) \longrightarrow OH + CH_3$$
 (4.19)

$$H_2 + O(^1D) \longrightarrow OH + H$$
 (4.20)

At the same time, water is also dominant sink of the hydrogen oxide family  $HO_x=H+OH+HO_2$ .

Catalytic  $O_x$  reactions involving the  $HO_x$  family are

#### CHAPTER 4. ATMOSPHERIC CHEMISTRY

$$OH + O \longrightarrow O_2 + H$$
 (4.21)

$$H + O_2 \xrightarrow{M} HO_2$$
 (4.22)

$$HO_2 + O \longrightarrow OH + O_2$$
 (4.23)

net :  $2O \longrightarrow O_2$ 

$$OH + O_3 \longrightarrow HO_2 + O_2$$
 (4.24)

$$HO_2 + O_3 \longrightarrow OH + 2O_2$$
 (4.25)

$$net: 2 O_3 \longrightarrow 3 O_2$$

As shown in the above reactions (4.24) and (4.25),  $HO_x$  can remove ozone even in the absence of atomic oxygen and, hence, affects the chemistry at lower altitudes.

Termination of the catalytic cycle requires sinks of  $HO_x$ , which arise from reactions such as

$$OH + HO_2 \longrightarrow H_2O + O_2$$
 (4.26)

in the upper and middle stratosphere, and from

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$$
 (4.27)

$$OH + H_2O_2 \longrightarrow H_2O + HO_2$$
 (4.28)

net : 
$$OH + HO_2 \longrightarrow H_2O + O_2$$

in the low stratosphere. Additionally,  $HO_x$  may react with  $NO_2$  and, through three-body reactions, get transformed into the  $HNO_3$  and the  $HO_2NO_2$  reservoirs.

The main oxidant in the troposphere is the hydroxyl radical and, since potentially harmful trace gases are emitted into that layer, OH is often referred to as the "cleansing agent" of the lower atmosphere. In fact, only few trace gases such as e.g. nitrous oxide (N<sub>2</sub>O), chlorofluorocarbons (CFC's), and carbon dioxide (CO<sub>2</sub>), do not get oxidized by the hydroxyl radical. The main source of OH is through reaction (4.18) after ozone photolysis (see Fig. 4.5), which in the troposphere takes place in the narrow spectral range of 290-320 nm (e.g. *Matsumi et al.*, 2002). Thus, some ozone molecules are needed in the troposphere in order to assure the production of OH and,

#### 4.3. NITROGEN OXIDE RADICALS

hence, to maintain a balance in the oxidising capacity of the atmosphere. The concentration of OH in the troposphere is of the order of  $10^6$  molec/cm<sup>3</sup>, however it is very variable due to its fast removal (~ 1 s). Although regenerated via NO<sub>x</sub> chemistry (see Sect. 4.3), major OH sinks are CO and CH<sub>4</sub>, which are pollution and greenhouse gases, respectively. Accordingly, the OH residence time in the atmosphere is often linked to anthropogenic emissions. Further details on OH sources such as the anthropogenic methylchloroform, as well as a summary of the OH trend since pre-industral times may be found in e.g. WMO (1995), Lelieveld et al. (2004), and Solomon et al. (2007).



Figure 4.5: Correlation of tropospheric  $O_3$  photolysis frequencies and OH concentration (16.08.1994; 53°N, 11°E). The correlation coefficient is 0.915. Adopted from Ehhalt (1999).

## 4.3 Nitrogen oxide radicals

The main source of the NO<sub>x</sub> species (NO<sub>x</sub>=NO+NO<sub>2</sub>) in the stratosphere involves O(<sup>1</sup>D), and the nitrous oxide (N<sub>2</sub>O):

$$O(^{1}D) + N_{2}O \longrightarrow 2NO \qquad (58\%)$$

$$(4.29)$$

$$\rightarrow$$
 N<sub>2</sub> + O<sub>2</sub> (4.30)

Nitrous oxide is a greenhouse gas resulting from natural and anthropogenic sources such as e.g. oceans, tropical forests, biomass burning and artificial fertilizers. In the troposphere there are no relevant sinks of this trace gas, which is eventually transported into the stratosphere. Once there, the main sinks of  $N_2O$  are photolysis

$$N_2O \xrightarrow{h\nu} N_2 + O(^1D) \qquad (\lambda \le 398 \text{ nm}) \qquad (4.31)$$

accounting for 90% of the N<sub>2</sub>O removal, and reaction (4.29). With a lifetime of 120 years (*Houghton et al.*, 2001), N<sub>2</sub>O has accumulated in the atmosphere from  $\sim 270$  to 322 ppbv (pre-industrial times to 2008), with an increasing rate of 0.78 ppbv per year from 1998 to 2008 (*WMO-GAW*, 2009).

Another source of stratospheric  $NO_x$  are aircraft emissions due to oxidation of atmospheric  $N_2$  to NO. Additionally, at mid to high-latitudes during winter and early spring,  $NO_x$  is transported into the stratosphere from the mesosphere and thermosphere. At those higher atmospheric layer, the solar proton events, galactic cosmic rays and energetic electron precipitation, represent sources of total reactive nitrogen  $NO_y^1$  (*Rozanov et al.*, 2005; *Engel et al.*, 2006). On the other hand, the removal of reactive nitrogen takes place mainly in the upper stratosphere through

$$NO + N \longrightarrow N_2 + O.$$
 (4.32)

Exchanges within the  $NO_x$  family occur through reactions such as

$$NO + HO_2 \longrightarrow NO_2 + OH$$
 (4.33)

$$NO + RO_2 \longrightarrow NO_2 + RO$$
 (4.34)

$$NO + XO \longrightarrow NO_2 + X$$
 (4.35)

where  $RO_2$  represents an organo peroxy radical (CH<sub>3</sub>O<sub>2</sub> is the most most abundant one in the stratosphere), and X stands for Cl or Br. Additionally, conversion of NO to NO<sub>2</sub> can also involve reactions with O<sub>x</sub> such as

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 (4.36)

$$\operatorname{NO}_2 \xrightarrow{h\nu} \operatorname{NO} + \operatorname{O} \qquad (\lambda \le 405 \text{ nm})$$
 (4.37)

$$O + O_2 \xrightarrow{M} O_3$$
 (4.38)

not affecting the net abundance of ozone, and also through catalytic reactions depleting ozone:

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 (4.39)

$$NO_2 + O \longrightarrow NO + O_2$$
 (4.40)

net: 
$$O_3 + O \longrightarrow 2O_2$$

<sup>1</sup>Chemical family  $NO_y = NO_x + NO_3 + 2 N_2O_5 + HNO_3 + ClONO_2 + HO_2NO_2 + BrONO_2$ 

Thus, reaction (4.40) is the limiting step in the ozone loss, and the O<sub>3</sub> concentration can be derived from the *Leighton ratio* (i.e.,  $\frac{NO}{NO_2}$ ). Termination of the ozone loss cycle implies oxidation of NO<sub>2</sub>, which during the day evolves as

$$NO_2 + OH \longrightarrow HNO_3$$
 (4.41)

$$\xrightarrow{M}$$
 HOONO (4.42)

$$\text{HNO}_3 \xrightarrow{h\nu} \text{NO}_2 + \text{OH}$$
 (4.43)

$$HNO_3 + OH \longrightarrow NO_3 + H_2O$$
 (4.44)

$$NO_3 \xrightarrow{h\nu} NO_2 + O$$
 (4.45)

where reaction (4.42) readily NO<sub>2</sub> and OH, and reaction (4.45) takes place within seconds. On the other hand, during dusk and over the night, the NO<sub>2</sub> oxidation yields  $N_2O_5$  through

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
 (4.46)

$$NO_3 + NO_2 \xrightarrow{M} N_2O_5.$$
 (4.47)

 $N_2O_5$  can then be removed by different mechanisms:

$$N_2O_5 \xrightarrow{n\nu} NO_3 + NO_2 \qquad (\lambda \le 1252 \text{ nm})$$
 (4.48)

$$N_2O_5 \xrightarrow{M} NO_3 + NO_2$$
 (4.49)

$$N_2O_5 + H_2O(s) \longrightarrow 2 HNO_3(s)$$
 (4.50)

where reaction (4.50) stands for hydrolysis on the surface of aerosols, and (s) represents the condensed phase (see Sect. 4.5). Thus, HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> serve as reservoirs of NO<sub>x</sub> and are part of the NO<sub>y</sub> family. Within weeks HNO<sub>3</sub> can be recycled back into NO<sub>x</sub> in the stratosphere, while in the lower troposphere HNO<sub>3</sub> gets ultimately removed by deposition within days. The stratospheric daily evolution of NO<sub>x</sub>, together with the NO<sub>3</sub>, HNO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> reservoirs are shown in Fig. 4.6.

Additional  $NO_x$  reservoirs comprise halogen compounds involving reactions such as



Figure 4.6: Modeled diurnal variation of NO<sub>2</sub>, NO, HNO<sub>3</sub>, NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> (25 km). The dashed lines show the time of sunrise and sunset (90° solar zenith angle, SZA). Model run for the 1-D chemical model LABMOS. Adopted from Butz (2006).

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$$NO_2 + ClO \xrightarrow{M} ClONO_2$$
 (4.51)

$$NO_2 + BrO \xrightarrow{M} BrONO_2$$
 (4.52)

followed by the NO<sub>2</sub> release through photolysis:

$$\text{ClONO}_2 \xrightarrow{h\nu} \text{Cl} + \text{NO}_3 \qquad (\lambda \le 735 \text{ nm}) \qquad (4.53)$$

$$\xrightarrow{n\nu} \text{ClO} + \text{NO}_2 \qquad (\lambda \le 1065 \text{ nm}) \qquad (4.54)$$

$$\operatorname{BrONO}_2 \xrightarrow{h\nu} \operatorname{Br} + \operatorname{NO}_3 \qquad (\lambda \le 861 \text{ nm}) \qquad (4.55)$$

$$\xrightarrow{n\nu} \text{BrO} + \text{NO}_2 \qquad (\lambda \le 1129 \text{ nm}) \qquad (4.56)$$

Overall, in the stratosphere the main  $NO_x$  reservoirs are inorganic compounds, and the main sink of stratospheric  $NO_y$  is its downward transport into the troposphere. In the troposphere organic forms of reactive nitrogen such as e.g the peroxyacetyl nitrate, also called PAN (CH3C(O)OONO<sub>2</sub>), can also act as a reservoir of  $NO_x$  (e.g., *Singh and Hanst*, 1981). PAN is generated from oxidation of hydrocarbons emitted from e.g. combustion and biomass burning. In the low troposphere PAN and NO<sub>x</sub> are near chemical equilibrium, but at lower temperatures in the upper troposphere, the residence time of PAN is of several months. Therefore, PAN represents a reservoir in the upper troposphere and, thus, serves as a long-transport carrier of NO<sub>x</sub> (e.g., Jacob, 1999; Glatthor et al., 2007).

In general, assuming a steady-state of  $HO_x$  in a clean environment (low  $NO_x$ ), the overall formation of tropospheric ozone follows the OH concentration. However, at very low  $NO_x$  levels, reactions resulting in ozone production slow down (e.g. photolysis of  $NO_2$ ), until a threshold of  $NO_x$  is reached (~0.07 ppbv), where ozone begins to be depleted (e.g. Fig. 4.7).



Figure 4.7: Tropospheric production rate of  $O_3$  in a clean environment based on the  $NO_x$  family (assuming a steady-state of  $HO_x$ ). Adopted from Ehhalt (1999).

## 4.4 Halogen oxide radicals

Although the sources of the halogen oxides have their origin in the troposphere, the importance of these radicals became clear nearly 40 years ago, when their ozone loss catalytic reactions taking place in the stratosphere were discovered (*Molina and Rowland*, 1974; *Wofsy et al.*, 1975; *Farman et al.*, 1985). These catalytic reactions leading to ozone loss are summarized as

$$X + O_3 \longrightarrow XO + O_2$$
 (4.57)

$$XO + O \longrightarrow X + O_2$$
 (4.58)

net: 
$$O_3 + O \longrightarrow 2O_2$$
 (4.59)

for X being atomic chlorine (Cl), bromine (Br) and iodine (I). The other two halogens, astatine (At) and fluorine (F), are not included in these reactions since At is not relevant for atmospheric

processes, and atmospheric F is rapidly converted to the stable trace gas HF by methane and water reactions. Additionally to reactions (4.57)-(4.59), catalytic ozone loss also occurs through

$$X + O_3 \longrightarrow XO + O_2$$
 (4.60)

$$Y + O_3 \longrightarrow YO + O_2 \tag{4.61}$$

$$XO + YO \longrightarrow X + Y + O_2$$
 (4.62)

net: 
$$2 O_3 \longrightarrow 3 O_2$$

where X=OH and Y=Cl, X=OH and Y=Br. If or X and Y are both halogen atoms, then their cross-reaction (4.62) may yield XY + O<sub>2</sub>, or OXO + Y.

The relative relevance of the  $\text{ClO}_x^2$ ,  $\text{BrO}_x^3$  and  $\text{IO}_x^4$  families as sinks of stratospheric odd oxygen depends not only on the efficiency of the catalytic cycle, but also on the distribution and residence times of their respective source gases. In general, the *Ozone Depletion Potential* ODP<sup>5</sup> of bromine compounds is about 60 times higher than the ODP of chlorine species (*WMO*, 2007). Although the ODP of the iodine species is even higher than for bromine and chlorine (e.g. *Solomon et al.*, 1994; *Davis and Marshak*, 1997; *WMO*, 2007), gaseous iodine radicals have not been unambiguously detected in the stratosphere (e.g. *Bösch et al.*, 2003; *Butz et al.*, 2009). Up to date, the effect of iodine on stratospheric ozone loss is considered "unlikely" (*WMO*, 2007). However, organic iodine compounds and iodinated particles have been found in the tropical UT/LS (e.g., *Davis et al.*, 1996; *Murphy et al.*, 1998; *Murphy and Thompson*, 2000). Hence, the budget and impact of the iodine radicals in the stratosphere remains an open question.

Since halogen compounds are a core topic in this work, this section reports on the overall **Reactive Halogen Species**  $(RHS)^6$ , addressing their major sources and sinks from a global perspective. Furthermore, this section gives details on the RHS reaction pathways, and their influence on the tropospheric and stratospheric chemistry, summarized in Fig. 4.8. Additionally Chap. 5 focuses on the processes involving RHS in the polar regions.

 $<sup>^{2}</sup>$ ClO<sub>x</sub>=Cl+ClO+2 Cl<sub>2</sub>O<sub>2</sub>

 $<sup>^{3}\</sup>text{BrO}_{x}=\text{Br}+\text{BrO}$ 

 $<sup>{}^{4}</sup>IO_{x} = I + IO$ 

<sup>&</sup>lt;sup>5</sup>Ozone Depletion Potential (ODP): effectiveness for global ozone depletion (per-atom basis)

 $<sup>^{6}</sup>$ RHS= X, XO, X<sub>2</sub>, XY, OXO, HOX, XONO<sub>2</sub> and XNO<sub>2</sub>, with X,Y being Cl, Br, and I

#### 4.4.1 Reactive halogen species in the troposphere

Triggered by their impact on the stratospheric ozone depletion, extensive laboratory studies and field measurements have been performed for over 30 years, aiming at the characterization of the tropospheric sources, pathways, sinks and impacts of RHS. A summary is given below.

#### Sources of tropospheric RHS

Main known sources of halogens in the troposphere involve (1) photolytic degradation of halogenated organic compounds (halocarbons) arising from terrestrial and marine emissions, and (2) the release of inorganic halogen compounds from aqueous sea salt aerosols and, to a lesser extend, also from volcanoes (e.g. *Symonds et al.*, 1988; *Bobrowski et al.*, 2003). While, together with  $I_2$ , (1) is believed to be the major source of iodine in the form of biogenic emissions in coastal areas, (2) represents a constant release mechanism of Cl and Br. A com-



Figure 4.8: Pathways scheme of the reactive halogen species. Note that hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are added on top of the chlorofluorocarbons (CFCs) based on WMO (2007) (refer to the text). Adapted from Von Glasow and Crutzen (2007).

prehensive summary of the different RHS sources are presented by e.g. Carpenter et al. (2003), Sander et al. (2003), Platt and Hönninger (2003), and Von Glasow and Crutzen (2007).

#### 1. Release of RHS from photolytic degradation of halocarbons

Organohalogens or halocarbons are emitted into the atmosphere by anthropogenic sources (e.g. biomass burning, industries), and also by natural sources (e.g. macroalgae at coastal sides, phytoplankton in the ocean, *Schall and Heumann*, 1993). Eventually, those organic compounds photodissociate, releasing halogen atoms into the troposphere (if short-lived), and also into the stratosphere (if long-lived).

While sea salt aerosol appears to be the major source of reactive bromine and chlorine compounds (see below), the emission of molecular iodine (from macroalgae and phytoplankton), and of halogenated hydrocarbons and their photolysis is the major source of reactive iodine species.

An overview of natural and anthropogenic emissions of organohalogens can be found in e.g. *Gribble* (2003), *Yang et al.* (2005), and *WMO* (2007), and a summary of their typical mixing ratios and atmospheric lifetimes is given in Table 4.1.

In general, tribromomethane or bromoform (CHBr<sub>3</sub>) is one of the main natural bromine source gases, with an oceanic emission rate of 0.2-1.0 Tg/y (e.g. Yang et al., 2005; *Carpenter and Liss*, 2000). Additionally, CHBr<sub>3</sub> also derives from human emissions (e.g. swimming pools). Bromomethane or methyl bromide (CH<sub>3</sub>Br), with an emission rate of ~ 0.131 Tg/y (*Montzka et al.*, 2003), has natural sources (oceans), and also anthropogenic ones (e.g. fumigants, leaded petrol, biomass burning). Main natural chlorine sources are CHCl<sub>3</sub> and CH<sub>3</sub>Cl (contributing ~ 45% of the chlorine budget). Iodine containing hydrocarbons like iodoform (triiodomethane, CHI<sub>3</sub>), diiodomethane (CH<sub>2</sub>I<sub>2</sub>) and short-chained organic halogens (e.g. CH<sub>2</sub>CII) are naturally emitted and rapidly photolysed into RHS (e.g.,  $CH_3I \xrightarrow{h\nu} CH_3 + I$ ). All these halogenated organic compounds emitted in the low troposphere are short-lived and, thus, may affect the tropospheric photochemistry.

On the other hand, the anthropogenic chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and halons (e.g. Halon-1301 or bromotrifluoromethane,  $CBrF_3$ ), are long-lived species and can eventually get transported into the stratosphere. Therefore, these halocarbons represent potential precursors of ozone depleting RHS in the stratosphere (see Sect. 4.4.2). Since 1987, their emissions have been regu-

Common name	Chemical formula	Lifetime	Mixing ratio	
		y ears	pptv	
Chlorine				
CFC-12	$\mathrm{CCl}_2\mathrm{F}_2$	100	540	
CFC-11	$CCl_3F$	45	254	
CFC-113	$\mathrm{CCl}_2\mathrm{FCClF}_2$	85	79	
HCFCs	$\mathrm{CH}_x\mathrm{Cl}_y\mathrm{F}_z$	1-20	205	
Carbon tetrachloride	$\operatorname{CCl}_4$	26	95	
Methyl chloride	$CH_3Cl$	1	527	
Methyl chloroform	$CH_3CCl_3$	0.5	22	
Bromine				
Halon-1211	$\mathrm{CBrClF}_2$	16	4.5	
Halon-1301	$\mathrm{CBrF}_3$	65	2.8	
Other halons		3-20	$\sim 1$	
Methyl bromide	$CH_3Br$	0.7	9	
Short lived species		12-150  days	variable	
Iodinine				
Methyl iodide	$CH_{3}I$	0.02	0.1-2	
Chloroiodomethane	$CH_2ICl$	Hours	0.35	

Table 4.1: Atmospheric lifetime and mixing ratios (in 2004) for the primary halogen source gases. Adapted from WMO (2007).

lated by the Montreal Protocol on Substances that Deplete the Ozone Layer and amendments. Moreover, these long-lived halocarbons are also considered greenhouse gases, and, as shown in Fig. 4.9, their effect on the radiative forcing has been dealt with since 1997 under the Kyoto Protocol (United Nations Framework Convention on Climate Change, UNFCCC). Thus, halogen compounds, their sources, sinks and pathways are actually a health-climate issue. A summary of the benefit of the Montreal Protocol toward climate protection is given e.g. by (*Velders et al.*, 2007).

#### 2. Release of RHS from sea salt

Sea salt aerosols are produced from air bubbles bursting as depicted in Fig. 4.10. The release of inorganic RHS from those sea salt aerosols, firstly introduced by *Holland* (1978), is the main source of halogen emissions into the lower troposphere.

Since oceans contain rather high amounts of Cl and Br ions, and to a lesser extend iodine ones (Table 4.2), ocean waters are considered large reservoirs of mainly chlorine and bromine. As exemplified for Cl in Fig. 4.11, the release of RHS from sea salt aerosols (and also deposits such as salt lakes) takes place through heterogeneous reactions comprising the following mechanisms: Table4.2: Sea water ionic composition.Adopted from Jaenicke (1988) andAndrews et al. (1996).

Ionic species	$Cl^{-}$	$Na^+$	$Mg^{2+}$	$\mathbf{SO}_4^{2-}$	$\mathbf{K}^+$	$Ca^{2+}$	$HCO_3^-$	$\mathrm{Br}^-$	$\mathbf{I}^{-}$
Concentration (mmol/l)	550	470	53	28	10	10	2	0.85	$10^{-3}$

(2.a) Release of gaseous hydrogen halides by acid displacement (e.g., Wayne et al., 1995). Strong acids such as  $HNO_3$  and  $H_2SO_4$  may react with the sea salt aerosol so that

$$H_2SO_4 + 2NaX(s) \longrightarrow 2HX + NaSO_4(s)$$
 (4.63)

$$HNO_3 + 2NaX(s) \longrightarrow HX + NaNO_3(s)$$
 (4.64)

where X = Cl, I, and (s) stands for aerosol surfaces. The released hydrogen halide may be then deposited, or taken-up by aerosols and recycled into RHS (see below).

(2.b) Release of halogenated nitrogen oxides from reactions involving  $NO_y$  (e.g., Finlayson-Pitts et al., 1989; Mozurkewich, 1995; Herrmann et al., 2003)



Figure 4.9: Relative contribution of the main greenhouse gases to the overall increase of the radiative forcing (based on 1750) between (a) 1979–1984, and (b) 2003–2008. Although the effect of halocarbons such as CFCs and halons has decreased, long-lived HCFCs and HFCs are gaining importance. Adopted from WMO-GAW (2009).



Figure 4.10: The bubble-burst mechanism. (a) Air bubble rises to the ocean surface creating a film interface (b) Rupture of the interface releasing sea-spray particles (c) Emission of large jet sea-spray droplets (d) Small salt particles result airborne. Adopted from Von Glasow and Crutzen (2007).

$$N_2O_5 + NaX(s) \longrightarrow XNO_2 + NaNO_3(s)$$
 (4.65)

$$XNO_2 \xrightarrow{h\nu} H + NO_2$$
 (4.66)

$$XNO_2 + NaY(s) \longrightarrow XY + NaNO_2(s)$$
 (4.67)

$$XY \xrightarrow{h\nu} X + Y \tag{4.68}$$

$$2NO_2 + NaX(s) \longrightarrow XNO + NaNO_3(s)$$
 (4.69)

$$NO_3 + NaX(s) \longrightarrow X + NaNO_3(s)$$
 (4.70)

For X,Y= Br, Cl. Hence, reactions (4.65) and (4.70) represent night-time accumulation sources of RHS (e.g., *Osthoff et al.*, 2008; *Gershenzon et al.*, 1999).

### (2.c) Oxidation of halides (e.g., Fan and Jacob, 1992; Sander et al., 1997)

Although ozone and OH react with halides (e.g., *Oum et al.*, 1998; *Knipping et al.*, ), their most likely oxidant are the inorganic halogen reservoirs  $XNO_3$  and mainly HOX (previously taken-up by aerosols):

$$HOX \longrightarrow HOX(aq)$$
 (4.71)

$$HOX(aq) + Y^{-}(aq) + H^{+}(aq) \longrightarrow XY(aq) + H_2O$$

$$(4.72)$$

$$XY(aq) \longrightarrow XY$$
 (4.73)

$$XY \xrightarrow{h\nu} X + Y$$
 (4.74)



Figure 4.11: Schematic of chlorine activation by night-time  $NO_x$  chemistry. Sources and mechanisms yielding the release of Cl from  $ClNO_2$  produced after heterogeneous reactions. Adopted from Thornton et al. (2010).

where (aq) stands for the liquid phase. Note that e.g., based on reaction (4.72), for X=I and Y=Br, the ocean serves as night-time reservoir of I and Br that may be activated in the marine boundary layer (MBL) upon sunrise (e.g., Fig. 4.12).

The autocatalytic release of bromine through these heterogeneous reactions (X=Y=Br) triggered the term "bromine explosions" (e.g., Fan and Jacob, 1992; Platt and Lehrer, 1996; Simpson et al., 2007). These bromine explosions, firstly discovered in the Arctic troposphere, yield extreme tropospheric Ozone Depletion Events (ODEs). As main topics of this work, sources for the bromine explosions in the polar regions will be address in Chap. 5.

#### Pathways and sinks of RHS

Once atomic halogens are released from organic or inorganic halogenated compounds into the troposphere, they get rapidly oxidised by ozone ( $\tau_{Cl} = 0.13$  s,  $\tau_{Br,I} = 1.3$  s, assuming a typical tropospheric vmr of 50 ppb), and eventually photolysed:

$$X + O_3 \longrightarrow XO + O_2$$
 (4.75)

$$XO \xrightarrow{h\nu} X + O$$
 (4.76)

where X denotes Cl, Br, or I. For reaction rates, the reader is kindly referred to e.g. *Atkinson et al.* (2007). The different pathways of these atomic and oxide halogens, summarized in Fig. 4.13, are described in the following, where *Ozone Depleting Cycles* are indicated as "*ODC*".



Figure 4.12: Monthly averaged diurnal evolution of vmr of IO and BrO in the marine boundary layer (16.85°N, 24.87°W, local noon is at GMT-1). Adopted from Mahajan et al. (2010).

- $XO_x$  and  $O_x$ 
  - \* Halogen oxides self-reactions:

$$2X + 2O_3 \longrightarrow 2XO + 2O_2 \tag{4.77}$$

$$XO + XO \longrightarrow 2X + O_2 85\%$$
 (4.78)

$$\longrightarrow$$
 X<sub>2</sub> + O<sub>2</sub> 15% (4.79)

$$X_2 \xrightarrow{h\nu} 2X$$
 (4.80)

net ODC I:  $2 O_3 \longrightarrow 3 O_2$ 

where if X=Cl, self-reaction may yield the  $Cl_2O_2$  dimer, that readily gets decomposed into ClO. In the case of X=Br, reaction (4.78) is favoured over reaction (4.79) (85%, 15% at SZA=70°). If X=I, the above self-reaction yields OIO and  $I_2O_2$ , which may lead to the formation of new particles (see below). \* Halogen oxides cross-reactions:

$$X + O_3 \longrightarrow XO + O_2$$
 (4.81)

$$Y + O_3 \longrightarrow YO + O_2 \tag{4.82}$$

$$XO + YO \longrightarrow X + Y + O_2$$
 (4.83)

$$\longrightarrow$$
 XY + O<sub>2</sub> (4.84)

$$\longrightarrow$$
 OXO + Y (4.85)

$$XY \xrightarrow{h\nu} X + Y$$
 (4.86)

net ODC II: 
$$2 O_3 \longrightarrow 3 O_2$$

with photolysis (4.86) is a very fast mechanism (X, Y= Cl, Br, or I). In general, halogen cross-reactions (X=Br and Y=Cl) are faster than the halogen self-reactions (ODC I).

This cross-halogen cycle is limited by reaction (4.83), which may be affected by the removal of halogen oxides through photolysis, and also through reactions with NO:

$$XO \xrightarrow{h\nu} X + O$$
 (4.87)

$$XO + NO \longrightarrow X + NO_2$$
 (4.88)

Cross-halogen reactions may also involve ozone null cycles:

$$X + O_3 \longrightarrow XO + O_2$$
 (4.89)

$$Y + O_3 \longrightarrow YO + O_2 \tag{4.90}$$

$$XO + YO \longrightarrow OXO + Y$$
 (4.91)

$$\xrightarrow{M} \text{XOYO} \tag{4.92}$$

$$OXO \xrightarrow{n\nu} XO + O \tag{4.93}$$

$$O + O_2 \xrightarrow{M} O_3$$
 (4.94)

and, additionally, the halogen dioxides may also react with NO  $(OXO + NO \longrightarrow XO + NO_2)$ , with the rate coefficient decreasing from iodine to bromine and chlorine.

If X=I and Y=Br, reaction (4.91) is favoured over reaction (4.83). Also, reaction (4.93) may lead to  $IO_2$  and, thus, to further ozone removal (e.g. *Hebestreit et al.*, 2000; *Sander et al.*, 2003). These iodine reactions are believed to be involved in particle bursting at coastal regions, which currently is a topic of active research due to its potential climate impact (e.g., *O'Dowd et al.*, 2002; *McFiggans et al.*, 2004; *McFiggans et al.*, 2010).

#### 4.4. HALOGEN OXIDE RADICALS

•  $XO_x$  and  $HO_x$  radicals

In the presence of the hydroperoxy radical resulting from

$$OH + O_3 \longrightarrow HO_2 + O_2$$
 (4.95)

halogen oxides may initiate an ozone loss catalytic cycle:

$$X + O_3 \longrightarrow XO + O_2$$
 (4.96)

$$XO + HO_2 \longrightarrow HOX + O_2$$
 (4.97)

$$HOX \xrightarrow{h\nu} X + OH \tag{4.98}$$

$$OH + CO \xrightarrow{O_2} CO_2 + HO_2$$
 (4.99)

net ODC III:  $CO + O_3 \longrightarrow CO_2 + O_2$ 

Thus, for high concentrations of halogen oxides, ODC I and II dominate the removal of ozone. For low XO abundances, however, ODC III determines the ozone loss.

Considering the above ODC I-III, and assuming no loss of RHS, an upper limit of the ozone loss rate as a function of XO concentration may be derived:

$$-\frac{d[O_3]}{dt} = 2 \cdot \left( \sum_{i,j} k_{X_i O + Y_j O} \cdot [X_i O] \cdot [Y_j O] \right) + \sum_i k_{X_i O + HO_2} \cdot [X_i O] \cdot [HO_2] \quad (4.100)$$

for X and Y = Br, Cl and I, and  $\sum_{i,j}$  represents the cross-halogen reactions between two halogens of index *i* and *j* (*Stutz et al.*, 1999).

Reaction (4.97) may undergo different pathways and, instead of HO<sub>2</sub>, the halogen oxides may react with organic peroxy radicals RO<sub>2</sub>, where R stands for the organic group (e.g., methyl peroxy radical, CH<sub>3</sub>O<sub>2</sub>). This branch may result in a rather effective way of recycling e.g. bromine oxide to hypobromus acid HOBr (*Aranda et al.*, 1997).

In general, hydroperoxy radicals and hydrocarbons (RH) may react with atomic halogens (instead of ozone in reaction (4.96)) resulting in halogen reservoirs:

$$X + RH \longrightarrow HX + R$$
 (4.101)

$$X + HO_2 \longrightarrow HX + O_2$$
 (4.102)

$$X + HO_2 \longrightarrow HOX + O_2$$
 (4.103)

Reaction (4.101) is in fact one of the major atmospheric sinks of active F (RH=CH<sub>4</sub>). Cl and Br may also react with RH, thus becoming reservoirs. However, the reaction  $X + O_3$ is favoured over X + RH for X = Cl (52%), Br (98%) and I (~100%). Furthermore, HX may be removed from the atmosphere by wet and dry deposition. Hence,  $HO_2$  and RHrepresent the main sinks of RHS in the troposphere.

•  $XO_x$  and  $NO_x$  radicals

In case of semi-polluted environments,

$$X + O_3 \longrightarrow XO + O_2$$
 (4.104)

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 (4.105)

$$\begin{array}{cccc} \mathrm{XO} + \mathrm{NO}_2 & \xrightarrow{M} & \mathrm{XNO}_3 & (4.106) \\ \mathrm{XNO}_3 & \xrightarrow{h\nu} & \mathrm{NO}_3 + \mathrm{X} & (4.107) \\ & \xrightarrow{h\nu} & \mathrm{NO}_2 + \mathrm{XO} & (4.108) \end{array}$$

$$\operatorname{NO}_3 \xrightarrow{h\nu} \operatorname{NO}_3 + \mathrm{X}$$
 (4.107)

$$\xrightarrow{\text{NO}} \text{NO}_2 + \text{XO} \qquad (4.108)$$

$$NO_3 \xrightarrow{h\nu} NO + O_2$$
 (4.109)

 $2O_3 \longrightarrow 3O_2$ net ODC IV:

Thus,  $XO + NO_x$  represent an ozone loss cycle. However, since reaction (4.108) yields an ozone null mechanism, this ODC is not as effective as ODC I-III. Additional pathways are also XNO<sub>3</sub> up-take by aerosols, and photolysis of NO<sub>3</sub> into NO<sub>2</sub> + O (null cycle).

Note that  $HO_2$  and XO may also act as oxidants to reconvert NO into  $NO_2$ :

$$NO + HO_2 \longrightarrow NO_2 + OH$$
 (4.110)

$$NO + XO \longrightarrow NO_2 + X$$
 (4.111)

#### • $XO_x$ and dimethylsulfied

Emitted mainly from phytoplankton into the MBL, dimethylsulfide (DMS,  $(CH_3)_2S$ ) is the major biogenic sulfur compound in the atmosphere, and its oxidation affects the aerosol budget in the MBL. Depending on the products, DMS is involved in creation of new small particles, or in the growth of existing ones and, thus, relevant from a climate perspective (e.g., Andreae, 1990). Toumi (1994) postulated that BrO may act as oxidant of DMS into dimethyl sulfoxide (BrO + DMS  $\rightarrow$  DMSO + Br). Since then, diverse studies aim at the characterization of the XO + DMS pathways, as well as their potential climate impact (e.g., von Glasow and Crutzen, 2004; Read et al., 2008).

#### • $XO_x$ and mercury

Mercury (Hg) is a toxic pollutant present in the atmosphere due to natural (e.g.,

#### 4.4. HALOGEN OXIDE RADICALS

volcanoes, oceans) and anthropogenic emissions (e.g., leaded petrol, coal combustion). In its gas phase (Hg<sup>0</sup>)– also referred to as Gaseous Elementary Mercury (GEM)– mercury can be worldwide transported from its sources (lifetime 0.5-1 year). Schroeder et al. (1998) reported depletion of GEM in the Arctic, correlated to ozone depletion events. Since then many attempts have been made to improve the understanding of these "Atmospheric Mercury Depletion Events", AMDEs (e.g. Ariya et al., 2004; Steffen et al. (2008); Lu et al., 2001). Studies indicate that halogens, in particular bromine, may act as oxidants of GEM (e.g.,  $Br + Hg^0 \rightarrow HgBr$ ,  $BrO + Hg^0 \rightarrow HgO + Br$ ). The result are oxidised inorganic Hg compounds (also called Reactive Gaseous Mercury, RGM). Snow and ice surfaces may then scavenge these RGM. In addition to polar regions, distribution of atmospheric Hg on a global scale, as well as the role of non-polar oceans and seas in the Hg cycle have been recently summarized by Sprovieri et al. (2010).



Figure 4.13: Simplified scheme of gas an aqueous phase halogen reactions (X=Cl, Br, I). The blue square comprises only iodine-related pathways. Adopted from Von Glasow and Crutzen (2007).

Impacts of RHS on the lower atmosphere

Summarizing the pathways detailed above, the relevance of the RHS in the troposphere is due

to their impact on:

- The oxidising capacity of the atmosphere (RHS alter the cycles of the main atmospheric oxidants  $O_x$ ,  $HO_x$ , and also the Leighton ratio, e.g., reaction (4.111)).
- Catalytic ozone removal (up to complete removal via the so-called Ozone Depletion Events, see Chap. 5).
- Atmospheric lifetimes of further relevant species such as e.g. hydrocarbons and volatile organic compounds, VOC (e.g. *von Glasow*, 2010).
- Oxidation of DMS (potential climate impact).
- New particle formation by iodine species (potential climate impact).
- Removal of atmospheric elemental mercury (environmental and human-health issue, see Chap. 5).

#### 4.4.2 Reactive halogen species in the stratosphere

#### Sources of RHS in the stratosphere

Halogen source gases (SG) are found in the stratosphere as a result of atmospheric transport (see Chap. 3). The most effective transport of air masses into the stratosphere is related to strong convective events taking place in the tropics. As a result, even very short-lived substances (VSLS<sup>7</sup>) can be injected straight into the tropical tropopause layer (TTL). In general, as depicted in Fig. 4.14, SG in the UT/LS can be transported into higher altitudes, and distributed worldwide through the Brewer-Dobson circulation. Once in the stratosphere, those SGs are converted into RHS.

Source gases of  $\text{ClO}_x$  and  $\text{BrO}_x$  in the stratosphere result from natural and anthropogenic emissions, the later being the main source of airborne chlorine-containing substances (Fig. 4.15). On the other hand, as detailed in Sect. 4.4.1, iodinated SG are related to natural emissions, with the ocean as major source. Overall, the stratospheric total chlorine concentration is about 160 times higher than the total bromine budget (see Fig. 4.15), while the extend of the iodine budget is an open debate (e.g., *Butz et al.*, 2009). For halogen budgets refer to Fig. 4.16.

#### Pathways, sinks and impacts of RHS in the stratosphere

Once the catalyst  $XO_x$  reaches the stratosphere (X= Cl, Br and I), the chemical pathways of the RHS in the stratosphere are analogous to the above described tropospheric mechanisms.

<sup>&</sup>lt;sup>7</sup>Very Short-Lived Substance (VSLS): Halogen-containing substances with a lifetime < 0.5 years WMO (2007)



Chemical and Dynamical Processes Affecting VSLS

Figure 4.14: Processes related to the transport of halogenated compounds into the stratosphere. Adopted from WMO (2007).

Firstly postulated by *Molina and Rowland* (1974), halogens are key species in the removal of the shielding stratospheric ozone layer. This fact was confirmed later by *Farman et al.* (1985) with the discovery of the stratospheric ozone hole over polar regions (see Chap. 5). That drastic depletion of the total ozone column over Antarctica was related to the  $ClO_x/NO_x$  interaction. Since then, RHS and in particular chlorine, became topics of thorough research and their emission have been restricted since 1987 by the Montreal Protocol of Substances that Deplete the Ozone Layer and its amendments (see Fig. 4.17). For X=Cl, Br, I, main reactions involved in this  $XO_x/NO_x$  cycle removing ozone are

$$X + O_3 \longrightarrow XO + O_2$$
 (4.112)

$$XO + O \longrightarrow X + O_2$$
 (4.113)

net: 
$$O_3 + O \longrightarrow 2O_2$$
 (4.114)

Additionally, reactions of XO with OH and NO yield HO<sub>2</sub> and NO<sub>2</sub> radicals, that may speed



Primary Sources of Chlorine and Bromine for the Stratosphere in 2004

Figure 4.15: Primary source gases of chlorine and bromine in the stratosphere as measured in 2004. Most important ones are CFCs for chlorine (anthropogenic), and methyl bromide for bromine (mostly naturally emitted). Adopted from WMO (2007).

up the ozone loss.

In addition to the release of RHS involving the gaseous phase, the halogen activation via heterogeneous reactions is very effective in the stratosphere (see below).

Cross-halogen reactions also contribute effectively to the ozone loss after photolysis of their product gases. As an example of these cross-reactions:

$$BrO + ClO \longrightarrow Br + OClO 59\%$$
 (4.115)

$$\longrightarrow$$
 Br + ClO<sub>2</sub> 34% (4.116)

$$\longrightarrow$$
 BrCl + O<sub>2</sub> 7% (4.117)

where reaction 4.115 is often used as a tracer for the efficiency of the ClO-BrO catalytic cycle.

Although bromine, for instance, can also be recycled through  $CH_2O$ ,  $XO_x$  is mainly recycled through reactions with  $HO_2$  and  $NO_2$  (e.g.,  $XONO_2$ , HOX, HX). For a daily evolution of  $Br_y$ , refer to Fig. 4.18. In the case of chlorine, the release through photolysis is rather slow. Hence,



(c) Vertical profile of  $I_y$  upper limits

Figure 4.16: Halogen species in the stratosphere. (a) VMR of chlorine species  $(30^{\circ}-60^{\circ}N, 2004)$ , from WMO (2007), (b) Concentration and vmr of modeled and measured (DOAS, Kiruna, March 2004) bromine species for SZA=80° (solid) and 90° (dashed). Note that the legends are valid for both panels. Adopted from Dorf (2005). (c)  $I_y$  upper limits derived from IO and OIO DOAS measurements (Brazil) during sunrise and sunset. Dotted lines give photochemical modeling uncertainties, and the horizontal line indicate the tropopause. Adopted from Butz et al. (2009).



Figure 4.17: Evolution of chlorine and bromine (Montreal Protocol 1987). (a) Evolution of total chlorine profile in the midlatitude stratosphere (contribution of VSLS is not included) (WMO, 2007), (b) Trend of the  $Br_y$  budget. Adopted from Dorf et al. (2006). Updated by M. Dorf.
below 30 km (e.g., *Solomon*, 1999), Cl is mostly present as HCl and ClONO<sub>2</sub>. Bromine, on the other hand, is effectively activated through photolysis and, hence,  $BrO_x$  ODP is higher than  $ClO_x$ . Gaseous and particulate iodine species are photolytically very active. Hence, the ODP of  $IO_x$  is the highest of the three RHS (e.g., *WMO*, 2007). However, due to its short lifetimes,  $IO_x$  impact is thought to be constrained to the low stratosphere (e.g., *WMO*, 2007).



Figure 4.18: Modeled diurnal cycle of bromine species (at 18 and 40 km) for 44°N, 6°E (top), and 60°N, 11°E (bottom). The dashed lines show the time of sunrise and sunset (SZA=90°). Adopted from Theys (2010a).

### 4.5 Aerosol particles and heterogeneous chemistry

Aerosols are small solid or liquid particles in suspension in the atmosphere. As detailed in Chap. 2, their presence in the atmosphere affects the radiative transfer influencing the energy budget, and also the availability of light for photochemical reactions (actinic fluxes, e.g., *Jacobson*, 2005). Furthermore, aerosol particles also influence chemical reaction pathways, yielding heterogeneous reactions, i.e., reactions involving reactants on different phases (e.g. *Seinfeld and Pandis*, 1998).

Aerosol particles that are emitted into the atmosphere, by natural or anthropogenic processes, are referred to as *primary aerosols* (e.g., sea spray, wind blown dust, volcanic dust, soot). Addi-

tionally, as a result of physical-chemical interactions, particles may be also formed directly in the atmosphere. Those are referred to as *secondary aerosols*, which often are related to condensation of gases, or gas-to-particle conversion. Example of these secondary aerosols are sulfates (from e.g., biogenic and volcanic emissions), organics (from VOCs) and nitrates (from NO<sub>x</sub> emissions).

For simplicity, aerosol particles are often assumed to be spherical and may be classified according to their diameter (D). Thus, two major types of particles may be described: fine  $(D < 2.5 \ \mu m)$  and coarse particles  $(D > 2.5 \ \mu m)$ . Overall, most of the primary aerosols are coarse particles, while secondary aerosols are fine ones. As for sinks of particles, wet and dry deposition on surfaces are the main pathways.

The atmospheric residence time of the coarse particles is often quite short since, due to their mass, they may readily precipitate. On the other hand, very small particles have no effective deposition pathways. In general, from the moment they are emitted (or built up) until they are removed from the atmosphere within days or weeks, aerosols undergo different transformation mechanisms comprising growth through nucleation, coagulation (very small particles sticking together) and condensation (due to partial pressure differences between the aerosol and its surroundings). Thus, particles are often subdivided based on three transformation modes. Very small fine particles, D<0.08 $\mu$ m, exist in the so-called *Aitken range*. Those are eventually transformed into the *accumulation mode* (D>0.08 $\mu$ m), which may also act as cloud condensation nuclei (CNN). If no removal processes take place, accumulation mode aerosols eventually become coarse particles which, finally, are deposited onto surfaces. Figure 4.19 depicts these transformation mechanisms, while Table 4.3 summarizes the main features of the different types of aerosols found in the troposphere.

Coarse and fine particles may also be transported into the stratosphere. As a result of volcanic emissions, and also due to anthropogenic and biogenic processes, stratospheric aerosols contain water, nitric acid and sulfuric acid. The stratospheric aerosols located between 10–30 km are usually referred to as the *Junge-Layer* or *background aerosols* (i.e., non-volcanic situation), which comprise  $H_2SO_4/H_2O$  droplets (e.g., *Junge*, 1961). Further stratospheric aerosol particles are e.g. those developing under specific circumstances in the polar winter: the *Polar Stratospheric Clouds* (*PSCs*), which will be addressed in Chap. 5.

In contact with the gas phase, aerosol particles serve as medium for inter-phase chemical reactions. In general, those heterogeneous reactions require less energy than gas phase reactions and, therefore, reaction rates are higher. Particles may hence serve as sources or sinks for e.g. halogen species, pathways that may be also related to day or night-time chemistry (e.g. *Thornton et al.*, 2010). Relevant halogen heterogeneous reactions in the low troposphere involve



Figure 4.19: Schematic description of the aerosol modes. Adopted from Seinfeld and Pandis (1998).

sea salt particles and hydrochloric acid:

$$\operatorname{NaCl}(s) + \operatorname{HNO}_3 \longrightarrow \operatorname{HCl} + \operatorname{NaNO}_3$$
 (4.118)

Additionally, as shown in Fig. 4.20, HCl may be taken up by aerosols. Particles may then harbor the halogen reservoir that, upon sunrise, can be released.

Recently, chlorine activation has also been reported in the tropical UT/LS, with low temper-



Figure 4.20: Model of the uptake of HCl and the  $NO_x$  reservoir  $N_2O_5$  on aerosol particles. Adopted from von Glasow (2010).

atures as key parameter (von Hobe et al., 2010). Halogens contained in the stratosphere also interact with aerosol particles. Particles reaching the stratosphere may e.g. evaporate. Otherwise, hydrohalogen acids reservoirs can be dissolved in the water contained in the particle, or adsorbed on its surface. The result is the conversion of gas-phase long-lived halogen species, into short-lived ones:

$$CINO_3 + HCl (s) \longrightarrow Cl_2 + HNO_3 (s)$$
 (4.119)

$$CINO_3 + H_2O(s) \longrightarrow HOCl + HNO_3(s)$$
 (4.120)

$$HOCl + HCl (s) \longrightarrow Cl_2 + H_2O (s)$$
 (4.121)

$$BrNO_3 + HCl (s) \longrightarrow BrCl + HNO_3 (s)$$
 (4.122)

$$BrNO_3 + H_2O$$
 (s)  $\longrightarrow$  HOBr + HNO<sub>3</sub> (s) (4.123)

$$HOBr + HCl (s) \longrightarrow BrCl + H_2O (s)$$
 (4.124)

In the daytime stratosphere, XY (X, Y = Cl, Br) can readily photolyse into RHS that may yield the removal of stratospheric ozone. This relevant issue is addressed in Chap. 5.

In general, the loss of a gaseous species into the aerosol phase can be approximated to a first

order loss rate coefficient given by

$$k_{het} = \frac{v_{th} \cdot A \cdot \gamma_{net}}{4} = \tau^{-1} \tag{4.125}$$

where  $\gamma_{net}$  is the net aerosol uptake coefficient, A the aerosol surface area, and  $v_{th} = \sqrt{\frac{8k_bT}{\pi m}}$ is the thermal velocity (where  $k_b$  is the Boltzmann constant, T the temperature and m the molecular mass). A heterogeneous reaction depends on the gas-phase diffusion (transport of the gas to the particle surroundings), number of successful collisions of the gas into the aerosol surface (mass accommodation coefficient  $\alpha$ ), the solubility ( $\Gamma_{sol}$ ) and the bulk reaction ( $\Gamma_{rxn}$ ). Hence, following the *Finlayson-Pitts and J. N. Pitts* (2000) notation, the net uptake coefficient may be expressed as a resistance and defined as

$$\frac{1}{\gamma_{net}} = \frac{1}{\Gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\Gamma_{sol} + \Gamma_{rxn}}.$$
(4.126)

For particle size range relevant to atmospheric chemistry, *Fuchs and Sutugin* (1970) simplified the  $\frac{1}{\Gamma_{diff}}$  as

$$\frac{1}{\Gamma_{diff}} = \frac{0.75 + 0.28K_n}{K_n(1+K_n)},\tag{4.127}$$

with the Knudsen number  $K_n = \frac{6D_g}{v_{th}d}$ , where  $D_g$  is the gaseous diffusion coefficient (0.2 cm<sup>2</sup>/s at sea level), and d is the particle diameter. Hence, for high soluble species and fast bulk reactions, Eq. (4.128) can be simplified as

$$\frac{1}{\gamma_{net}} \sim \frac{1}{\Gamma_{diff}} + \frac{1}{\alpha}.$$
(4.128)

Thus, as shown in the following chapter, the type of the aerosols and also their location in the atmosphere (i.e., T), are key parameters for the efficiency of these multi-phase reactions.

Туре	Concentration $(cm^{-3})$	Characteristics
Marine	100-400	Three modes >95% of particle mass, but only 5-10% of total number , in largest mode. Large particles mainly sea-salt aerosol, smallest are products (e.g. $SO_4^{2-}$ ) of gas-to-particle conversion (e.g. DMS).
Remote continental	$\sim 10^4$	Three modes centered at D~ 0.02, 0.12 and 1.8 $\mu$ m. Includes products of gas-to-particle conversion and biological sources, e.g. pollens.
Urban aerosol	$\geq 10^5$	Three modes. Larger particles contain crustal elements (Fe, Si, etc.). Smaller contain nitrate, sulphate, ammonium, and elemental and organic carbon.
$Non-urban\ continental$	$\sim 10^3$	Similar to urban aerosol.
Desert	Variable	Most are large (D>1 $\mu$ m). Contain desert soil elements such as Fe, Si, Al, and Ca.
Polar	$\sim$ 15-150	Typical D~ 0.15 $\mu$ m. Contain gas-to-particle conversion products (e.g. sulphate, ammonium).
Free troposphere	$\sim 30$	Monodisperse. D~ 0.2–0.5 $\mu$ m Major source: nucleation. Sulphate is major component.
Biomass burning	$\sim 10^4$	Two modes. D~ 0.1- 0.4 and D> 2 $\mu$ m. Smaller mode contains gas-to-particle conversion products (sulphate, nitrate, ammonium, organics). Larger mode has soil and ash particles.

Table 4.3: Tropospheric aerosol particles: abundance, sources and characteristics. Adapted fromFinlayson-Pitts and J. N. Pitts (2000).

# Chapter 5

# The Arctic environment

Since data presented in this work were gathered during campaigns taking place in the High Arctic, this chapter provides the main features of that unique environment. Section 5.1 addresses the different definitions of the Arctic region, the Arctic Ocean circulation and the sea ice properties, as well as main features related to the measurements herein presented. Additionally, Sect. 5.1.4 briefly introduces the particles and pollution in the Arctic atmosphere.

Section 5.2 referrers to the unique pathways and effects of the RHS in the polar atmosphere. It addresses the *Stratospheric Ozone Hole* related to the formation of *Polar Stratospheric Clouds* and, in particular, the tropospheric *Ozone Depletion Events* related to the *Bromine Explosions* linked to the sea ice.

Section 5.3 closes this chapter by presenting the Arctic in the context of climate change, focusing on the current sea ice status.

For additional details and for information in ongoing polar research, the reader is kindly referred to e.g. the Arctic Monitoring and Assessment Programme (AMAP, http://amap.no/), the International Polar Year programme (IPY, http://www.ipy.org/) or the National Snow and Ice Data Center (NSIDC, http://nsidc.org).

## 5.1 Defining the Arctic

## 5.1.1 Geographical extension

Probably the term most commonly used to delimit the Arctic region is the north parallel  $66^{\circ}$  33' 44": the Arctic Circle (also referred to as *High Arctic*). This definition is related to the summer and winter solstices (e.g. midnight Sun). Additionally, as shown in Fig. 5.1, the Arctic can also be demarcated based on climatic conditions such as, e.g., the permafrost location

(Barry and Ives, 1974), the tree line, the 10°C-July isotherm (Linell and Tedrow, 1981), and also by the ocean salinity.

Within the frame of this thesis the author participated in two campaigns that took place in the High Arctic. Named as the *Arctic Study of Tropospheric Aerosols, Clouds and Radiation* ASTAR 2007 campaign, and the *Greenland Aerosol and Chemistry Experiment GRACE 2008* campaign, their details are given in Sect. 7.3. Additionally, Fig. 5.1 provides a context for the geographical location (and coverage) of the given campaigns.



Figure 5.1: Different definitions of the Arctic (adopted from NPI, 2010). Additionally included are the red shadows delimiting approximately the regions covered during the aircraft campaigns reported in this thesis. The ASTAR 2007 campaign took place in spring 2007, with base in Longyearbyen, Norway (LYN in the map). The GRACE 2008 campaign took place in summer 2008, with base in Kangerlussuaq, Greenland (KGL in the map).

#### 5.1.2 The Arctic Ocean

Besides mean temperatures, flora and fauna, or native inhabitants, one factor distinguishing the Arctic from the Antarctic is that the former consists on an ocean surrounded by continents and islands. On the other hand, the Antarctic consists on a continent by itself, surrounded by the Southern Ocean.

The main distribution of the energy in the Earth-atmosphere system evolves through the atmosphere (see Chap. 3). However, the ocean currents actively participate also in the transport of heat from the tropics to the polar regions (e.g. *Sverdrup and Johnson*, 1942, *Pedlosky*, 1996). In the northern hemisphere, the ocean circulation transports water masses through the Gulf Stream by the North Atlantic Current to the Hight Arctic. In the Arctic heat, nutrients, and gases (e.g.  $CO_2$ ) are brought to the surface, mainly in the Norwegian Sea. There, very low atmospheric temperatures evaporates and cool the water, which becomes denser and sinks into the deep basins. This process, intuitively shown in Fig. 5.2, is called *deep water formation*. That densercolder and more saline– water eventually leaves the Arctic basin through the Farm Strait, moved south slowly by thermohaline forcing. Additionally, the surface water in the Arctic Ocean is wind driven by the Beaufort Gyre circulation (see 5.2), which also directs the movement of the sea ice.

#### 5.1.3 Sea ice

This work investigates the bromine monoxide abundance in the polar troposphere, where the main bromine source is related to the frozen ocean: the sea ice. Hence, in order to assist the understanding of the results presented in this work, this section features the sea ice growth process, as well as its composition and types.

• Sea ice formation

As a result of the contact of the warm ocean waters and the cold atmosphere characterizing the polar regions, sea water freezes. Due to the salt content, sea water freezing point is below  $0^{\circ}$ C. In general, an increase of 15 psu yields  $1.12^{\circ}$ C decrease of the freezing point. The ocean salinity ranges between 30–35 psu and, therefore, the ocean waters begin to freeze at roughly -1.7°C (e.g. *Thomas and Dieckmann*, 2003).

As waters freezes, its molecules are rearranged, and hydrogen bonds are created between adjacent oxygen and hydrogen atoms forming hexagonal crystals expelling any impurity from its structure. This crystal distribution yields an overall increase of volume, and a decrease of density. As sea water freezes, those ice crystals stick to each other resulting on small (mm) needle-shaped crystals that float above the liquid water. These crystals are called *frazil ice*, and consists mainly on fresh water. In the freezing process of oceanic



(a) Arctic ocean circulation



Figure 5.2: (a) The Arctic Ocean. (b) The global thermohaline circulation and salinity distribution. Classic units of ppt (parts per thousand, in weight). However, salinity may also be given in practical salinity units, psu, related to the conductivity of the solution. In general ppt and psu are quite similar and, hence, psu units are given in this work. In the figures, warm water masses are indicated with red arrows, and the colder and denser ones with blue. In this work the Norwegian Arctic, and in particular the surroundings of Svalbard, is a region of main interest. Compared to other polar regions this area is characterized by mild temperatures as a result of deep and superficial ocean currents.

waters, the salt is expelled in any direction of the ice crystal, yielding a saturated liquid layer called *brine*. Table 5.1 summarizes the composition of frozen sea water, and Table 5.2 the one of the resulting brine.

Table 5.1: Composition of 1 kg of frozen sea water  $(T=-30^{\circ}C)$ , with initial salinity of 35 psu. Adapted from Sverdrup and Johnson (1942).

Tracers	Mass (g)
Ice crystals	931.9
NaCl crystals	20.23
$Na_2SO_4$ crystals	3.95
CaCO <sub>3</sub> crystals	Trace
Brine	43.95

Table 5.2: Inorganic composition of 43.95 g of brine resulting after freezing 1 kg of sea water (initial salinity 35 psu,  $T=-30^{\circ}C$ , refer to Table 5.1). Adapted from Sverdrup and Johnson (1942).

Tracers	Mass (g)	
$H_2O$	23.31	
$Cl^{-}$	7.03	
$Na^+$	1.42	
$Mg^{++}$	1.31	
$K^+$	0.38	
$Ca^{++}$	0.39	
$\mathrm{Br}^-$	0.08	
$SO4^-$	0.03	

If the freezing process is fast, some air bubbles and impurities may be trapped between the ice crystals. The trapped brine droplets are referred to as *brine pockets*. In the first state of the freezing process, the salinity of the brine increases under cooling conditions (additionally frozen water supplying additional salts). Overtime, those brine pockets may be released through sea ice movements, and also salts drain downward driven by gravity and temperatures differences. This drainage creates the so called *brine channels*, shown in Fig. 5.3. Eventually that salty solution reaches the bottom of the sea ice and sinks downward in the ocean (deep water formation).

Additionally to this downward release of the brine, brine is also rejected and deposited on top of the newly-formed sea ice, in a very thin (nm to mm) and highly saline *quasi liquid layer* (*QQL*, e.g., *Carignano et al.*, 2007). This warm brine layer above very thin ice releases water vapor to the cold atmosphere. Under very cold conditions (below approx. -15°C), this water vapor condenses close to the brine surface in form of needleshaped crystals that accumulate and yield the so-called *frost flowers* (*FF*) (see Fig. 5.3).

### CHAPTER 5. THE ARCTIC ENVIRONMENT

Through capillarity, brine is transported to the tips of the "needles" and, therefore, FF are very salty surfaces exposed to the atmosphere (for detail description of FF refer to e.g. *Domine et al.*, 2005). Additionally brine and, therefore, frost flowers host heterogeneous reactions resulting in the release of halogens to the atmosphere (e.g., *Lehrer et al.*, 2004, *Kaleschke et al.*, 2004) and, hence, are important features in this work (see Sect. 5.2.2 and Chap. 9).



Figure 5.3: Brine and sea ice. (a) Frost flowers over QQL brine. Adopted from Kaleschke et al. (2004), (b) Brine channels formed as brine pockets travel downward toward the warmer ocean. in the bottom of the sea ice (the image width is 5 mm width). Adopted from NSIDC (2010).

The salt contained in the brine depends strongly on temperature, as well as the amount of brine in contact with the frozen water. Figure 5.4 provides a schematic description of the temperature dependent salt content of the brine in contact with sea ice, and the brine related to sea ice at a given temperature. Moreover, Table 5.3 gives an overview of the salinity of the newly formed sea ice depending on the air temperature.

Table 5.3: Temperature dependent salinity of newly-formed see ice (salinity of the initial surface water was about 30 psu). Adopted from Sverdrup and Johnson (1942).

Air temperature	Salinity of ice	
$(^{o}C)$	(psu)	
- 16	5.64	
- 28	8.01	
- 30	8.77	
- 40	10.16	



Figure 5.4: (A) Temperature dependent salt content of brine in contact with sea ice. (B) Temperature dependent amount (grams) of brine contained in 1 kg of sea ice with salinity 1 psu. Adapted from Sverdrup and Johnson (1942).

• Sea ice types

As shown in Fig. 5.5, as new-formed ice grows thicker, its properties change and, with them, the name assigned (summarized in Fig. 5.6, e.g., *Thomas and Dieckmann*, 2003).

In general, based on its depth and age the sea ice is classified as:

- New ice or *nilas*: described above (<10 cm thick). Thin and smooth floating ice with a dark colored flat surface <10 cm thick.
- Young ice: 10–30 cm thick, characterized by its color (gray ice: 10–15 cm, gray-white ice: 15–30 cm).
- First-year sea ice (FY): less than 1 year old ice with typical thicknesses of 0.3-1.5 m (up to 2 m winter). As shown in Fig. 5.5, a snow deposit may be found on top of this ice (5-30 cm). As shown also in the figure, the salinity profile of the FY sea ice is characterized by a C-shape due to the released of brine in the upward and downward direction. Hence, the upper layer of the FY sea ice in highly saline and is believed to be the main source of halogenated species into the Arctic troposphere. Additionally, the halogen content of the snow cover depends strongly on the location of the sea ice (detailed study presented by Domine et al., 2004).
- Multi-year (MY): with a thickness of 2–4 m, this sea ice has survived at least one melt season (>1 year old).

Resulting from movements of the sea ice, cracks may appear. The narrow and linear ones are called *leads*. These leads may contained open water (*open leads*), or on growing



Figure 5.5: Sea ice properties as it grows older and thicker. Adopted from Thomas and Dieckmann (2003).

ice (e.g., Fig. 5.7). Big cracks in the ice with areas of permanent open water are called *polynyas*. In both cases, the warm ocean is exposed to the cold environment and, hence, leads and polynyas are sources of heat and moisture to the atmosphere influencing the atmosphere thermodynamics (e.g., *Alam and Curry*, 1997, *Nilsson et al.*, 2001, *Morales Maqueda et al.*, 2004). Additionally, these cracks affect the radiative transfer in the atmosphere (their albedo is much lower than its surroundings), and also in the ocean by heating up the superficial layers.

• Monitoring sea ice

In addition to field campaigns and ice breakers campaigns, sea ice research is performed by remote sensing observations on aircraft and satellite platforms. The sea ice thickness and evolution may be monitored e.g. by radar observations, where the salinity of the different



Figure 5.6: Pathways of the sea ice formation. Adapted from NSIDC (2010).

types of sea ice yield a unique scattering of the light. As shown in Fig. 5.8, in radar images, the low saline and rough MY sea ice appears brighter than the younger FY sea ice. Also, dark and bright areas may be also spotted on FY sea ice regions, corresponding to the highly saline and rough FF (very strong backscattering, e.g., *Fetterer et al.*, 1994,



Figure 5.7: Lead with young sea ice. Adopted from *Renfrow* (2010).



Steffen and Heinrichs, 1994, Renfrow, 2010). These kind of studies will be use in Sect. 9.2.

Figure 5.8: Retrieval of sea ice properties by satellite. Synthetic Aperture Radar (SAR) image shown the multi-year ice (MY), first-year rough ice (FYR), first-year smooth ice (FYS), and new ice or open water (NI/OW). Adopted from Fetterer et al. (1994).

#### 5.1.4 Particles and pollution in the Arctic atmosphere

An extensive list of gas-phase and aerosol particles measurements within the polar region is given by e.g. *Sander* (2007). Also, Arctic pollution issues are addressed in detail in e.g. *Barrie* (1986) and *AMAP* (1997). Moreover, *Fisher et al.* (2010) reports on the sources and the interannual variability of the pollution in the Arctic. There, here only main features of these topics are given.

In addition to the locally produced, pollution reaches the Arctic through the ocean and atmospheric circulations. In the Arctic environment mercury and cadmium are the main toxic pollutants. Also, persistent organic pollutants (POPs), released in lower latitudes by insecticides and industries emission, have been found in the Arctic environment. An important transported POP also found in the Arctic is the polychlorinated biphenyl (PCB). Also brominated fire retardants have been found in plants and animals in the polar regions. Based on AMAP (1997), the main identified source of sulfuric species into the Arctic is an smelter at Norilsk (Siberia), and probably a coal-fired power plant in Chukotka (Russia). Long-term trends of black carbon and sulphate aerosols transported into the Arctic have been recently published by *Hirdman et al.* (2010). As an example, Fig. 5.9 shows anthropogenic aerosol constituents measured in the Canadian Arctic. For recent publications regarding aerosol particles in the Arctic refer to e.g. *Yamagata et al.* (2009), *Khosrawi et al.* (2010), *Dörnbrack et al.* (2010).

One characteristic seasonal particle transport into the Arctic is the so-called *Arctic haze* (e.g. *Barrie*, 1986, *Shaw*, 1995, *Quinn et al.*, 2007, *Law et al.*, 2007). This phenomenon, firstly reported by pilots as brown layers of particles in the troposphere, occurs typically in winter, increases toward spring, and diminishes in summer. Haze comprises acidifying pollutants such as sulfates, soot and hydrocarbons. During winter, those pollutants get distributed and isolated into stable layers in the low troposphere. After the polar sunrise, the isentropic transport barrier referred to as the *polar dome* disappears, and turbulences and displacement of these layers take place. Figure 5.10 shows examples of this phenomenon.

### 5.2 Halogen species in the Arctic atmosphere

Since the ozone hole was discovered over Antarctica (*Farman et al.*, 1985), numerous investigations have focused on the description of the processes involved in the physics and chemistry of the polar atmospheres. This section focuses on the uniqueness of the polar atmosphere for the activation of halogen radicals that yield the removal of ozone in the stratosphere, and also in the troposphere. For studies on  $NO_x$  and  $HO_x$  radicals in the polar atmosphere the reader is kindly referred to e.g. *Stroud et al.* (2003) and *Mao et al.* (2010). Additionally dynamics in the polar atmosphere are addressed by the analysis of e.g. the tropopause folds (e.g., *Shapiro et al.*, 1987, *Kunz*, 2010), and boundary layer over snow or ice (*Anderson and Neff*, 2008 and references therein).

#### 5.2.1 Polar Stratospheric Clouds and the Ozone Hole

The lack of solar radiation over the winter cools down the air which sinks. As a result, the winter polar atmosphere is characterized by a persistent large-scale cyclone in the middle-upper troposphere and stratosphere, called *the polar vortex*. This vortex, which strength is given by its potential vorticity (see Sect. 3.2.3), isolates the polar atmosphere from southernly air intrusions. Inside of the polar vortex temperatures may drop even below 196 K. These low temperatures facilitate the development of the *Polar Stratospheric Clouds (PSCs)* (e.g., *Crutzen and Arnold*, 1986, *Toon et al.*, 1986). PSCs, often classified based on their optical properties, are believed to contain NAT or NAD particles (HNO<sub>3</sub>+ 3H<sub>2</sub>O and HNO<sub>3</sub>+ 2H<sub>2</sub>O, respectively), water, and Stratospheric Sulfate Aerosol (SSA) particles (e.g., *Fahey et al.*, 2000).

In the absence of light,  $NO_x$  radicals are transformed via  $N_2O_5$  hydrolysis (denoxification), into nitric acid that may be up-taken by these PSCs. PSCs then serve as surfaces for heterogeneous reactions that convert e.g. halogen reservoirs into more reactive ones. In this way, chlorine species may be activated by:



Figure 5.9: Air chemistry in the Canadian arctic (winters 1980/81 and 1981/82). Averaged seasonal variation of the ratio of weekly-average to annual-average concentration  $(C/\bar{C})$  for anthropogenic aerosol constituents. Adopted from Barrie and Hoff (1985).



Figure 5.10: Pollution into the Arctic. (A) Satellite image of the Moderate Resolution Imaging Spectroradiometer (MODIS) of smoke from boreal fires entering in the Canadian Arctic region. (B) Non-haze situation in Svalvard (April 2006), and (C) the same viewing but in case of reduced visibility associated with the haze phenomenon (May 2006). Adopted from Law et al. (2007).

$$\text{ClONO}_2 + \text{HCl}(s) \xrightarrow{het} \text{Cl}_2 + \text{HNO}_3(s)$$
 (5.1)

$$IONO_2 + H_2O(s) \xrightarrow{het} HOCl + HNO_3(s)$$
(5.2)

- $HOCl + HCl(s) \xrightarrow{het} Cl_2 + H_2O(s)$  (5.3)
- $N_2O_5 + HCl(s) \xrightarrow{het} ClONO + HNO_3(s)$  (5.4)

and bromine species by:

С

- $BrONO_2 + HCl(s) \xrightarrow{het} BrCl + HNO_3(s)$ (5.5)
- $BrONO_2 + H_2O(s) \xrightarrow{het} HOBr + HNO_3(s)$  (5.6)
  - $HOBr + HCl(s) \xrightarrow{het} BrCl + H_2O(s)$  (5.7)

With the polar sunrise, photochemistry gets activated and the more reactive halogens photodissociate readily, yielding the stratospheric ozone loss: *ClO-ClO cycle:* 

$$ClO + ClO \xrightarrow{M} Cl_2O_2$$
 (5.8)

$$\operatorname{Cl}_2\operatorname{O}_2 \xrightarrow{h\nu} \operatorname{Cl} + \operatorname{ClO}_2$$
 (5.9)

$$ClO_2 \xrightarrow{M} Cl + O_2$$
 (5.10)

$$2Cl + 2O_3 \longrightarrow 2ClO + 2O_2 \tag{5.11}$$

net ODC: 
$$2O_3 \longrightarrow 3O_2$$

ClO-BrO cycle:

$$ClO + BrO \longrightarrow Br + OClO$$
 (5.12)

$$\longrightarrow$$
 Br + ClO<sub>2</sub> (5.13)

$$\longrightarrow$$
 BrCl + O<sub>2</sub> (5.14)

$$ClO_2 \xrightarrow{M} Cl + O_2$$
 (5.15)

$$BrCl \xrightarrow{n\nu} Br + Cl \tag{5.16}$$

$$Cl + O_3 \longrightarrow ClO + O_2$$
 (5.17)

$$Br + O_3 \longrightarrow BrO + O_2$$
 (5.18)

net ODC: 
$$2O_3 \longrightarrow 3O_2$$

As an example of these reactions, Fig. 5.11 shows the evolution of PSCs, chlorine species and ozone inside of the Arctic vortex.

Since the ClO-ClO cycle described above depends directly on the existence of PSCs (very low temperatures), that cycle is believed to dominate the dramatic ozone holes of the cold Antarctic stratosphere. On the other hand, the ClO-BrO cycle, which can also take place in the absence of light, dominates the removal of the ozone in the (warmer) Arctic stratosphere (e.g., *WMO*, 2003).

The strength of the ozone hole is given by measurements of the ozone total column, and its extension is estimated to address areas within the constant ozone column threshold of 220 DU. Major stratospheric ozone loss were reported in 2006 over Antarctica, and in 1997 over the Arctic (e.g., *WMO*, 2007). Figure 5.12 compares these measurements, to the ozone column measured over the poles in 2008.

Climatologies show that indeed the strength of the ozone removal differs from pole to pole (e.g., *Solomon et al.*, 2007). Figure 5.13 illustrates the vertical distribution of the ozone loss



Figure 5.11: Evolution of PSCs, chlorines species and ozone inside the vortex (460K) during the Arctic sunrise after the 2004/2005 winter. Adopted from Harris et al. (2010).

in each pole, comparing measurements over the North Pole in the one of the coldest winters (1999/2000), with a typical ozone hole situation over the South Pole.

#### 5.2.2 Bromine explosion and Ozone Depletion Events

As discussed in Sect. 4.4.1, removal of ozone via reactive halogen species occurs not only in the stratosphere but also in the low troposphere. While the depletion of ozone in the former is known as the "Ozone Hole", the later is commonly referred to as *Ozone Depletion Events (ODEs)*. In the polar regions, where background ozone may drop to values below the detection limit of most instruments (from 25–50 ppbv to <0.4 ppbv), the understanding of ODEs gained a new perspective when measurements in the Arctic region showed a correlation of these events, with high concentration of filterable bromine (*Barrie et al.*, 1988, Fig. 5.14).

While the gas-phase reactions addressed in Sect. 4.4.1 could explain the measured ODEs, only heterogeneous reactions involving inert halide salt ions could reproduce such an enhancement



Figure 5.12: Monthly mean total ozone columns over the poles (Dobson Units). Obtained from a multisensor reanalysis from KNMI/TEMIS (van der A et al., 2010).



Figure 5.13: Stratospheric ozone hole: Arctic vs. Antarctic. Vertical profiles of  $O_3$  concentration (red lines report the ozone hole situation, and blue ones illustrate the ozone profile in a non-ozone hole situation profile). Adapted from Rex et al. (2002).

of tropospheric bromine (e.g., *Fan and Jacob*, 1992, *McConnell et al.*, 1992). The proposed autocatalytic reactions involve bromide ions:



Figure 5.14: First report of bromine correlation with Ozone Deplation Events. Open squares show ozone vmr (ppb), and filled squares the filterable Br concentration (f-Br, ng/m<sup>3</sup>. Adopted from Barrie et al. (1988).

$$HOBr(aq) + Br^{-}(aq) + H^{+}(aq) \longrightarrow Br_{2}(aq) + H_{2}O$$
(5.19)

$$Br_2(aq) \longrightarrow Br_2$$
 (5.20)

$$Br_2 \xrightarrow{h\nu} 2Br$$
 (5.21)

$$Br + O_3 \longrightarrow BrO + O_2$$
 (5.22)

$$BrO + HO_2 \longrightarrow HOBr + O_2$$
 (5.23)

$$HOBr \xrightarrow{M} HOBr(aq)$$
(5.24)

$$netODC: H^+(aq) + Br^-(aq) + HO_2 + O_3 \xrightarrow{M,n\nu} Br + H_2O + 2O_2,$$

and also chloride ones:

$$HOBr(aq) + Cl^{-}(aq) + H^{+}(aq) \quad \rightleftharpoons \quad BrCl(aq) + H_2O \tag{5.25}$$

$$BrCl(aq) + Br^{-}(aq) \rightleftharpoons Br_2Cl^{-}(aq)$$
 (5.26)

$$Br_2Cl^-(aq) \rightleftharpoons Br_2(aq) + Cl^-(aq)$$

$$(5.27)$$

$$net: HOBr(aq) + H^+(aq) + Br^-(aq) \xrightarrow{M} Br_2(aq) + H_2O$$

However, in case of low bromide, the Eq. (5.26) yields BrCl. After photolysis of BrCl, the released chlorine atoms may react with e.g. hydrocarbons, transforming Cl into the HCl reservoir. Hence, chlorine is believed to contribute only to 2% of the measured ODE in polar regions, and mainly at the beginning of the ODE ( $O_3 > 10$  ppbv, *Evans et al.*, 2003; *Simpson et al.*, 2007).

Once gas-phase  $Br_2$  or BrCl are released and atomic bromine is created through photolysis, the Ozone Depletion Cycles given in Sect. 4.4.1 may proceed. From these cycles, the BrO self-reaction is considered to be the limiting rate reaction for the removal of ozone in polar regions (e.g., *Simpson et al.*, 2007). Figure 5.15 presents a simplified scheme of these bromine explosions and the removal of ozone, and Table 5.4 the associated reaction rates. In addition to the ozone removal, as mentioned in Sect. 4 and depicted in Fig. 5.16, the enhancement of reactive bromine species in the atmosphere also renders the atmospheric mercury depletion events, which eventually support the scavenge of Hg by snow and particles. As a result, about 300 tonnes of toxic Hg is deposited per year in the polar ecosystems (e.g., *Steffen et al.*, 2008).

The above described bromine activation through heterogeneous reactions are not exclusive to polar regions but also take place in the marine boundary layer, over salt lakes, and volcanic plumes (e.g., *Hebestreit et al.*, 1999; *Bobrowski et al.*, 2003; *Von Glasow and Crutzen*, 2007; *Mahajan et al.*, 2010). However, their frequency and extent during the polar spring triggered the term "bromine explosions" (Fan and Jacob, 1992; *Platt and Lehrer*, 1996). Therefore, the



Figure 5.15: Simplified scheme of the bromine explosions. The yellow arrows indicate photolysis processes, while the uptake and recycling processes involving particles are given by the black arrows.

Arctic and Antarctic present themselves as unique environments for the study of reactive bromine species (Br and BrO) and ODEs.

The detection of reactive bromine activation (BrO) and ODEs was first reported for DOAS measurements by *Hausmann and Platt* (1994). Since then, many measurements in both poles have aimed at the characterization of the sources, processes and impacts of these events.



Figure 5.16: Bromine and mercury in the polar regions. Adopted from Steffen et al. (2008).

Reaction	Rate	Reference
	$J(s^{-1})$	
	$k (cm^3 molec^{-1} s^{-1})$	
	$k_M \ (cm^6 \ molec^{-2} \ s^{-1})$	
$\operatorname{Br}_2 \xrightarrow{h\nu} 2\operatorname{Br}$	$J = 10^{-2}$	Impey et al. (1999)
$Br + O_3 \rightarrow BrO + O_2$	$k = 7.8 \cdot 10^{-13}$	Atkinson et al. (2007)
BrO $\xrightarrow{h\nu}$ Br	$J = 1.4 \cdot 10^{-2}$	Simpson et al. (2002)
$BrO + BrO \rightarrow 2Br + O_2$	$k = 2.8 \cdot 10^{-12}$	Sander et al. (2003)
$BrO + BrO \rightarrow Br_2 + O_2$	$k = 7.9 \cdot 10^{-13}$	Sander et al. $(2003)$
$BrO + HO_2 \rightarrow HOBr + O_2$	$k = 4.5 \cdot 10^{-12}$	Atkinson et al. (2007)
$BrO + NO \rightarrow Br + NO_2$	$k = 2.4 \cdot 10^{-11}$	$Atkinson \ et \ al. \ (2007)$
$BrO + NO_2 \xrightarrow{M} BrNO_3$	$k_M = 3.7 \cdot 10^{-12}$	Sander et al. (2006)
$BrNO_3 \xrightarrow{h\nu} NO_2 + BrO$	$J = 2.9 \cdot 10^{-4}$	Simpson et al. $(2002)$
$\mathrm{HOBr} \xrightarrow{h\nu} \mathrm{Br} + \mathrm{OH}$	$J=0.05 \cdot J_{Br_2}$	Tackett et al. (2007)
$Br + HO_2 \rightarrow HBr + O_2$	$k = 1.3 \cdot 10^{-12}$	Tackett et al. (2007)
$\mathrm{HBr} + \mathrm{OH} \rightarrow \mathrm{Br} + \mathrm{H_2O}$	$k = 2.5 \cdot 10^{-12}$	Atkinson et al. (2007)
$Br + HCHO \rightarrow HCO + HBr$	$k = 6.63 \cdot 10^{-13}$	Atkinson et al. (2007)
$NO_2 \xrightarrow{h\nu} NO + O$	$J = 3.63 \cdot 10^{-3}$	Simpson et al. (2002)
$\rm NO + O_3 \rightarrow \rm NO_2 + O_2$	$k = 9.4 \cdot 10^{-15}$	Sander et al. (2003)
$\rm NO + HO_2 \rightarrow NO_2 + OH$	$k = 9.15 \cdot 10^{-12}$	Atkinson et al. (2007)

Table 5.4: ODEs-related reaction rates  $(T = 260 \text{ K}, SZA = 80^{\circ})$ 

Hence, herein only main concepts are summarized. For a detailed assessment of the effect and pathways of halogen species in the polar atmosphere the reader is kindly referred to *Simpson et al.* (2007), references therein and supplement. Also, seasonal variations of halogens in the Antarctic atmosphere are given by *Saiz-Lopez et al.* (2007), and a comprehensive climatology of measured ODEs in the polar spring is given by e.g. *Solberg et al.* (1996).

In general, main sources of salt bromide in the polar regions are the brine, the first-year sea ice, and the frost flowers (e.g., *Wagner et al.*, 2001; *Kaleschke et al.*, 2004; *Simpson et al.*, 2007; *Piot and von Glasow*, 2008). At the same time, those sources may serve as surfaces for taking up the RHS and transforming them into reservoirs, becoming therefore key parameters in the bromine explosions. Moreover, once halogenated particles are airborne, they may be transported to e.g. snow surfaces on top of the nearby sea ice (see Fig. 5.17), or even further distances with a postulated impact on the mid-latitudes troposphere (e.g., *Yang et al.*, 2010).

Additionally to heterogeneous reactions, gas-phase bromine may also derive from CHBr<sub>3</sub> emitted from algae (e.g. *Bottenheim et al.*, 1990), from frost flowers and, as reported by e.g. *Foster et al.* (2001), also from the snow pack (Br<sub>2</sub>, BrCl), refer to Fig. 5.18. Further snow pack trace gas emissions relevant for catalytic removal of ozone (e.g., NO<sub>x</sub> and HO<sub>x</sub>) are summarized by *Grannas et al.* (2007).



Figure 5.17: Vertical concentration of Na<sup>+</sup>, Cl<sup>-</sup>, and Br<sup>-</sup> in snow sampled from the frozen Northern Arctic Ocean (84°N, 67°W, 25 April 2000). Origin of these ions are believed to be related to transport of sea spray, upward migration of brine, and frost flowers deposited on top after being wind-blown. Adopted from Domine et al. (2004).

The abundance of halogen species and the extent of the ODE depend on the halogen primary sources, the amount of ozone available for oxidation of halogen atoms (e.g., Fig. 5.19), the different halogen recycling pathways, sinks and, moreover, of the synoptic conditions (e.g., *Jones et al.*, 2010). In fact, due to the complexity of the processes involved not only in the activation of RHS, but also in the chain reactions leading to the removal of ozone, chemical and transport models constrained by measurements are probably the best way for improving our current understanding of these events (e.g., *von Glasow et al.*, 2002; *Yang et al.*, 2005; *Piot, 2007; Piot and von Glasow, 2008; Saiz-Lopez et al.*, 2008; *Yang et al.*, 2010).

In general, typical duration of the ODEs are 1–5 days. However, shorter and longer periods have also been reported (7h – 9 days, e.g., *Bottenheim et al.*, 2002; *Jacobi et al.*, 2006). Chlorine,



Figure 5.18: Daily evolution of  $O_3$ ,  $Br_2$  and BrCl above snow (Alert, March 2000). Adopted from Spicer et al. (2002).

iodine and bromine species are linked to these polar ODEs. However, as mention above, chlorine species are believed to play a minor role. On the other hand, and maybe due to biochemistry (e.g. microalgae), high abundances of iodine species have only been found in Antarctica (e.g., *Frieß*, 2001; *Saiz-Lopez et al.*, 2007; *Saiz-Lopez et al.*, 2008; *Frieß et al.*, 2010). Hence, in the Arctic the reactive bromine species direct the ODEs, with BrO lifetime of ~ 1 day in the boundary layer (e.g., *Simpson et al.*, 2007). In this work, possible BrO sources, pathways and transport processes in the polar boundary layer are assessed in detail in Sect. 9.2.2.

## 5.3 Arctic and Climate Change

While scientists debate about global warming and climate change, the faster increase of temperatures in the Arctic as compared to other latitudes is not a question, but a fact. Time series of the temperature anomalies given at in different latitudes are presented in Fig. 5.20. As shown in the figure, the increase of temperatures in the Arctic is the last decades is about twice the anomaly detected at other latitudes. This is referred to as *the Arctic amplification*. Despite whether the change in the Arctic climate has an anthropogenic or a natural origin, the numerous uncertainties of its effects and feedbacks have yielded active interdisciplinary research (e.g., *Serreze et al.*, 2000, IPY).

Temperature changes in the polar stratosphere (e.g., Randel and Wu, 1999), possible conse-



Figure 5.19: Modeled evolution of bromine and chlorine species as a function of ozone concentration (simulation initialized with 43 pptv of bromide). Adopted from Evans et al. (2003).



Figure 5.20: The Arctic amplification. Annual zonal mean temperature changes in the Arctic  $(90.0 - 64.2^{\circ}N)$ , northern Mid-Latitudes  $(64.2 - 23.6^{\circ}N)$ , Tropical  $(23.6^{\circ}N - 23.6^{\circ}S)$ , southern Mid-Latitudes  $(23.6 - 64.2^{\circ}S)$ , and Antarctic  $(64.2 - 90.0^{\circ}S)$ . Right figure compares temperature anomalies in both poles. Anomalies based on 1951–1980 period. Updated on 12 Aug. 2010. Adopted from (NASA, 2010a).

quences of increased UV radiation reaching the ground and the ocean surface as a result of a decrease of total O<sub>3</sub> column, effects on the atmospheric chemistry, atmospheric and ocean circulation, sustainability of the aboriginal ways of life, survival of the polar bears and ice-related species (e.g., microalgae), increase of the sea level (melting of e.g. Greenlandic glaciers), atmospheric release of CH<sub>4</sub> from thawing permafrost, exploitation of natural resources and opening new commercial routes in an sea ice free Arctic, etc. Many are the issues and open questions regarding the consequences of a change in the Arctic climate. Since part of this work is related to the sea ice as a source of bromine species, here some graphical facts regarding the Arctic sea ice current state are presented. Figure 5.21 shows an aerial view of the mean sea ice extent for the 1979-2000 period, as compared to August 2010. Figure 5.22 details the evolution of the summer minimum sea ice extent of 2007–2010, as compared to the 1979-2000 period. Overall, the Arctic summer sea ice is shrinking and, up to date, the summer of 2007 presented the lowest sea ice coverage record. But the Arctic sea ice is not only changing its extension in summer, but also its properties, even in the winter season. Figure 5.23 presents the trend of the type of sea ice for the 2004–2008 period. Despite a general decrease in volume, between 2004–2006 the type of sea ice was mainly multiyear sea ice. However, from winter 2006 to winter 2007, the dominant type of sea ice switched from multiyear to an overall first-year sea ice (potential bromine source). This work presents measurements performed during an aircraft-borne campaign that took place in the High Arctic in the spring 2007, and Sect. 9.2.2 focuses in particular on the relation of the measured BrO within the polar marine boundary layer, to the properties of sea ice.



Figure 5.21: Arctic sea ice extent. Adopted from Cook (2010).



Figure 5.22: Arctic sea ice extent minimum. Adopted from Cook (2010).



Figure 5.23: Sea ice trend of the Arctic Ocean in winter (2004–2008). The images on top present the multiyear sea ice fraction. The black line indicates the overall volume. The red line indicates the trend of the total volume corresponding to multiyear sea ice, and the blue line to first-year sea ice. Adopted from (Kwok, 2010).

# Chapter 6

# Remote sensing of the atmosphere

For decades, remote sensing measurement techniques such as LIDAR or absorption spectroscopy, have been proved to be highly versatile and sensitive, with broad capabilities for atmospheric monitoring (e.g., *Dobson*, 1968; *Stolarski et al.*, 1991). This thesis reports on measurements gathered by a passive UV/vis absorption spectroscopic technique to assess atmospheric trace gas abundances.

Section 6.1 summarizes some general concepts in atmospheric optical absorption spectroscopy. Section 6.2 details the *Differential Optical Absorption Spectroscopy* (DOAS) method applied herein, addressing its principle, error treatment and limitations, as well as some DOAS measurements instrumental setups. When detecting scattered skylight, like in this study, the radiative transfer modeling (RTM) becomes a key process in the retrieval of atmospheric trace gas abundances. Hence, Sect. 6.3 focuses on the RTM used in this work.

## 6.1 Basics of the optical absorption spectroscopy

By definition, "spectroscopy" is the study of spectra, which derives from the Latin word "specter" or ghost. Thus, conceptually, the optical absorption spectroscopy is the study of matter by analyzing the "shadows" arising from its interaction with light, i.e., by analyzing its absorption lines. Each of those observed spectral lines is characterized by the absorption probability (refer to Eq. (2.18)), as well as by the line width, strength and shape:

#### • Absorption line width

Due to the lifetime of an excited state and as a result of the Heisenberg's energy-time uncertainty principle, absorption (and emission) lines have a non-zero line width (nondelta functions). In fact, each transition has an associated *natural line width*, which is given by the full width half maximum (FWHM) of a Lorentzian intensity distribution centered at  $\lambda_0$ . For transitions following the selection rules (details in e.g. *Herzberg*, 1950), the typical lifetime is about  $10^{-8}$  s. Hence, transitions in the visible range have a natural line width of about  $10^{-5}$  nm (FWHM). This natural line width may undergo thermal and collision broadening. The thermal broadening is a consequence of the motion of the absorbing (emitting) molecule relative to the detector. This broadening, also referred to as *Doppler broadening*, follows a velocity-dependent Gaussian distribution. In addition, as a consequence of molecules interactions, spectral lines may also experience the so-called *pressure or collisional broadening*, characterized by a Lorentzian distribution. Therefore, the physical line (i.e., the *Voigt profile*), is a convolution of the natural line width and the broadening processes.

#### • Strength and shape of an absorption line

The intensity or strength of each possible absorption  $S_N$  is given by the area under the curve of the wavelength distribution of the absorption coefficient:

$$S_N = \int_{\lambda} \mathcal{E}_a(\lambda) d\lambda \tag{6.1}$$

Thus, following Eq. (2.19) and Eq. (2.23), for an infinitesimal volume dl with n molecules, the absorption line strength is  $S = \frac{S_N}{\int n dl}$ . If  $f(\lambda)$  is the spectral line shape factor describing the profiles of absorption lines, normalized as  $\int_0^\infty f(\lambda) = 1$ , then the absorption coefficient reads as  $\sigma_a(\lambda) = S \cdot f(\lambda)$ .

Despite the natural properties of absorption lines, atmospheric optical spectroscopic measurements yield an inherent transformation of the incoming spectrum as a result of instrumental characteristics (see also Chap. 7). In general, the Doppler and collisional broadening detailed above dominate the shape of the transition lines detected with UV/vis absorption spectroscopy (optical spectrometers not highly resolved). Moreover, the measured spectrum  $I^*(\lambda)$  is in fact the result of the incoming continuous spectrum  $I(\lambda)$ , modified (convolved) by the instrumental line shape (slit) function  $H(\lambda)$ , so that:

$$I^*(\lambda) = I(\lambda) \otimes g(\lambda) = \int_{-\infty}^{\infty} I(\lambda') H(\lambda - \lambda') d\lambda'.$$
(6.2)

The slit function  $H(\lambda)$  is specific to each apparatus and may experimentally be approximated to the spectrum of an atomic emission line from a low pressure lamp such as a mercury or cadmium lamp.

In addition, using a multi-channel detector yields the  $I^*(\lambda)$  mapped onto a detector of n discrete pixels. Each pixel integrates the light in a wavelength interval  $\Delta\lambda(n)$  around the central wavelength  $\lambda(n)$ . Thus, in optical spectroscopic measurements, the incoming radiation is detected as

$$I^*(n) = \int_{\lambda(n) - \frac{\Delta\lambda(n)}{2}}^{\lambda(n) + \frac{\Delta\lambda(n)}{2}} I^*(\lambda') d\lambda'.$$
(6.3)

The integrating interval for each pixel is defined by the *wavelength-pixel mapping*, also referred to as the *wavelength calibration* function of the instrument, often approximated by a polynomial. For a linear dispersion the spectral width of a pixel is constant. However, changes in pressure and temperature may lead to a shift, stretch or squeeze of the wavelength-pixel mapping, needed to be accounted for when performing spectral analyses.

Moreover, as a consequence of the photo-diodes thermal discharge (e.g. in silicon detectors), and the electronic offset added before the A/D conversion,  $I^*(n)$  comprises not only the spectrum to study, but also dark current and electronic offset spectra. Therefore, before any spectroscopic analysis is performed,  $I^*(n)$  is often corrected for those instrumental contributions.

## 6.2 Differential Optical Absorption Spectroscopy in the UV/vis

In addition to instrumental calibration, the main challenge in atmospheric optical measurements is to solve the Beer-Lambert equation (Eq. 2.26), since different extinction processes may attenuate the incoming light beam and, also, different substances may simultaneously cause that attenuation. In the 1970s, the solution to these issues arose by realizing that Rayleigh and Mie scattering yielded only broadband structures in the measured spectra, while absorption processes produced broadband as well as narrow or *differential* structures. That new approach for analyzing measured spectra was named as *Differential Optical Absorption Spectroscopy*, DOAS (*Noxon*, 1975; *Perner and Platt*, 1979; *Platt et al.*, 1979). Since then, the DOAS has become a well known and established atmospheric measurement technique (e.g., *Platt and Stutz*, 2008). Here a description of the DOAS method is given in Sect. 6.2.1, while experimental setups of DOAS measurements are introduced in Sect. 6.2.2.

### 6.2.1 The DOAS principle

According to the DOAS principle, the molecular absorption cross-section of a given molecule comprises low frequency or broadband absorption structures (indicated with subscript b), and also high frequency or differential absorption ones (indicated with apostrophe), so that

$$\sigma_a(\lambda) = \sigma_b(\lambda) + \sigma'(\lambda). \tag{6.4}$$

If  $\mathcal{E}_s$  is the extinction coefficient of Rayleigh and Mie scattering, the optical density from Eq.



Figure 6.1: Illustration of the DOAS principle. Measured radiances and absorption cross-sections are split up into narrow and broadband components. Adopted from Stutz and Platt (1996).

(2.27) may be also regarded by its broad and differential components:

$$\tau(\lambda) = \int_{L} \left( \sum_{i=1}^{N} (\sigma_{b,i}(\lambda) + \sigma'_{i}(\lambda)) n_{i} + \mathcal{E}_{s}(\lambda) \right) dl = \tau_{b}(\lambda) + \tau'(\lambda)$$
(6.5)

where L is the light path, N the number of absorbers, and  $n_i$  represents the atmospheric concentration of each absorbing molecule. Moreover, if molecular absorption cross-sections are considered independent of temperature and pressure, then the differential absorption cross-section of a molecule may be regarded as independent of the light path L through the atmosphere. Therefore, the differential or narrow band component of the optical density reads as

$$\tau'(\lambda) \approx \sum_{i=1}^{N} \sigma'_i(\lambda) \int_L n_i \cdot dl = \sum_{i=1}^{N} \sigma'_i(\lambda) \cdot SCD_i$$
(6.6)

where SCD is the slant column density of each molecule given by

$$SCD_i = \int_L n_i \cdot dl.$$
 (6.7)

Therefore the SCD is the number density n of an absorbing molecule integrated along the line-of-sight or light path, and is the quantity inferred by the spectral DOAS retrieval method.

The nature of the DOAS technique is that of a mathematical inversion problem (e.g., *Rodgers*, 2000). Hence, the DOAS retrieval relies on constructing a forward model function  $\mathbf{F}$  containing the physics needed to model the measurement vector  $\mathbf{y}$  (measured radiance spectra), so that

$$\mathbf{y} = \mathbf{F}(\mathbf{x}, \mathbf{b}) + \epsilon, \tag{6.8}$$

where  $\mathbf{x}$  is the state vector to be inferred (comprising the absorption of a certain trace gas along
the line-of-sight,  $SCD_i$ ), **b** is the vector consisting of all the forward model parameters that will not be retrieved (e.g., absorption cross-sections), and  $\epsilon$  represents the inherent measurement error. Here details of the approximations involved in the construction of the DOAS forward model function and the solution to the inverse problem are given. In addition, the error treatment and limitations of the DOAS method are also addressed.

### The DOAS model function

Considering the narrow and broadband structures of the absorption cross-section as explained above, the Beer-Lambert's law from Eq. (2.26) may be transformed as

$$I(\lambda) = I_0(\lambda) \cdot e^{-(\tau_b(\lambda) + \tau'(\lambda))} = I(\lambda) = I_{0,b}(\lambda) \cdot e^{-\tau'(\lambda)}$$
(6.9)

where  $I_{0,b}(\lambda)$  consists of the source spectrum (without any absorption feature), and all broadband extinction processes so that:

$$I_{0,b}(\lambda) = I_0(\lambda) \cdot e^{-\tau_b(\lambda)}.$$
(6.10)

As mentioned in Sect. 6.1, as a result of the instrumental characteristics, the measured radiance gets degraded by the instrumental slit function  $H(\lambda)$ , so that

$$\ln I^*(\lambda) \approx \ln \left[ \left( I_{0,b}(\lambda) \cdot e^{-\tau'(\lambda)} \right) \right] \otimes H(\lambda).$$
(6.11)

Assuming small differential optical densities ( $\tau'(\lambda) \ll 1$ ), and regarding  $I_{0,b}$  as weakly  $\lambda$  dependent ( $I_{0,b} \sim \text{const.}$ ), this equation may be expressed as a linear function **F** given by:

$$F(\lambda) = \ln I^*(\lambda) \approx \ln \left[ I_{0,b}(\lambda) \otimes H(\lambda) \right] - \tau'(\lambda) \otimes H(\lambda).$$
(6.12)

In atmospheric UV/vis spectroscopy, the assumption of  $\tau'(\lambda) \ll 1$  is usually justified since the encountered optical densities in the measured spectra range between  $10^{-3}$  and  $10^{-1}$ . However, regarding  $I_{0,b}$  as a constant may lead to systematic errors in the DOAS retrieval (e.g., *Huppert*, 2000) and, moreover, the temperature and pressure independence of molecular cross-section may not be negligible. Both limitations of the forward model function are addressed later in this section.

Considering these approximations, the DOAS model function for the spectral retrieval in the UV/vis reads as

$$F(\lambda) = \ln \left[ I_0^*(\lambda, d_{0,0}, d_{1,0}, \cdots) \right] + P(\lambda, p_0, p_m, \cdots) - \sum_{i=1}^N a_i \sigma_i'(\lambda, d_{0,i}, d_{1,i}, \cdots).$$
(6.13)

where  $I_0^*$  is the source spectrum, P is a polynomial of degree M –usually between  $2^{nd}$  and  $5^{th}$  degree– approximating the broadband processes, and the term  $a_i \sigma'_i$  describes the (scaled) molecular absorption cross-sections (often taken from high resolution measurements). The parameters  $d_{j,i}$  are the spectra alignment parameters giving the possible shift and squeeze of the wavelength-pixel mapping between the spectra to be analyzed, the reference spectrum (i=0), and the absorption cross-sections (see also Sect. 6.1).

In atmospheric measurements using the Sun as a light source,  $I_0$  usually stands for the extraterrestrial solar spectrum without any extinction process. However, many optical instruments like the passive DOAS instrument used in this work, do not perform measurements outside the Earth's atmosphere, so there is no direct measurement of the incoming radiation  $I_0$ . In this case measurements are often regarded as relative to a reference spectrum  $I_{ref}$ . This  $I_{ref}$  is considered as a background spectrum shaped by minimal absorption processes ( $\tau_{ref}$  min.), and reads as:

$$I_{ref}(\lambda) = I_0(\lambda) \cdot e^{-\tau_{ref}(\lambda)}.$$
(6.14)

The use of this pseudo-solar spectrum, actually measured by the spectrometer, renders a proper representation of the Fraunhofer lines in the forward model.

Hence, accounting for the discretization of the measured radiance in n pixels as detailed in Sect. 6.1, the linear forward model function becomes

$$F(n) = \ln \left[ I_{ref}^*(n, d_{0, ref}, d_{1, ref}, \cdots) \right] + P(n, p_0, p_m, \cdots) - \sum_{i=1}^N a_i \sigma'_i(n, d_{0, i}, d_{1, i}, \cdots).$$
(6.15)

Summarizing, the DOAS model function comprises the logarithm of the measured radiance spectrum  $\ln I^*(n)$  as the measurement vector  $\mathbf{y}$ , and the forward model parameters  $\mathbf{b}$  which consist of the absorption cross-sections  $\sigma'_i$ , and  $I^*_{ref}(n, d_{0,ref}, d_{1,ref}, \cdots)$ . Thus, the inversion problem aims to retrieve the state vector  $\mathbf{x}$ , which includes the N scaling factors  $a_i$  (corresponding to the SCD<sub>i</sub> of the  $n_i$  absorbers), the M polynomial coefficients of P, and the  $d_{j,i}$  spectra alignment parameters. Since the measurements are referred to a reference spectrum, the difference between the slant column density from the spectrum to be analyzed, and that from the reference spectrum defines the differential slant column density dSCD of each absorbing species, so that

$$dSCD_i = SCD_i - SCD_{ref,i}.$$
(6.16)

#### Solution of the inverse problem

The mathematical inversion of the DOAS model function is performed by combining a linear least square fitting method (e.g., *Bevington*, 1969; *Albritton et al.*, 1976), and a non-linear Levenberg-Marquardt algorithm which merges the steepest gradient and the Gauss-Newton method (*Marquardt*, 1963; *Levenberg*, 1944).

In the spectral analysis, the least square fitting approach is applied for inferring the scaling parameters  $a_i$  and P, and the Levenberg-Marquardt method to define the shift and squeeze parameters  $d_{j,i}$ . The goal is to minimize the cost function

$$\chi^{2} = \sum_{n=1}^{W} \left( \frac{\ln I^{*}(n) - F(n)}{\epsilon_{n}} \right)^{2}$$
(6.17)

where W stands for the number of pixels comprising the spectral range used for the retrieval, and  $\epsilon_n$  is the measurement error of the n<sup>th</sup> diode resulting from the measurement noise. Often, a constant measurement error is assumed for all diodes so that  $\epsilon_n = \epsilon = \text{const.}$  (see bellow). Hence, in the spectral analysis, the parameters  $a_i$  (and P) are first inferred by the least square fitting considering fixed  $d_{j,i}$ . The outputs of this linear fit are then used as input parameters in the Levenberg-Marquardt equation. After one step, the non-linear method provides new  $d_{j,i}$ that are used again in the linear approach, hence setting an iterative fitting procedure until the  $\chi^2$  converges, or a certain number of iterations is fulfilled (e.g., *Stutz and Platt*, 1996). In this thesis the spectral analysis procedure is performed with the WinDOAS software package (*Fayt and van Roozendael*, 2001).

### Characterization of the spectral retrieval and error analysis

According to Eq. (6.8), the errors of the state vector **x** result from the retrieval noise due to measurement errors, errors of the forward model **b** parameters, errors due to correlations of the retrieval parameters, and errors of the forward model function itself (e.g., *Rodgers*, 2000). These different error sources are addressed below.

#### Measurement error

Once the measured spectra are corrected for dark current and electronic offset noise (see Sect. 6.1), the total error of the measured radiances comprises the different instrumental error: the photo-electron shot noise ( $\epsilon_{ph}$ ), the dark current ( $\epsilon_{dc}$ ) and the electronic noise ( $\epsilon_{el}$ ), so that

$$\epsilon = \sqrt{\epsilon_{ph}^2 + \epsilon_{dc}^2 + \epsilon_{el}^2}.$$
(6.18)

The dominant instrument noise, the photo-electron shot noise, is due to the statistical distribu-

tion of the number of electrons generated by the photons illuminating the detector pixels. Since the number of photo-electrons N is distributed according to Poisson statistics, the noise is given by

$$\epsilon_{ph} = \sqrt{\alpha \cdot N},\tag{6.19}$$

where  $\alpha$  the is the saturation level of the recorded spectrum.

The *electronic offset noise* is a random noise resulting from electronic processes such as the A/D conversion, the pre-amplifying of the signal or the read-out.

The dark current noise of a single detector photo-diode is caused by the statistical variance of the dark current across the junction. As in the  $\epsilon_{ph}$ , the dark current electrons are Poisson distributed. For an integration time  $T_{int}$ , and a mean number of dark current electrons per time n, the dark current noise may be inferred as

$$\epsilon_{dc} = \sqrt{n \cdot T_{int}}.\tag{6.20}$$

The retrieval noise due to the measurement noise  $\epsilon$  is given by the error deriving from the DOAS fitting procedure. A thorough study of the error treatment in the DOAS retrieval is given by *Stutz and Platt* (1996), and *Platt and Stutz* (2008). In summary, considering the number of absorption bands, the number of pixels considered in the retrieval, the intensity of the recorded spectrum, and the instrumental wavelength-pixel mapping, the overall fitting routine provides the standard deviations of the retrieval parameters as output, i.e., the true value of each retrieved parameter lies with 68.3% probability within the boundaries of the given error.

The residual spectrum  $R(n) = \ln I^*(n) - F(n)$  provides the quality of the retrieval and may be employed to determine the detection limit of each measurement. If the residual spectrum consists of pure noise, the fitting errors represent the retrieval noise, and the real measurement error may be regarded as twice the 1- $\sigma$  fitting error (i.e., the probability of finding the true value is 95%). This confidence may be regarded as the measurement *detection limit* in case of purely noise residum (mostly photo-electron shot noise). However, if the detectors used in the DOAS instruments present cross dependencies between neighboring pixels, or if a trace gas with relevant absorption bands in the fit window is omitted from the fit, structures may result in the residual spectrum and generate systematic errors. Since the minimum differential optical density detectable must be larger than the differential optical density of the fit residual, the amplitude of the structured residual spectrum may be used to derive the detection limit of a specific DOAS retrieval (see also Sect. 8.1).

### Forward model parameter error

Forward model parameters **b** are the molecular absorption cross-sections, and the reference spectrum. From a set of measured spectra, an ideal reference spectrum will not show any narrow band structures. However, in the case of e.g. scattered light measurements performed with airborne DOAS instruments like in this study, since spectra are gathered within the troposphere and low stratosphere atmosphere, there is no opportunity of measuring extraterrestrial spectra with complete absence of absorption structures. In these cases,  $I_{ref}$  may be measured e.g. at highest altitude or smallest solar zenith angle SZA (to minimize overhead-stratospheric absorption structures). Also, if the aim is to retrieve e.g. tropospheric trace gases associated to pollution,  $I_{ref}$  should be chosen in a non-polluted scenario, with the instrument looking in a direction in which the absorber of interest is not present, or present but at lower abundances than in the area of interest. The possible absorption inherent to the reference spectrum may yield a retrieval error derived from the offset of the retrieved parameters. Although under some circumstances this offset may be calculated up to a certain degree (e.g., Langley's extrapolation, e.g., *Platt and Stutz*, 2008), in general this reference offset represents a limitation of the scattered light measurements.

Regarding the *molecular absorption cross-sections*, the main errors originate from uncertainties of their absolute magnitude, and their pressure and temperature dependence (e.g., Orphal, 2003). In the case of this work and due to the instrumental resolution, the pressure dependency of the absorption cross-sections may be neglected. On the other hand, a change in temperature causes significant change in the absolute value and shape of the cross-sections, perceptible in UV/vis spectroscopic measurements. If not accounted for in the DOAS routine, the temperature dependence may lead to inappropriate fit parameters  $a_i$ , to an inadequate model of the measured radiances, and to large residual structures. Hence, if strong absorbers have temperature dependent cross-sections and this is not considered, those structures may obscure the targeted weak absorbers. This limitation in the DOAS retrieval can be minimized by including absorption cross-sections measured at different temperatures. If the temperature dependence is approximately linear, two cross-sections are sufficient to cover a large temperature region. In order to avoid correlations between the two cross-sections at different temperatures, one of them is orthogonalized with respect to the other so that their differential structure is obtained by fitting a polynomial. However, the retrieval of the SCDs of an absorber with temperature dependent cross-section is often not straight forward. Diverse approaches to overcome this issue imply e.g. approximation by a linear temperature dependence of the cross-section, or corrected SCDs retrieved at a given temperature by interpolation to an effective temperature (Butz, 2006). In this work, bromine monoxide is the main target of study. Therefore, BrO is the chosen absorber for a closer analysis of its absorption cross-section. Diverse studies report on the BrO  $\sigma_a$  at different spectral resolutions and temperatures (e.g., Cox et al., 1982; Wahner et al., 1988; Wilmouth et al., 1999). In summary, like other halogen radicals, BrO  $\sigma_a$  in the UV-A spectral range consists of a  $A \leftarrow X^2 \Pi$  transition, with several well-defined vibrational bands, and some rotational bands. As shown in Fig. 6.2, the BrO  $\sigma_a$ is characterized by a peak absorption band at 338.3 nm  $(A(^2\Pi_{3/2}) \leftarrow X(^2\Pi_{3/2}))$  electronic transition), a weak broadband structure, and a non negligible temperature dependency.



Figure 6.2: BrO absorption cross-section- temperature dependent- corresponding to the  $A(^{2}\Pi_{3/2}) \leftarrow X(^{2}\Pi_{3/2})$  transition, with indication of the vibrational transitions (1) and (7). (Wilmouth et al., 1999)

Diverse studies address the temperature dependence of the BrO absorption cross-section absolute values (e.g., Wilmouth et al., 1999; Fleischmann et al., 2004). In general, although the integrated absorption cross-section remains rather constant for atmospheric temperature ranges (Fleischmann et al., 2004), the strength of the temperature dependency depends on each  $\sigma_a$ band. A summary of the T dependence of band (7) at a spectral resolution FWHM = 0.4 nm, is given in Dorf (2005) and shown in Fig. 6.3. With a decrease of roughly 15% from 200 K to 250 K, the BrO peak absorption-cross section band presents a linear temperature dependence. This linearity will be considered in the retrieval of BrO dSCDs shown in Chap. 8.

### Correlations of retrieval parameters

Systematical errors may arise from correlations of retrieval parameters such the absorption cross-sections included in the fit (e.g., *Bösch*, 2002), and from correlations of retrieval parameters with the fitting polynomial. In general, these correlations decrease with the number of pixels of the selected fit window, and increase with the degrees of freedom of the fit, i.e., with the number of absorption cross-sections included in the fit, and with the polynomial degree.



Figure 6.3: Temperature dependence of the differential BrO absorption cross-section of the vibrational band (7). Literature and laboratory measured values are compared. Adopted from Dorf (2005).

#### Solar $I_0$ effect

One of the conditions for the linearisation of the Beer-Lambert's law to formulate the DOAS forward model function is based on assuming  $I_{ref,b}$  as wavelength independent. However, in the case of passive DOAS measurements, the reference spectrum comprises many strong wavelengthdependent Fraunhofer absorption lines. This fact, referred to as the solar  $I_0$  effect, represents a limitation of the forward model DOAS function, and yields systematic retrieval errors. For an estimated  $SCD_i$ , that limitation can be corrected by attributing the residual structures to the molecular absorption cross-sections (e.g. Platt et al., 1997), so that

$$\sigma_{i,corr}'(\lambda) = \frac{1}{SCD_i} \ln \frac{\left(I_0(\lambda) e^{-\sigma_i'(\lambda) SCD_i}\right) \otimes H(\lambda)}{I_0(\lambda) \otimes H(\lambda)},\tag{6.21}$$

where  $\sigma'_{i,corr}$  is the I<sub>0</sub>-corrected molecular absorption cross-section,  $\sigma'_i$  is the highly resolved absorption cross-section, H is the instrument slit function, and I<sub>ref</sub> a high resolution solar spectrum (e.g. *Kurucz et al.*, 1984).

### The Ring effect

As a result of inelastic rotational Raman scattering by atmospheric molecules (see Sect. 2.3.1),

the spectra measured from scattered light show reduced optical densities of the solar Fraunhofer lines as compared to direct solar spectra. This "filling-in" of the Fraunhofer lines is called *Ring effect*, after *Grainger and Ring* (1962), and depends on the SZA (on the atmospheric light path). These changes of the Fraunhofer lines optical densities are about one order of magnitude higher than the  $\tau$  of the absorbers herein detected and, hence, may strongly affect the DOAS retrieval. Since  $\ln I_{measured} = \ln(I_{elastic} + I_{Raman})$ , the Ring effect can be corrected by including a so called *Ring cross-section* as pseudo-absorber in the DOAS fit. According to *Chance and Spurr* (1997), that Ring cross-section is given as

$$\sigma_{Ring} = \frac{I_{Raman}}{I_{Rayleigh}} \sim \frac{I_{Raman}}{I} \tag{6.22}$$

where  $I = I_{Raman} + I_{Rayleigh}$  is the total intensity. In this work the Ring cross-section is modeled with the software package DOASIS<sup>1</sup>, and included in the DOAS retrievals (see Chap. 8).

### Instrumental stray light

Light reflected at the inner parts of the spectrometer (second or higher orders) can reach the detector and lead to an artificial offset in the measured signal. In the DOAS retrieval this offset due to the spectrometer stray light can be corrected by introducing a polynomial O(n) of maximal  $2^{nd}$  order, which coefficients are determined by the Levenberg-Marquardt fitting algorithm. Thus, the cost function given in Eq. (6.17) is transformed into:

$$\chi^{2} = \sum_{n=1}^{W} \left( \frac{\ln \left[ I^{*}(n) - O(n) \right] - F(n)}{\epsilon_{n}} \right)^{2}.$$
 (6.23)

### 6.2.2 Experimental DOAS measurements setups

For over more than 30 years many different experimental DOAS measurements setups have been developed. In general, DOAS measurements setups can be divided in active or passive (artificial or natural radiant source). Passive DOAS instruments can measure either direct (Sun, Moon or stars), or scattered light. Regarding the viewing geometry, passive scattered DOAS can operate in limb geometry, or measure in multi-angle (MAXDOAS). Currently there are passive DOAS instruments operating from the ground, from cars, aircrafts, stratospheric balloons and also from satellites. Some of these setups are depicted in Fig. 6.4.

### The mini-DOAS instrument concept

This work reports on measurements performed with a mini-DOAS instrument. Here, the background of measurement concept of these instruments is summarized as follows.

 $<sup>^1</sup> A vailable \ under: \ http://www.iup.uni-heidelberg.de/bugtracker/projects/doas is a state of the state$ 



Figure 6.4: Experimental DOAS measurement setups. Example of active DOAS setups are given in (a) and (b), i.e., Long-path DOAS (LP-DOAS) with or without reflectors. Passive DOAS setups examples are given in figures (c) to (f). An example of direct sunlight DOAS is given by (c), while examples (d) to (f) are based on scattered skylight measurements. These measurements may be performed in limb geometry (d), or in multi-axis (MAXDOAS) mode from ground based (e), satellites, or aircraft platforms (AMAXDOAS) (f). Figure adopted from Platt and Stutz (2008).

For over a decade, stratospheric profiles of trace gas abundances have been successfully inferred from direct sunlight DOAS measurements performed on board stratospheric balloons (e.g., *Ferlemann et al.*, 1998; *Harder et al.*, 1998; *Dorf et al.*, 2006; *Butz et al.*, 2005). With the benefit of the balloon Lagrangian measurements, results obtained from those measurements have addressed photochemical and transport issues of relevant stratospheric compounds (*Butz et al.*, 2005; *Dorf et al.*, 2006; *Butz et al.*, 2005; *Dorf et al.*, 2006; *Butz et al.*, 2009). The direct sunlight balloon-borne DOAS instrument is a highly precise, stable, and quite big apparatus. Vertical profiles of atmospheric substances can be inferred when either the light source changes its position (sunrise/sunset), or when the measurement platform performs ascents and descents. Thus, despite of the high accuracy, measurements of the balloon-borne direct sunlight DOAS instrument are restricted to the above mentioned viewing geometries. As a result, a smaller and more versatile version of that instrument was built at the IUP-HD in 2005, and referred to as "mini-DOAS instrument" (*Weidner*, 2005). The concept of that novel mini-DOAS was to perform limb scattered skylight

measurements on board balloon platforms, aiming also at the profile retrieval of stratospheric trace gas abundances (*Weidner et al.*, 2005). In the mini-DOAS setup, the viewing geometry may be changed not only due to a displacement of the measurement platform, but also as a result of telescopes mounted on stepper-motors. Thus, vertical information of the atmosphere may also be gained at float altitude by operating the instrument in limb scanning mode. A sketch of these mini-DOAS viewing geometries is given in Fig. 6.5. Moreover, recently a further advance in the application of the mini-DOAS instruments has been presented by *Kritten et al.* (2010), where time-dependent stratospheric profiles of UV/vis absorbing radicals are inferred from balloon-borne measurements.

The mini-DOAS instrument used in this work was built in 2007 based on the experiences gained from the 2005 mini-DOAS instrument. Specific details will be given in Chap. 7.



Figure 6.5: Viewing geometry of balloon-borne mini-DOAS instruments. Letf: Fixed limb mode (during balloon ascent/descent). Right: Limb scanning mode (at balloon float altitude). Adopted from Kritten (2009).

### 6.3 Radiative transfer modeling

Once the (differential) slant column densities of a given absorber have been retrieved by the DOAS fitting procedure, a further step is needed to infer the concentration c corresponding to the measured SCDs. Since  $SCD = \int c \cdot dl$ , this step implies solving the radiative transfer equation RTE (Eq. 2.25), i.e., to define the effective path of the photons through the sampled atmospheric volume. For measurements obtained by active or direct sunlight DOAS setups, this can be handled by calculating the light path geometrically. However, for scattered light measurements solving the RTE is not straight forward. In these cases, the light path-dependent SCD is often compared to the light path-independent vertical columns densities (VCD). This

comparison is addressed via the air mass factors (AMF), defined as

$$AMF = \frac{SCD}{VCD} = \frac{\int c \cdot dl}{\int c \cdot dz}.$$
(6.24)

Thus, the AMF for a column of height z represents the ratio of the traveled light path inside the column, and z. Therefore, the AMFs can be understood as weighting factors related to the effective photon path length in the given column.

Based on the viewing geometry of the measurements, some simplifications can be done for an analytical calculation of the AMF (details given in e.g. *Platt and Stutz*, 2008). For instance, in the case of a trace gas layer located above the detector, most of the scattering events take place between the trace gas layer and the instrument. Thus, the light path may be simplified by  $AMF \sim \frac{1}{\cos(SZA)}$ , where SZA is the solar zenith angle. On the other hand, for ground based measurements targeting trace gas layers located near the surface, the AMF  $\sim \frac{1}{\sin(\alpha)}$ , where  $\alpha$  is the angle between the viewing direction of the instrument and the horizon. However, in complex RT atmospheres where multiple scattering takes place, these geometrical simplifications are no longer valid. In those cases, the need of a thorough study of the different processes that photons may undergo before reaching the detector, implies the use of *radiative transfer models* (RTM).

The RTM used throughout this work is the fully spherical 3-D model McArtim ("Monte Carlo Atmospheric Radiative Transfer Inversion Model"), detailed in *Deutschmann*, 2008. McArtim was designed for simulating the radiative transfer in the UV/vis/NIR spectral range, and its performance was successfully compared to other RTM (*Wagner et al.*, 2007), and validated with measurements (*Deutschmann*, 2008; *Deutschmann et al.*, 2010). The McArtim principle addresses the adjoint monochromatic RTE (Eq. 2.25). By modeling the physical processes that a single photon of a given wavelength undergoes in a simulated atmosphere, McArtim generates light trajectories by modeling the physical processes that a single photon of a given wavelength. Undergoes in a simulated atmosphere. This is modeled from the moment the photon leaves a detector in a certain line-of-sight, until the photon escapes from the top of the atmosphere to the Sun (backward RTM). McArtim operates with a statistical Monte Carlo approach, assigning probability distributions to each light extinction process. Therefore, through repeated random sampling in a simulated atmosphere, the derivatives can be modeled for each measured quantity (e.g., SCD or radiances).

The main parameters characterizing the simulated atmosphere in the RTM are the vertical and/or horizontal discretization (grid), the vertical profiles of temperature, pressure, and humidity, the ground albedo, the vertical distribution of the concentration of trace gases, absorption cross-section associated to those trace gases, optical properties of aerosol and

Layer number	Altitude range (km)
1	0-0.1
2	0.1-0.6
3	0.6-1.2
4	1.2-2
5	2-3.5
6	3.5-5
7	5-6
8	6-7
9	7-8.5
10	8.5-9.5
11	9.5-10.5

Table 6.1: Vertical grid of the simulated atmosphere chosen for the RTM detailed in Chap. 8.

cloud particles, and their vertical distribution. In the McArtim interface, those atmospheric parameters can be defined by the user. Herein, the RT in the true 3-D atmosphere is simulated in a 1-D modeled atmosphere divided in concentric spherical cells (i.e., vertical grid), as given in Table 6.1. In this case, the atmospheric conditions in each of those vertical layers are assumed to be horizontally homogeneous and to remain unaltered for the time of the measurements (limitations of this assumption are addressed in Chap. 9). Additionally, the viewing geometry related to each measurement is defined by the field-of-view of the detector (in this case rectangular, as given in Chap. 7), and the attitude of the detector during each of the measurements, i.e., the solar zenith and solar relative azimuth angles, the latitude, longitude, and altitude of the measurement location, as well as the elevation angle of the telescope relative to the horizon.

Hence, in the simulated atmosphere with n discrete layers of height  $h_n$  (referred to as *boxes*), a weighting factor similar to Eq. (6.24) can be inferred for each box. This weighting factor is called *box air mass factor (boxAMF)*, and may be understood as the ratio between the effective light path inside a given box n, and the height of the box  $h_n$  (i.e., the sensitivity weighted light path length inside the box). Besides boxAMF, McArtim is able to compute other physical quantities such as e.g. radiances, dSCD, and aerosol optical properties, as well as their Jacobians. Details and application of those quantities are given in *Deutschmann et al.* (2010).

Proof and constrains of the physical quantities inferred by the RTM may arise from the comparison of modeled and measured quantities (usually dSCDs or radiances). Also, stable known atmospheric gases such as the oxygen dimer  $O_4$  ( $O_2$ - $O_2$ ) may serve for calibration and validation of the RT calculations. The remain part of this section aims at the description of the oxygen dimer and its possible applications related to RT calculations. In this work the absorption of  $O_4$  is used for probing the characterization of the light path in the RTM, and also for the validation of a novel algorithm for the retrieval of trace gas concentration vertical profiles (Sect. 8.2).

The oxygen dimer  $O_4$  is an atmospheric trace gas which vertical distribution, fairly constant in the atmosphere, is related to the squared oxygen number density  $[O_2]$  and, thus,  $O_4$  has a scale height of roughly 4 km.  $O_4$  is a (weak) absorber of light in the UV/vis spectral range (e.g., *Perner and Platt*, 1980; *Pfeilsticker et al.*, 2001; *Wagner et al.*, 2002), and its absorption cross-section is temperature dependent. However, its absolute value is not known up to date (*Pfeilsticker et al.*, 2001). The vertical distribution of the  $O_4$  extinction coefficient  $\mathcal{E}_{O_4}$  may be calculated as

$$\mathcal{E}_{O_4}(z) = \sigma(T) \cdot [O_4(z)] = \sigma \cdot K_{eq}(T) \cdot [O_2(z)]^2$$
(6.25)

where  $K_{eq}$  is the equilibrium constant of O<sub>4</sub> and, at 360.5 nm and 296 K, the O<sub>4</sub> peak collision pair absorption cross-section ( $\sigma \cdot K_{eq}$ ) has a value of  $4.1 \cdot 10^{-46} \frac{cm^5}{molec^2}$ , known with an accuracy of around 10% (e.g., *Greenblatt et al.*, 1990, *Pfeilsticker et al.*, 2001).

Therefore, the  $O_4$  optical densities can generally be inferred from the atmospheric temperature and pressure. As a result, the  $O_4$  absorption may be used for the characterization of the light path distribution through the atmosphere (e.g., Wagner et al., 2004). For instance, the boxAMF related to the SCD of a species located close to the ground and (weakly) absorbing in similar wavelengths as the oxygen dimer, may be approximated to the boxAMF related to the  $O_4$  optical density at the same height. This approximation implies the assumption of the trace gas being horizontally homogeneously distributed (as it is the oxygen dimer), and also the assumption of the shape of the vertical distribution of the trace gas in question being similar to the  $O_4$  vertical distribution. Additionally,  $O_4$  absorption and its measured dSCD may be used for describing optical properties of aerosol and cloud particles affecting the light path, as well as their vertical distributions. This is the so-called " $O_4$  method", and is often applied for the retrieval of aerosol vertical distributions in combination with DOAS measurements (e.g., Wagner et al., 2004; Frieß et al., 2006). However, disadvantages of this method are the restriction to the absorption bands of  $O_4$  and, more important, the decreasing sensitivity of the method with altitude. In order to overcome these limitations, and since this work relies on aircraft-borne measurements probing the atmosphere from the boundary layer up to the UT/LS, Section 8.2 presents an algorithm for the profile retrieval of aerosol extinction coefficients, not based on measurements of O<sub>4</sub> dSCDs, but on measured monochromatic radiances.

### CHAPTER 6. REMOTE SENSING OF THE ATMOSPHERE

# Chapter 7

# The mini-DOAS instrument on board the Falcon aircraft

Based on the balloon-borne mini-DOAS instrument built in 2005 (see Sect. 6.2.2), in 2007 a new airborne mini-DOAS instrument was built intended for aircraft deployments, but versatile enough to be set up on board other measurement platforms (*Simmes*, 2007). Results presented in this work derive from measurements performed during the first deployments of that 2007 mini-DOAS instrument (also referred to as "Oskar"). Here the "Oskar" instrumental setup and its deployment on the DLR-Falcon aircraft are described. In addition, the first research campaigns were the instrument operated are introduced.

### 7.1 Description of the mini-DOAS instrument

The mini-DOAS instrument from 2005 consists of two commercial USB2000 spectrometers from Ocean Optics<sup>1</sup> for the detection of skylight in the spectral range of 330-550 nm (details on design and performance are given in *Weidner*, 2005). Likewise, the new instrument includes two commercial Ocean Optics spectrometers covering similar wavelengths (320-550 nm) and using scattered skylight received from the horizon for the detection of trace gases such us  $O_3$ , NO<sub>2</sub>, BrO, OCIO, IO, OIO, HNO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>, CH<sub>2</sub>O, H<sub>2</sub>O and O<sub>4</sub>. However, the exchange of the USB2000 spectrometer covering the UV spectral range by a QE65000 spectrometer in the new version, resulted not only in a higher resolution capability of the novel instrument but also in a better performance (higher signal-to-noise ratio). While details on the design and characterization of the improved instrument are given in *Simmes* (2007), herein a basic description is provided.

The core of the mini-DOAS "Oskar" instrument, sketched in Fig. 7.1, consists of a housing

<sup>&</sup>lt;sup>1</sup>Ocean Optics, for detailed information: www.oceanoptics.com

	USB2000	QE65000	
	vis channel	$UV \ channel$	
Detector type <sup>*</sup>	Sony ILX511	Hamamatsu S7031	
	1-D array	2-D array	
Num. pixels <sup>*</sup>	2048	1024	
$Well-depth^*(e^-)$	$62.5 \cdot 10^3 \text{/pixel}$	$1.5 \cdot 10^6 / \text{column}$	
A/D resolution (bit)	12	16	
Num. counts (full sat.)	4096	$65 \cdot 10^3$	
$photo-e^-/count$	15.3	23.1	
Quantum efficiency <sup>*</sup> (at 400 nm)	0.1	0.5	
Total num. photons	$625 \cdot 10^3 / \text{pixel}$	$3 \cdot 10^6 / \text{column}$	
	150 /pixel	46 /column	
Wavelength range (nm)	336-551	320-402	
Slit entrance (width, $\mu m$ )	50	100**	
Dispersion (nm/pixel)	0.105	0.08	
FWHM	6.2 pixels	4.75 pixels	
	0.68 nm	0.38 nm	

 Table 7.1: Technical details of the mini-DOAS spectrometers.

\* Ocean Optics, 2006

\*\* Changed to 200  $\mu \mathrm{m}$  width in 2008

with two Ocean Optics spectrometers (QE65000/USB2000 for UV/vis). The spectrometer operating under cross Czerny-Turner geometry, and with linear/array CCD detectors (USB2000/QE65000). Their properties are given in Table 7.1.



Figure 7.1: Sketch of the mini-DOAS housing containing the two spectrometers. Adopted from *Simmes* (2007).

	<b>USB2000</b>	$\mathbf{QE65000}$
Integration Time (ms)	50	1500
Photo-electron Noise $\epsilon_{ph}$ (e <sup>-</sup> )	224	1095
Dark Current Noise $\epsilon_{dc}$ (e <sup>-</sup> )	2	44
Electronic Offset Noise $\epsilon_{el}$ (e <sup>-</sup> )	47	123
Sum $\epsilon_{single} = \sqrt{\epsilon_{ph}^2 + \epsilon_{dc}^2 + \epsilon_{el}^2} \ (e^-)$	229	1103
Corresponding N/S	0.458%	0.092%

Table 7.2: Noise contribution for a single scan (saturation level of 80%) for the UV/vis channels (QE65000/USB2000) of the mini-DOAS instrument. Adopted from Simmes (2007).

The instrumental noise is defined as the root-mean-square of the photo-electron shot noise  $(\epsilon_{ph})$ , the dark current  $\epsilon_{dc}$  and the electronic noise  $(\epsilon_{el})$ . The  $\epsilon_{el}$  is a random noise resulting from electronic processes such as the A/D conversion, the pre-amplifying of the signal or the read-out. The  $\epsilon_{dc}$  is related to the thermal energy (discharge) within the silicon detector and may, therefore, be decreased by low and stable temperatures, and by reducing the integration time  $(\epsilon_{dc} \sim \sqrt{T_{int}})$ . The  $\epsilon_{ph}$  depends on the well-depth and the saturation level of the measurement, i.e., by the number of photons N reaching the detector  $(\epsilon_{ph} \sim \sqrt{N})$ . Thus, this noise limits the accuracy of radiance measurements (e.g., *Stutz and Platt*, 1996). In addition, since the DOAS evaluation relies on the division of two spectra, that physical limit increases by a factor of  $\sqrt{2}$ . Details on different noise contributions of the mini-DOAS instrument used in the framework of this work are given in Table 7.2.

As long as the photo-electron shot noise dominates (e.g., Table 7.2), the total noise may be reduced by adding up spectra since  $\epsilon_{total} = \epsilon_{single}/\sqrt{N}$  (N is the number of co-added spectra). The number of spectra usually co-added in this work are  $10^3$  (up to  $10^4$ ) spectra in the case of the USB2000, and 100 (up to  $10^4$ ) spectra in the case of the QE65000. Under atmospheric measurements, at a 80% saturation level, and for standard integration times (see Table 7.2), these co-added spectra result in a total  $1-\sigma$  noise contribution of  $1.5 \cdot 10^{-4}$  and  $9.2 \cdot 10^{-5}$  for the USB2000 and QE650000, respectively. In order to assure optical stability, the spectrometers housing is evacuated, vacuum-sealed and temperature stabilized with an ice-water mixture (see Fig. 7.2, a). The temperature stability of the mini-DOAS is about 12 h (depending on the external temperature), and its pressure can be kept ~1 mbar for roughly 1 week.

### 7.2 Deployment on the DLR-Falcon aircraft

For the deployment on the DLR-Falcon aircraft, two telescopes with spherical quartz lenses of 12.7 mm diameter and 30 mm of focal length are mounted on two stepper-motors<sup>2</sup> with a step size of  $0.04^{\circ}$ . The telescopes and stepper-motors are mounted on an aluminum air-tight window of 4.5 kg (see Fig. 7.2, e). The window is located in the left side of the aircraft and has two slits (5x80 mm<sup>2</sup>, see Fig. 7.2, f). Hence, embedded in the window, the telescopes may perform scans from  $-35^{\circ}$ , up to  $+10^{\circ}$ .

Two quartz glass fiber bundles<sup>3</sup> directed the light from the two telescopes to the spectrometers (see 7.2, f). These fiber bundles partly depolarize the incoming light and also allow for a flexible instrument set-up. The UV fiber bundle consists of 8 individual fibers with a diameter of  $200\mu$ m each. The fiber bundle directed to the USB2000 spectrometer consists of 10 individual fibers with a diameter of  $100\mu$ m each. Both (2 m) fiber bundles have a numerical aperture of 0.22, and their individual glass fiber entrances are linearly aligned. This allows a field-of-view (FOV) of  $0.19^{\circ}$  in the vertical and  $2.1^{\circ}$  in the horizontal.

One single board computer<sup>4</sup> (see 7.2, c), with Compact Flash Card for data storage (4GB), operates the measuring software DOASIS with the Windows XP operative system (*Kraus*, 2004). Unfortunately, under DOASIS, the stepper-motors (directed by a single controller), failed to operate simultaneously. Therefore, most of the deployments of the mini-DOAS in this configuration where performed with the telescopes fixed parallel to the horizon. Therefore, the viewing geometry of the mini-DOAS is given by a viewing direction perpendicular (anticlockwise) to the flight direction, and the elevation angle of the telescopes is directly given by the roll angle of the aircraft (see 7.2, h). Thus, the viewing geometry of the instrument is provided by the basic instrumentation of the Falcon aircraft (with 1 Hz resolution). During the Falcon deployment, the two spectrometers, the stepper-motor controller, the computer and the display are integrated into a 19-inch rack inside of the pressurized cabin (see 7.2, b and d).

The small size ( $483x400x270 \text{ mm}^3$ , w/o fibers), weight (25 kg, including 5 kg of water), and power consumption (14 W), make this mini-DOAS a versatile instrument for many measurement platforms. Indeed, since the instrument was built in 2007, the specific instrument has been deployed on the Falcon aircraft (this work and *O'Brien*, 2008), on balloon gondolas (*Werner*, 2009), and on manned (Geophysica) and in future unmanned (Global Hawk) high-altitude aircrafts.

However, since Oskar was built and based on the experience gained after its first deployment

<sup>&</sup>lt;sup>2</sup>Hofmann Meßtechnique, Germany

<sup>&</sup>lt;sup>3</sup>Built by FiberTech GmbH, details in http://fibertech.de

<sup>&</sup>lt;sup>4</sup>1GB RAM, EPIC format, type Huricane, from Lippert Automationstechnik GmbH. Details in http://www.lippert-at.com



Figure 7.2: The mini-DOAS instrument on board the Falcon aircraft (adopted from Simmes, 2007). Details are given in the text.

during the ASTAR 2007 aircraft campaign (see Chap. 5), some shortcoming were also found:

## 7.3 Aircraft-borne limb DOAS measurements in the Arctic troposphere

Within the International Polar Year 2007/08<sup>5</sup>, and as part of the POLARCAT project<sup>6</sup>, the mini-DOAS instrument was deployed on the Falcon aircraft in two campaigns in the framework of this thesis : the ASTAR 2007 and the GRACE 2008 campaigns.

During these field campaigns, target trace gases to be detected from the boundary layer up to the UT/LS with the mini-DOAS instrument were  $O_3$ ,  $NO_2$ , BrO, OClO, IO, HNO<sub>2</sub>,  $C_2H_2O_2$ , CH<sub>2</sub>O, H<sub>2</sub>O and O<sub>4</sub>. In this work, measurements of bromine monoxide are the ones addressed in detail.

This section introduces both campaigns, providing their general objectives, the instruments on board the DLR-Falcon aircraft, and a summary of the deployments for each campaign. In addition, the particular sorties studied within this work are briefly explained.

### 7.3.1 The ASTAR 2007 campaign

The first deployment of this mini-DOAS instrument was during the ASTAR 2007 campaign ("Arctic Study of Aerosol, Clouds and Radiation"), based on Longyearbyen (LYN), Spitsbergen (78°N, 18°E).

Main objectives of this campaign, that took place during March and April 2007, were:

- the characterization of the aerosol microphysical, optical and chemical properties during the Arctic haze season,
- the investigation of microphysical and optical properties of Arctic clouds,
- the identification of pollutants transport pathways,
- the study of the halogen activation in the polar troposphere, main objective of this work (Chap. 9).

Table 7.3 provides a summary of all the instruments deployed on the Falcon aircraft during the ASTAR 2007 campaign. In addition, an overview of the research flights performed during the

<sup>&</sup>lt;sup>5</sup>Details given in *http* : //www.ipy.org/

<sup>&</sup>lt;sup>6</sup> "Polar study using aircraft, remote sensing, surface measurements and modeling of climate, chemistry, aerosols and transport". Details given in http://www.polarcat.no/

campaign is given in Table 7.4, where the main features of each flight regarding the mini-DOAS measurements are also included.

The particular deployments studied in this work are the 1<sup>st</sup> April, and the 8<sup>th</sup> April ones. Figures 7.3.1 and 7.3.1 present the flight trajectories of both sorties. In general, prior to the flights the housing of the vacuum instrument was filled up with a mixture of water-ice in order to assure instrumental optical stability. Also, offset and dark current spectra were measured for posterior spectra correction (10<sup>4</sup> scans with integration time  $T_{int} = 8$  ms, and 1 scan with  $T_{int} = 10^4$  ms, resp.). Before taxi of the aircraft to the runway, the measurement script was set and started for fix-mode telescopes (script given by *Simmes*, 2007). During the flight, detailed in Sect. 7.3.1, the aircraft performed different ascents and descents probing the Arctic atmosphere from the BL up to the UT/LS. Unique to this deployment was the very low flight passage over the High Arctic sea ice (60–100 m during 25 min), followed by a steep ascent to the LS. The aircraft landed after 3.30 h of flight.

### 7.3.2 The GRACE 2008 campaign

The GRACE 2008 field campaign ("Greenland Aerosol and Chemistry Experiment"), took place in June-July 2008, based in Kangerlussuaq (67°N, 50°W). Before the campaign, same changes were done on the above described mini-DOAS instrument. The focus of the QE65000 focus was optimized for ~ 0°C, the slit of the QE65000 needs to be replaced by one of 200  $\mu$ m width, and the USB2000 was replaced by a counterpart covering the 410–532 nm spectral range and with a FWHM = 0.8 nm (see *O'Brien*, 2008).

General objectives of the GRACE 2008 campaign were:

- to study the annual variation of the distribution of trace gases and aerosols in the Arctic
- to examine processing (chemistry, aerosol aging) in pollution plumes during long-range transport for different sources (forest fires, urban pollution)
- to determine the pathways and dispersion of boreal forest fire emissions at high latitudes
- to investigate the distribution and impact of reactive halogen compounds in the Arctic
- to study the role of mixing during long-range transport using ambient and artificial tracer
- to sample in situ data for validation of space-borne observations

Table 7.5 provides a summary of all the instruments deployed on the Falcon aircraft during this campaign. An overview of the research flights performed during the GRACE 2008 campaign is

Category	Instrument	Method	Measurement	Institute
Aerosols	CPSA/CPC system	6-channel condensation	Nucleation and Aitken	DLR-IPA
		particle counter system	mode aerosol number conc.	
		(unheated/heated)	Semi-/non-volatile particle fraction	DLR-IPA
	PCASP-100X FSSP-300	Aerosol spectrometer probes	Accum. and coarse	DLR-IPA
			mode particle size distrib.,	
			cloud elements	
	Grimm OPC	Optical particle	Accum. mode	MISU/ITM
		counter	particle size distrib.	
	(Tandem-)	Differential mobility analyzer	Aitken and accum.	MISU/ITM
	DMA	(unheated/heated)	particle size distrib.	
		Volatility tandem mode	Aerosol mixing state	
	PSAP	Particle soot	Aerosol absorption	MISU/ITM
		absorption photometer	coefficient	
	$3\dot{A}$ PSAP	3-wavelength Particle soot	Aerosol absorption	FMI
		absorption photometer	coefficient	and DLR-IPA
	IN	Integrating nephelometer	Aerosol scattering	NIPR
			coefficient	
	Aerosol sampling	Filter/impactor sampling for	Aerosol chemistry	TU Darmstadt
		single particle element analysis		
Trace gases	$NO/NO_y$ and	Chemi-luminescence	NO and $NO_y$ vmr	DLR-IPA
	$J(NO_2)$	filter radiometer	calculation of $NO_2$	
	CO	VUV fluorescence	Carbon monoxide vmr	DLR-IPA
	Ozone	UV absorption	Ozone vmr	DLR-IPA
	IT-CIMS	Chemical ionization	SO <sub>2</sub> vmr	MPI-K
		mass spectrometry	$HNO_3$ , $HCl$ possible	and DLR-IPA
	CR-2	Frost point hygrometer	humidity	DLR-IPA
	Mini-DOAS	Differential Optical	Halogen compounds	Uni-HD
		Absorption Spectroscopy		
Aircraft data	Aircraft position	Falcon basic sensor inst.	Aircraft position data	DLR-FB
	Atmospheric state	Falcon basic sensor inst.	P, T, humidity, wind	DLR-FB

Table 7.3: Summary of the instruments deployed on the DLR-Falcon aircraft during the ASTAR 2007 campaign.

Date	Location	Geophysical condition	Limb observation	Deployment notes
dd.m.yyyy	Place	Description	Scanning mode (Sc)	
(UT)	(Lat., Long.)	$(SZA \ range)$	Fixed mode $(F)$	
28.3.2007	LYN <sup>a</sup>	high latitude	$\operatorname{Sc}$	Mostly in
(17:31:13-20:11:47)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(88^{o}-95.6^{o})$		darkness
30.3.2007	LYN	high latitude	$\operatorname{Sc}$	Test flight
(15:21:31-16:48:08)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(81^{o} - 85.4^{o})$		Script test
31.3.2007	LYN	high latitude	$\operatorname{Sc}$	Stepper motors
(07:07:41-10:49:26)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(79.9^{o}-73.9^{o})$		failure
1.4.2007	LYN	high latitude	F	BrO over sea ice
(10:46:21-14:24:15)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(73.5^{o}-77.8^{o})$		$(HONO, CH_2O?)$
3.4.2007	LYN	high latitude	$\mathbf{Sc}$	Scientist on board
(16:54:18-19:20:18)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(84.3^{o}-91.4^{o})$		(Stepper motor test)
4.4.2007	LYN	high latitude	$\operatorname{Sc}$	Cirrus clouds
(10:50:38-12:54:44)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(72.3^{o}-73.7^{o})$		Script problem
8.4.2007	LYN	high latitude	F	BrO over sea ice
(12:03:54-16:01:56)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(71.2^{\circ}-79.8^{\circ})$		$(HONO, OClO, CH_2O?)$
10.4.2007	LYN	high latitude	$\mathbf{Sc}$	Spectrum ref. test
(09:52:36-13:57:46)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(70.6^{o} - 73.5^{o})$		(BrO, IO?)
14.4.2007	LYN	high latitude	Sc and F	Spectrum ref. test
(12:15:19-14:56:38)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(69.3^{o}-75.6^{o})$		STP <sup>e</sup> , Cirrus clouds
14.4.2007	LYN	high latitude	F	Pollution layers, cirrus clouds
(16:06:27-19:09:18)	$(78.1^{\circ}N, 15.3^{\circ}E)$	$(78^{o}-87^{o})$		$(CH_2O, BrO?)$
15.4.2007	LYN-TRH <sup>b</sup>	high latitude	Sc and F	Spectrum ref. test, STP
(16:06:27-19:09:18)	$(78.1^{\circ}N, 15.3^{\circ}E - 63.25^{\circ}N, 10.23^{\circ}E)$	$(79.2^{o}-96.3^{o})$		Darkness
15.4.2007	TRH-LYN	high latitude	Sc and F	STP
(21:19:47-00:26:22(+1))	$(63.25^{\circ}N, 10.23^{\circ}E - 78.1^{\circ}N, 15.3^{\circ}E)$	$(99^{o}-91.2^{o})$		Darkness
17.4.2007	LYN-K <sup>c</sup>	high latitude	F	Transfer flight
(08:10:45-10:09:42)	$(78.1^{\circ}N, 15.3^{\circ}E - 67.9^{\circ}N, 21.1^{\circ}E)$	$(70.9^{o}-57.7^{o})$		(BrO?)
17.4.2007	K-OBPH <sup>d</sup>	mid latitude	F	Transfer flight
(10:58:54-14:29:11)	$(67.9^{\circ}N, 21.1^{\circ}E-48.4^{\circ}N, 11.16^{\circ}E)$	$(57.7^{o}-55^{o})$		Warm instrument

<sup>a</sup> Longyearbyen, Svalbard <sup>b</sup> Trondheim, Norway <sup>c</sup> Kiruna, Sweden <sup>d</sup> Oberpaffenhofen, Germany <sup>e</sup> Stepper motor problem

Table 7.4: Overview of the mini-DOAS deployments during the ASTAR 2007 aircraft campaign. Trace gases ambiguously detected (due to clouds or poor signal-to-noise ratio) are given in parenthesis.

### 124 CHAPTER 7. AIRCRAFT DEPLOYMENT OF THE MINI-DOAS INSTRUMENT



(a) 1 April 2007: Flight trajectory



(b) 1 April 2007:  $O_3$  and BrO measurements, and selected passage

Figure 7.3: 1 April 2007 sortie. (a) Flight trajectory, (b) Left panel: Flight profile (gray), and measurements of BrO dSCDs (red), and  $O_3$  vmr (blue) provided by H. Schlager (DLR). Note the anti-correlation of both trace gases at 12–12:30 UT. Right panel: Passage of the flight chosen for the retrieval of BrO vmr vertical profile (detailed in Chap. 9).



(a) 8 April 2007: Flight trajectory



(b) 8 April 2007:  $O_3$  and BrO measurements, and selected passages

Figure 7.4: 8 April 2007 sortie. (a) Flight trajectory, (b) Left panel: Flight profile (gray), and measurements of BrO dSCDs (red), and  $O_3$  vmr (blue) provided by H. Schlager (DLR). Note the anti-correlation of both trace gases for altitudes below ~2 km. Right panel: Passages of the flight chosen for the retrieval of BrO vmr vertical profiles. In particular, the measurements performed during the ascent starting at 14:30 UT are used in this work for the validation of the novel retrieval of vmr vertical profile of tropospheric trace gases. In addition, the horizontal passage 14:10–14:30 UT is analyzed for the characterization of the BrO-induced ozone depletion event in the boundary layer. Details are provided in Chap. 9.

given in Table 7.6, where the main features of each flight regarding the mini-DOAS measurements are also included. Details of the mini-DOAS dSCDs measurements gathered during this campaign are given by *O'Brien* (2008). Overall, main issues encountered during the GRACE 2008 campaign where related to the abundant cloud and aerosol particles present during most of the campaign, and the low altitude of most of the flights. As a result, the majority of the spectra recorded presented a rather poor signal-to-noise ratio. In this work only one sortie that took off from Kangerlussuaq and landed in Longyearbyen (15 July 2008, Fig. 7.3.2), will be briefly addressed in Sect. 9.2.1.

Institute	Meaurement	Technique
DLR	$O_3$ UV absorption	
	CO	VUV flouorescence
	$\mathrm{CO}_2$	IR absorption
	NO	CL
CAO	$NO_2 CL$	
DLR	$NO_y$ Reduction converter + CL	
	$J(NO_2)$	Filter radiometer
	PAN, PPN, MPAN	CIMS
	PFC (C6F12, C9F18) samples $+$ GC	CIMS
FZJ	$H_2O$ (total)	Lyman-alpha hygrometer
Uni-HD	$O_3, O_4, NO_2, BrO, OClO, CH_2O, \ldots$	mini-DOAS
DLR	Nucleation and Aitken mode aerosol	2-channel CPC system + DMA
	concentration and size distribution	
DLR	Accumulation and coarse mode aerosol	PCASP-100X, FSSP-300
	size distribution	
DLR	Non-volatile aerosol size	3-channel CPC system + OPC
	distribution + thermodenuder $(250 \text{ degC})$	
DLR	Absorption coefficient	PSAP (3 wavelengths)
	Single particle composition	Aerosol impactor sampling
DLR	Meteorological parameters: p, T, wind,	Standard probes
	relative humidity	
DLR	Aircraft position	INS, GPS

Table 7.5: Summary of the instruments deployed in the DLR-Falcon aircraft during the GRACE2008 campaign.

Date	Location	Geophysical condition	Deployment notes
dd.m.yyyy	Place	Description	
(UT)	(Lat., Long.)	(SZA range)	
30.6.2008	OBPH <sup>a</sup> -Scotland	mid latitude	Transfer flight
(08:33:35-10:50:31)	$(48.4^{\circ}N, 11.16^{\circ}E-55.5^{\circ}N, 3.1^{\circ}W)$	$(41.2^{o}-36^{o})$	$(O_3, NO_2, BrO?)$
30.6.2008	Scotland-Iceland	high latitude	Transfer flight, warm inst.
(12:08:24-14:26:33)	$(55.5^{\circ}N, 3.1^{\circ}W- 64^{\circ}N, 21.56^{\circ}W)$	$(32.4^{o} - 42^{o})$	$(O_3, NO_2, BrO?)$
30.6.2008	Iceland-KGL <sup>b</sup>	mid latitude	Transfer flight, warm inst.
(15:48:50-17:55:46)	$(64^{\circ}N, 21.56^{\circ}W - 67^{\circ}N, 50.4^{\circ}W)$	$(46.7^{o} - 49.7^{o})$	$(O_3, NO_2, BrO?)$
2.7.2008	KGL	high latitude	Script problem
(15:17:39-16:59:58)	$(67^{\circ}N, 50.4^{\circ}W)$	$(44^{o} - 46.4^{o})$	(BrO?)
4.7.2008	KGL	high latitude	Script problem
(17:41:38-21:22:19)	$(67^{\circ}N, 50.4^{\circ}W)$	$(49^{o} - 68.7^{o})$	
7.72008	KGL	high latitude	$\rm VC^d$
(12:42:23-16:06:33)	$(67^{\circ}N, 50.4^{\circ}W)$	$(51.3^{o} - 44.9^{o})$	$(O_3, H_2O, BrO?)$
8.7.2008	KGL	high latitude	MA <sup>e</sup> 8km, VC
(11:13:25-14:03:10)	$(67^{\circ}N, 50.4^{\circ}W)$	$(59.1^{o} - 49.9^{o})$	Tracing Canadian BBP <sup>f</sup>
			$(O_3, H_2O, CH_2O, C_2H_2O_2?)$
9.7.2008	KGL	high latitude	MA 6km, VC
(11:58:08-15:09:48)	$(67^{\circ}N, 50.4^{\circ}W)$	$(55.2^{\circ}-44.8^{\circ})$	Comparison flight $(DC-8)$
			$(O_3, H_2O?)$
9.7.2008	KGL	high latitude	MA 8km, VC
(18:02:11-21:10:54)	$(67^{\circ}N, 50.4^{\circ}W)$	$(50.9^{o} - 68^{o})$	$(O_3, NO_2, H_2O?)$
10.7.2008	KGL	high latitude	MA 11km
(14:26:38-18:35:26)	$(67^{\circ}N, 50.4^{\circ}W)$	$(45.9^{o} - 53.6^{o})$	Siberian BBP
			$(O_3, NO_2, H_2O, BrO?)$
12.7.2008	KGL	high latitude	MA 6km, VC
(16:43:03-20:32:47)	$(67^{\circ}N, 50.4^{\circ}W)$	$(46.7^{o} - 64.6^{o})$	$(H_2O?)$
13.7.2008	KGL	high latitude	MA 6km, VC
(12:58:04-16:42:23)	$(67^{\circ}N, 50.4^{\circ}W)$	$(51^{o} - 46.8^{o})$	$(O_3, H_2O?)$
14.72008	KGL	high latitude	MA 5km, VC
(11:20:01-12:44:30)	$(67^{\circ}N, 50.4^{\circ}W)$	$(59.3^{o} - 52.2^{o})$	Comparison flight (ATR-42)
			$(NO_2, H_2O?)$
14.7.2008	KGL	high latitude	MA 9km, VC
(16:13:30-19:10:24)	$(67^{\circ}N, 50.4^{\circ}W)$	$(46^{o} - 57^{o})$	$(NO_2, H_2O?)$
15.7.2008	KGL- LYN <sup>c</sup>	high latitude	Clean Arctic air
(11:04:38-14:59:03)	$(67^{\circ}N, 50.4^{\circ}W$ -78.1°N, 15.3°E)	$(61^{o} - 62.7^{o})$	UV channel problems
			$(O_3, H_2O?)$
15.72008	LYN-KGL	high latitude	Clean Arctic air
(16:27:42-19:59:19)	$(78.1^{\circ}\text{N}, 15.3^{\circ}\text{E} - 67^{\circ}\text{N}, 50.4^{\circ}\text{W})$	$(67^{o}-61.9^{o})$	$(BrO, O_3, H_2O?)$
17.7.2008	KGL	high latitude	Summit station over-flight, VC
(13:36:31-16:47:53)	$(67^{\circ}N, 50.4^{\circ}W)$	$(49.2^{o}-47.6^{o})$	$(BrO, O_3, NO_2, H_2O?)$
18.7.2008	KGL- Iceland	high latitude	Transfer flight
(10:15:04-12:11:32)	$(67^{\circ}N, 50.4^{\circ}W- 64^{\circ}N, 21.56^{\circ}W)$	$(66.2^{o} - 45.2^{o})$	$(BrO, O_3, NO_2, H_2O?)$

<sup>a</sup> Oberpaffenhofen, Germany <sup>b</sup> Kangerlussuaq, Greenland <sup>c</sup> Longyearbyen, Svalbard <sup>d</sup> Very cloudy conditions <sup>e</sup> Maximum altitude reached <sup>f</sup> Biomass burning plume

Table 7.6: Overview of the mini-DOAS deployments during the GRACE 2008 aircraft campaign. Trace gases ambiguously detected (due to clouds or poor signal-to-noise ratio) are given in parenthesis.



Flight Time: 11:04:38 to 14:59:03 System Time from DAQ\_SCALE=1:1.40000e+007



(a) 15 July 2008: Flight trajectory

(b) 15 July 2008: BrO dSCD measurements, and selected passage

Figure 7.5: 15 July 2008 sortie (a) Flight trajectory, (b) Flight profile (gray) and BrO dSCDs measurements (red). Section 9.2.1 addresses the passage in the low stratosphere indicated with an arrow.

# Chapter 8

# Procedure for the retrieval of tropospheric trace gas abundances

The measurements presented in this work were gathered during the ASTAR 2007 aircraft campaign with the UV channel of the mini-DOAS instrument introduced in the previous chapter. This section addresses the different steps involved in the algorithm for the retrieval of trace gas abundances from measured quantities.

Section 8.1 presents the parameters used for the retrieval of trace gas differential slant column densities (dSCDs) by the DOAS method, which is detailed in Sect. 6.2.

The retrieval of trace gas concentration or mixing ratios from inferred dSCDs requires the knowledge of the light path (i.e., boxAMF). As described in Sect. 6.3, for clear sky conditions the  $O_4$  method may be used for obtaining the boxAMF of a trace gas located within the BL. However, for retrieving vertical profile abundances of a given trace gas from the BL to the UT/LS, this proxy is not longer sensitive. Section 8.2 details a novel algorithm for that vertical profile retrieval. The method comprises a non-linear mathematical inversion of a measurement vector (radiances) in order to retrieve a vertical profile of the aerosol load affecting the RT, and a linear mathematical inversion of a measurement vector (dSCDs) to infer the targeted trace gas abundance vertical profile. The theory, application and validation of this method, developed in the framework of this work, is presented here. For an overview of mathematical inversion techniques generally applied for the profile retrieval of species, the reader is kindly referred to e.g. *Rodgers* (2000).

Trace gas	Temperature (K)	Reference
$O_3$	$T_{low} = 221, T_{high} = 241^*$	Burrows et al. (1999)
$NO_2$	220	Vandaele et al. (1998)
BrO	$T_{low}=228, T_{high}=298^*$	$Wilmouth \ et \ al. \ (1999)$
$HNO_2$	294	Stutz et al. $(2000)$
$\rm CH_2O$	260	Meller and Moortgat (2000)
OClO	233	Kromminga et al. (2003)
$O_4$	Room temp.	Hermans (2002)

\* Orthogonalized to  $T_{low}$ 

Table 8.1: List of trace gases considered for the DOAS retrieval

## 8.1 Spectral retrieval of tropospheric trace gases absorbing in the UV-A spectral range

Depending on the absorption cross-section of the targeted trace gas and its vertical profile concentration, the spectral retrieval of a tropospheric trace gas weakly absorbing in the UV-A spectral range is a challenge due to the absorption of UV light in the high parts of the atmosphere, and to Rayleigh scattering of air molecules (see Chap. 2). This relatively low incoming signal reaching the spectrometer (compared to e.g. visible light) renders the measurements close to the instrumental detection limit. Additionally, depending on cloud and aerosol particles present in the troposphere, the incoming signal may be decreased even further. Hence, unless a high signal-to-noise ratio is reached in the measurements, systematic structures in the OD retrieval of a trace gas may hinder the trace gas absorption signatures (for a theoretical background refer to Sect. 6.2). In the case of tropospheric aircraft deployments where strong changes in pressure and temperature can occur on short time scales, an optically stable instrument like the mini-DOAS instrument is therefore essential.

This section presents the DOAS analysis procedure for the spectral retrieval of some UV light absorbing species followed in this work. The list of the absorbers considered is given in Table 8.1, and their absorption cross-section spectra are presented in Fig. 8.1.

Prior to the spectral retrieval of trace gas dSCDs, the measured spectra are corrected for the electronic dark current and offset, and all the trace gas cross-sections  $\sigma$  are convolved to the instrumental resolution with the instrumental slit function determined from a pre-flight recorded line spectra of a mercury-cadmium lamp.

The DOAS method is applied for the spectral retrieval of trace gases using the WinDOAS software (*Fayt and van Roozendael*, 2001). The measured spectra are analyzed with respect to a spectrum measured when the aircraft entered the LS ( $\sim 10$  km), referred to as *refer*-



Figure 8.1: UV spectra of the absorption cross-sections used in this work, given at mini-DOAS's resolution.

ence or Fraunhofer spectrum  $I_{ref}$  in Sect. 6.2.1. As a result, the trace gas dSCDs can be inferred.

The spectral retrieval for the 8 April 2007, case study of this work, was tested for trace gases such as BrO,  $O_4$ ,  $NO_2$ ,  $O_3$ ,  $HNO_2$ , OCIO and  $CH_2O$ . However, only the retrieval of BrO,  $O_4$  and (partly) OCIO resulted stable toward sensitivity studies. The settings for the DOAS retrieval of the later trace gases are given in the following.

### 8.1.1 BrO spectral retrieval

Based on the detailed study presented by Aliwell et al. (2002), herein the spectral retrieval of bromine monoxide in the Arctic atmosphere is performed in the 346-359 nm spectral range, comprising the (4-0) and (5-0) vibrational bands of the  $A({}^{2}\Pi_{3/2}) \leftarrow X({}^{2}\Pi_{3/2})$  transition (see e.g. Fig. 6.2), using the BrO  $T_{low}$  absorption cross-sections from Table 8.1. Included in the DOAS fit are also the interfering absorbing species NO<sub>2</sub>, O<sub>4</sub>, OCIO and O<sub>3</sub> ( $T_{low}$ ), the later orthogonalized with respect to  $T_{high}$  to account for temperature effects (refer to Table 8.1). As suggested by Aliwell et al. (2002), the O<sub>3</sub>, NO<sub>2</sub> and BrO absorption cross-sections are corrected for the solar I<sub>0</sub> effect explained in Sect. 6.2.1. These cross-sections  $\sigma$  are shown in Fig. 8.2.

To correct for the "filling-in" of the Fraunhofer lines detailed in Sect. 6.2.1, a synthetic Ring spectrum is calculated with the software DOASIS, and included in the BrO DOAS fit. Additionally, a  $2^{nd}$  and a  $1^{st}$  degree polynomial are included in order to account for the broadband extinction processes and the instrumental stray light, respectively. Theoretical details of these fitting parameters are provided in Chap. 6.

Figure 8.3 gives an example of the BrO DOAS fit using the parameters described above. Further, Fig. 8.4 presents the BrO spectral fit for measurements performed in the boundary layer, compared to those performed in the free troposphere and in the lower stratosphere. As shown in Fig. 8.4(a), there is a residual systematic structure at around 353 nm in the BrO spectral fit. This structure may be cause by e.g. the  $I_0$  effect and by the Ring effect (both effects are described in Sect. 6.2.1). Here, the Ring effect is closer analyzed. As shown in Fig. 8.4(a), since the BrO absorption in the BL is strong, its detection is not compromised by the above mentioned retrieval artifact. However, the systematic structure weakens the quality of the BrO spectral retrieval in the free troposphere. In the LS, where the absorption of BrO is again higher, the BrO signal is again clearly above the instrumental noise. Figure 8.4(b) shows in the Ring cross-section calculated for a spectrum measured in the LS (reference spectrum), and one calculated for a spectrum measured in the BL. Since all spectra are analyzed relative to a reference spectrum which Ring cross-section is included in the fit, systematic structures may result in the spectral retrieval. Figure 8.4(b) shows the relative error when assuming that the Ring cross-section is independent of the viewing geometry (i.e., altitude). This altitude effect yields an error of 1% in the Ring cross-section (a detailed study on calculated Ring cross-section spectra is given by e.g. Weidner, 2005). Since the Ring optical density is about one order of manitude higher than for tropospheric BrO, this issue complicates the unambiguous detection of BrO in regions where its absorption signature is weak (e.g. the free troposphere).

Sensitivity studies were also performed to analyze the influence of including or excluding the



Figure 8.2: Absorption cross-sections considered in the BrO spectral retrieval (given at instrumental resolution). The spectral range corresponds to the window chosen for the DOAS fit.

OCIO absorption cross-section in the BrO spectral retrieval. Results showed that, for the given spectral window, the residual spectrum appeared to be independent of including or not the OCIO absorption cross-section. This may be due to the Ring effect dominating the residuum spectra as addressed above, since the resulting retrieval structures coincide with the OCIO absorption cross-section peak of this spectral window. However, OCIO is herein included since that trace gas is related to the polar lower stratosphere. The presence of OCIO in the Arctic atmosphere is discussed in Sect. 8.1.2.

Additionally, the effect that the temperature dependent BrO  $\sigma$  may have on the BrO spectral retrieval is also investigated. The Wilmouth et al. (1999) BrO absorption cross-section is given at  $T_{low} = 228$  K and  $T_{high} = 298$  K.  $T_{low}$  is commonly used for the BrO spectral retrieval of



Figure 8.3: BrO evaluation in the UV-A spectral range for a spectrum measured at  $81^{\circ}N$ ,  $7^{\circ}E$ , 70 m above sea ice, on April 8, 2007 (14:35:15 UT, SZA= 78°, 10 scans,  $T_{int}$ = 10 s). The upper panel shows the reference spectrum (red line) and the measured spectrum (black line). In the panels below, the retrieved trace gas absorptions of  $O_3$  (\* indicates that  $\sigma_{T=241K}$  is orthogonalized to  $\sigma_{T=221K}$ ), NO<sub>2</sub>, OCIO, O<sub>4</sub>, and also of the Ring spectrum are shown. The lowest panel illustrates the remaining residual of the fitting procedure. The black lines indicate the spectral absorption and the red lines the sum of the spectral absorption and the residual.

measurements performed in the stratosphere, and  $T_{high}$  in those performed at mid-latitudes ground level. During the ASTAR 2007 campaign the atmosphere was probed from the ground level (with temperatures between 245–265 K), up to the UT/LS (at approx. 225 K). Sensitivity studies performed with the temperature dependent BrO  $\sigma$  show non-negligible influence of the temperature on the retrieved BrO dSCDs in the BL. Indeed, within the BL, the BrO dSCDs retrieved considering the BrO  $\sigma_{T_{low}}$  differ by ca. 20% from those retrieved using  $\sigma_{T_{high}}$ . In order to take this into account and considering that the measurements in the BL were performed at



(a) BrO spectral retrieval vs. altitude.



(b) Ring cross-sections vs. altitude.

Figure 8.4: BrO spectral retrieval and the Ring effect. (a) BrO spectral retrieval vs. altitude. Note the different scales between the left and the two right figures. The black lines indicate the modeled spectral absorptions, the red lines the measured ones (sum of the spectral absorption and residual), and the gray ones the residual. (b) Upper panel: Ring cross-section from a spectrum measured in the LS, and of one measured in the BL. Lower panel: Relative error in the calculation of the Ring cross-section for a spectrum measured in the BL, toward one measured in the LS.

T~260 K, the BrO dSCD measurement vector used in Chap. 9 for retriving BrO abundance consists of an average of the BrO dSCDs retrieved at  $\sigma_{T_{low}}$  and at  $\sigma_{T_{high}}$ . This is shown in Fig. 8.5. The error of the averaged dSCDs is calculated by Gaussian error propagation. With

this approximation the linear dependence of the BrO  $\sigma$  shown in Sect. 6.2.1 is assumed (note that  $T_{average} = \frac{T_{low}+T_{high}}{2} \sim 260K \equiv T_{BL}$ ). Moreover, the error of the retrieved dSCDs are considered independent of T. Noteworthy is that this temperature dependency of the retrieved BrO dSCDs becomes imperceptible in the UT/LS (the BrO dSCDs<sub>228K</sub> fall within the error margins of the BrO dSCDs<sub>298K</sub>). The detection limit for BrO absorption may be calculated as double of the dSCD error (see Sect. 6.2.1). However, as mentioned above, some structures appear in the spectral retrieval of BrO. Hence, a closer look is taken for the estimation of the spectral detection limit, since the minimum differential optical density detectable must be larger than the differential optical density of the fit residual. Therefore, the detection limit of a trace gas can be calculated as

$$D_{lim} = \frac{R_{ptp}}{\sigma(\lambda) \cdot AMF(\psi)}$$
(8.1)

where  $R_{ptp}$  is the peak-to-peak of the residual of the retrieval fit, and  $AMF(\psi)$  the airmass factor associated with a measurement of viewing geometry  $\psi^1$ . Hence, considering the  $R_{ptp}$ of each of the BrO spectral retrievals shown in Fig. 8.4(a), the BrO detection limit results in 3.2 pptv, 0.9 pptv and 0.6 pptv for measurements performed in the boundary layer, free troposphere and low stratosphere, respectively. Thus, the average BrO vmr detection limit during an aircraft ascent is 1.6 ppt.



Figure 8.5: BrO dSCDs retrieved from measurements performed during one aircraft ascent, using the BrO  $\sigma$  for different temperatures. The (black) BrO<sub>av</sub> dSCDs resulting from averaging the retrieved dSCD<sub>228K</sub> and dSCD<sub>298K</sub> are referred to as the BrO measurement vector for further studies. The solid gray line indicates the estimated BrO detection limit (double of the dSCD<sub>av</sub> error). The gray dashed line shows the flight profile.

<sup>&</sup>lt;sup>1</sup>For tropospheric AMF( $\psi$ ) refer to Chap. 9
#### 8.1.2 OClO spectral retrieval

In the stratosphere, the bromine and chlorine catalytic ozone depletion cycles are coupled via the reaction of BrO and ClO (Sect. 4.4.2). Although in a sunlit atmosphere chlorine dioxide OClO photolyses readily, in the polar regions OClO has been detected with DOAS setup measurements (e.g., *Fitzenberger*, 2000; *Frieß*, 2001; *Dorf*, 2005). These measurements were performed in the proximity or inside the polar vortex in twilight conditions.

Since the ASTAR 2007 campaign took place during the polar sunrise after a winter with actived polar vortex, the presence of OClO in the lower stratosphere is investigated herein. The spectral retrieval of chlorine dioxide is performed in the 365–389 nm spectral range. Note that a wider spectral fit window toward smaller wavelengths will include interferences with other absorbing species such as BrO or O<sub>4</sub> (see Fig. 6.2). Included in the DOAS fit are also BrO ( $T_{low}$ ), NO<sub>2</sub>, O<sub>4</sub> and O<sub>3</sub> ( $T_{low}$ ), the latter orthogonalized with respect to  $T_{high}$  (refer to Table 8.1). As for the BrO spectral retrieval, the O<sub>3</sub>, NO<sub>2</sub> and BrO absorption cross-sections are corrected for the solar I<sub>0</sub> effect.

To correct for the Ring effect, a synthetic Ring spectrum is also included in the OCIO DOAS fit. Additionally, a  $5^{th}$  and a  $2^{nd}$  degree polynomial are included in order to account for the broadband extinction processes and the instrumental stray light (resp.).

For measurements performed in the troposphere, OClO absorption is not detected. The OClO spectral retrieval from measurements performed in the low stratosphere, presented in Fig. 8.6, show ambiguous OClO signatures to what would correspond to 1.1 pptv (upper limit). Following Eq. (8.1), the residual spectrum of the spectral fit is used for defining the detection limit for the OClO absorption in the LS, resulting in 0.5 pptv.

In addition the spectra were analyzed for HONO,  $CH_2O$ ,  $O_3$ ,  $NO_2$  and IO (the later three from measurements performed with the visible channel). However, their spectral retrieval were not stable toward sensitivity studies and therefore are not given herein. Since HONO,  $CH_2O$  and IO may be related to snow and sea ice emissions (e.g., *Hutterli et al.*, 1999; *Perrier et al.*, 2002; *Amoroso et al.*, 2006; *Saiz-Lopez et al.*, 2007; *Beine et al.*, 2008; *Frieß et al.*, 2010), their detection limits are calculated in order to establish vmr upper limits of these trace gases in the BL. Estimations are 0.2 ppbv, 5 ppbv and 2 pptv for HONO,  $CH_2O$  and IO, respectively. Similarly, the vmr upper limit of IO in the low stratosphere is estimated to be 1.5 pptv. Due to the high spectral resolution of the UV channel and its good signal-to-noise ratio, the calculated upper limits of HONO and  $CH_2O$  may be trust worthy. Nevertheless, the coarser spectral spectral resolution of the visible channel used for the detection of IO, renders its upper limits questionable.



Figure 8.6: OCIO spectral fit for measurements performed in the Arctic at SZA= 80° on April 8, 2007. Left: measurement performed at 10.9 km. Right: measurement performed at 10.2 km. In both cases the measured spectra comprise 100 scans with  $T_{int}$ = 27.8 s. The black lines indicate the modeled spectral absorptions, the red lines the measured ones (sum of the spectral absorption and residual), and the gray ones the residual of the fit.

## 8.1.3 O<sub>4</sub> spectral retrieval

The UV spectral retrieval of  $O_4$  is performed in the 346–366 nm wavelength interval. Included in the DOAS fit are also NO<sub>2</sub>, O<sub>4</sub>, BrO and O<sub>3</sub>, the later two cross-sections with  $T_{low}$  and  $T_{high}$ orthogonalized (refer to Table 8.1). O<sub>3</sub>, NO<sub>2</sub> and BrO absorption cross-sections are corrected for the solar I<sub>0</sub> effect. To correct for the Ring effect, a synthetic Ring spectrum is also included. Additionally, a  $3^{rd}$  degree and a constant additive polynomial are included in order to account for the broadband extinction processes and for the instrumental stray light (resp.). Figure 8.7 gives an example of the O<sub>4</sub> DOAS fit using this procedure.

This work aims at the description of the abundances of bromine monoxide in the Arctic troposphere, and simultaneously measured  $O_4$  ODs assist in that description by (1) characterizing the light path associated to measurements performed within the boundary layer, and (2) validating a novel algorithm for the retrieval of vertical profiles of tropospheric trace gas abundances presented in this thesis. Hence, (1) for measurements performed during horizontal aircraft passages within the boundary layer, the  $O_4$  method<sup>2</sup> is used in Sect. 9.2 for inferring AMF and boundary layer BrO abundances. (2) For measurements performed during aircraft ascents/descents, a new method for the retrieval of vertical profiles of tropospheric trace gas abundances is used. Major challenges of this vertical profile retrieval arise from modeling the

<sup>&</sup>lt;sup>2</sup>The theory behind the  $O_4$  method is described in Sect. 6.3.



Figure 8.7:  $O_4$  evaluation in the UV-A spectral range for a spectrum measured at 50 m altitude, on April 8, 2007 (SZA= 78°, 10 scans,  $T_{int}$ = 10 s). The upper panel shows the reference spectrum (red line) and the measured spectrum (black line). In the panels below, the retrieved trace gas absorptions of  $O_3$  (T=221 K and T=241 K orthogonalized to each other), NO<sub>2</sub>, OCIO, BrO (T=228 K and T=298 K orthogonalized to each other), and also of the Ring spectrum are shown. The lowest panel illustrates the remaining residual of the fitting procedure. The black lines indicate the spectral absorption and the red lines the sum of the spectral absorption and the residual.

radiative transfer in an aerosol and cloud particle loaded atmosphere, and from overcoming the lack of a priori knowledge of the tropospheric BrO vertical distribution. In Sect. 8.2, those challenges are tackled by a mathematical inversion of tropospheric trace gas profiles using a regularization approach constrained by a retrieved vertical profile of the aerosols extinction coefficient  $\mathcal{E}_{\mathcal{M}}$ . The validity and limitations of the algorithm are tested with in situ measured  $\mathcal{E}_{\mathcal{M}}$ , and also with the known vertical profile of O<sub>4</sub>.

## 8.2 Profile retrieval of tropospheric trace gas abundances from aircraft-borne limb DOAS measurements

The theoretical background of a novel algorithm for the vertical profile retrieval of tropospheric trace gas abundances from aircraft-borne limb DOAS measurements is given in Sect. 8.2.1, and applied in Sect. 8.2.2. Finally, Sect. 8.2.3 validates the algorithm with the vertical profile mathematical inversion of a known absorber  $(O_4)$ .

## 8.2.1 Theory



1st) Characterization of scattering processes affecting the light path

Figure 8.8: Summary of the retrieval method in a two-step process: (1) inversion of the vertical distribution of the aerosols extinction coefficient affecting the RT ( $\mathcal{E}_{\mathcal{M}}$ ), and (2) inversion of the vertical profile concentration of the trace gas. Sensitivity studies of each step are performed via RT forward modeling (dashed arrows).

In general, optically thin absorbers in a given spectral ranges (e.g., BrO in the UV), do not substantially affect the RT. Thus, the vertical concentration profile retrieval of such a trace gas may be performed in a two-step process, detailed in Fig. 8.8. First, the influence of Rayleigh and Mie scattering affecting the RT during the observations may be studied by measuring and modeling Sun normalized radiances at a given wavelength. If Mie scattering dominates the RT then, via non-linear inversion from relative radiance measurements, a vertical profile of the aerosol's extinction coefficient  $(\mathcal{E}_{\mathcal{M}})$  may be retrieved on a certain vertical grid. Once the light path lengths in the respective layers are modeled with the RT model, the inversion of the targeted trace gas vertical profile from measured dSCDs may be performed using the Phillips-Tikhonov approach, including the formerly retrieved  $\mathcal{E}_{\mathcal{M}}$  profile as a forward parameter in the RT calculations. The mathematical description of these steps is given as following.

#### Non-linear inversion of the aerosol's extinction coefficient vertical profile

A key step of the retrieval of a trace gas abundance from scattered skylight measurements is to infer the light path associated with each of the measurements, and the possible absorption and scattering events influencing those observations. In order to determine the light path in an artificial 1-D atmosphere, a vertical profile of the  $\mathcal{E}_{\mathcal{M}}$  of aerosols (i.e., combination of cloud and aerosol particles) is herein retrieved.

Since the retrieved  $\mathcal{E}_{\mathcal{M}}$  profile is included in the forward RT calculations of the targeted trace gas profile retrieval, the chosen wavelength for the  $\mathcal{E}_{\mathcal{M}}$  study is  $\lambda = 353$  nm, where there is no major trace gas absorption (see e.g. Fig. 8.2).

Logarithmic radiance ratios may be modeled by a RT model capable of simulating Sun normalized radiances  $I_{i/ref}$ , thus avoiding any absolute calibrating factor  $c(\lambda)$ :

$$y_i = \ln\left(\frac{L_i(\lambda)}{L_{ref}(\lambda)}\right) = \ln\left(\frac{c(\lambda)I_i(\lambda)}{c(\lambda)I_{ref}(\lambda)}\right) = \ln\left(\frac{I_i(\lambda)}{I_{ref}(\lambda)}\right)$$
(8.2)

where  $L_{i/ref}$  are the measured radiances at a certain geometry with index *i* related to the reference geometry *ref*. In this work the RTM used is the McArtim model, introduced in Sect. 6.3.

The cost function of the relative radiances is given by

$$\chi^{2} = \left\| \mathbf{S}_{\in}^{-1/2} \left( \mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}) \right) \right\|_{2} = (\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}))^{\mathrm{T}} \mathbf{S}_{\in}^{-1} (\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}))$$
(8.3)

where the state vector  $\mathbf{x}$  is the  $\mathcal{E}_{\mathcal{M}}$  vertical profile. In Eq. (8.3), the measurement vector  $\mathbf{y}$  is given by the measured Sun normalized radiances  $L_{i/ref}$ , and  $\mathbf{F}(\mathbf{x}, \mathbf{b})$  by the simulated Sun normalized radiances vector, where  $\mathbf{b}$  represents the auxiliary parameters that will not be retrieved (atmospheric pressure, ground albedo, etc.). The diagonal measurement covariance matrix  $\mathbf{S}_{\in}$ contains the squared errors of each measurement, chosen here as 4% in order to account for systematic RT uncertainties such as the Ring effect, the used trace gas cross-sections, etc.

Following a standard Levenberg-Marquardt approach, Eq. (8.3) is minimized (e.g., *Marquardt*, 1963; *Levenberg*, 1944; *Rodgers*, 2000). In the next step, the inferred vertical profile of the  $\mathcal{E}_{\mathcal{M}}$  serves to constrain the inversion of tropospheric trace gas vertical profiles.

#### Mathematical inversion of trace gas profiles: the regularization method

The optimal estimation using a priori information of the targeted trace gas is an inversion technique commonly applied for the profile retrieval of trace gases (*Rodgers*, 2000). Nevertheless, if the a priori covariance  $\mathbf{S}_a$  of the targeted trace gas concentration is not known, or if there is no knowledge of the a priori profile  $\mathbf{x}_a$  (e.g., unknown vertical distribution of BrO in the troposphere), the regularization method is a more appropriate approach for the retrieval of trace gas profiles (e.g., *Hasekamp and Landgraf*, 2001). Following the notation given in (*Rodgers*, 2000), generally in the regularization method the inverse of the a priori covariance  $\mathbf{S}_a^{-1}$  is replaced by a smoothing operator  $\mathbf{R}$ . The output is then a smoothed version of the true profile where the retrieved absolute values are not compromised.

One of the most widely used regularization methods is the Phillips-Tikhonov approach (*Phillips*, 1962; *Tikhonov*, 1963; *Tikhonov et al.*, 1977). In this method the cost function to be minimized reads

$$\left\| \mathbf{S}_{\in}^{-1/2} \left( \mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}) \right) \right\|_{2} + \alpha \left\| \mathbf{L} \mathbf{x} \right\|_{2}$$
(8.4)

where  $\mathbf{y} \in \Re^m$  represents the measurement vector and  $\mathbf{S}_{\in}$  its covariance matrix. In this case the measurement vector consists of the dSCDs inferred after the DOAS routine (Sect. 8.1). The diagonal of  $\mathbf{S}_{\in}$  is built considering the squared of one standard deviation of the DOAS fit error, and the off-diagonal elements of  $\mathbf{S}_{\in}$  are set to zero. The expression  $\mathbf{F}(\mathbf{x}, \mathbf{b})$  in Eq. (8.4) stands for the RT forward model that estimates the light path through the atmosphere for each viewing geometry, and therefore provides the modeled dSCDs. The true state (the true vertical profile of the trace gas) is given by  $\mathbf{x} \in \Re^n$ , and  $\mathbf{b}$  are the auxiliary parameters that will not be retrieved (trace gas absorption cross-sections, atmospheric pressure,  $\mathcal{E}_{\mathcal{M}}$  profile, etc.). In Eq. (8.4),  $\mathbf{L}$  is the constraint operator which, in this case, is a discrete approximation to the first derivative operator (e.g., *Steck*, 2002), and  $\alpha$  is the regularization parameter giving the strength of the constraint. Therefore, if  $\mathbf{R} = \alpha \mathbf{L}^T \mathbf{L}$  is the the smoothing operator, the dSCDs cost function to be minimized is

$$(\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}))^{\mathbf{T}} \mathbf{S}_{\in}^{-1} (\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b})) + \mathbf{x}^{\mathbf{T}} \mathbf{R} \mathbf{x} \to min.$$
 (8.5)

The state vector minimizing Eq. (8.5) is given by

$$\hat{\mathbf{x}}_{\mathrm{reg}} = (\mathbf{K}^{\mathrm{T}} \mathbf{S}_{\in}^{-1} \mathbf{K} + \mathbf{R})^{-1} \mathbf{K}^{\mathrm{T}} \mathbf{S}_{\in}^{-1} \mathbf{y}$$
(8.6)

where  $\mathbf{K} \in \Re^{m \times n}$  is the Jacobian matrix providing the sensitivity of the (simulated) measurements to the true state  $(\frac{\partial \mathbf{F}}{\partial \mathbf{x}})$ , therefore giving an insight into the light path.

One of the main challenges of the regularization method is to determine which regularization

parameter  $\alpha$  provides the most realistic retrieved profile. Although analytical formulas have been suggested where some a priori knowledge ( $\mathbf{x}_{\mathbf{a}}$  and  $\mathbf{S}_{a}$ ) is recommended (e.g., *Ceccherini*, 2005), one of the approaches most widely used to determine  $\alpha$  is the *L*-curve method (e.g., Hansen, 1992; *Steck*, 2002). In this work,  $\alpha$  is defined by the graphical approach of the L-curve, cross-checked with the numerical approach of the maximum curvature (e.g., *Hansen*, 2007). The goal is indeed to keep a balance between the applied constraint, and the information content provided by the averaging kernel matrix given by

$$\mathbf{A} = (\mathbf{K}^T \mathbf{S}_{\in}^{-1} \mathbf{K} + \mathbf{R})^{-1} \mathbf{K}^T \mathbf{S}_{\in}^{-1} \mathbf{K}$$
(8.7)

Following the notation in (*Rodgers*, 2000), if there is no null-space of **K**, then the aimed profile  $\hat{\mathbf{x}}_{reg}$  from Eq. (8.6). Thus, the retrieved profile ( $\hat{\mathbf{x}}_{reg}$ ) is the sum of the true profile smoothed by the averaging kernel matrix and the measurement error, i.e.,  $\hat{\mathbf{x}}_{reg} = \mathbf{A}\mathbf{x} + \epsilon$  (e.g., *Hasekamp and Landgraf*, 2001). The quality of the retrieval is therefore described by the difference between the retrieved state and the true state (*Rodgers*, 2000):

$$\hat{\mathbf{x}}_{\mathrm{reg}} - \mathbf{A}\mathbf{x} = \epsilon_{\mathrm{noise}} + \epsilon_{\mathrm{frw}} \tag{8.8}$$

where  $\epsilon_{noise}$  represents the retrieval noise. On the other hand,  $\epsilon_{frw}$  symbolizes the error in the forward model  $\mathbf{F}(\mathbf{x}, \mathbf{b})$ , originating from uncertainties of each of the forward model parameters  $\mathbf{b}$ . This  $\mathbf{e_{frw}}$  is not straight forward to calculate if the true state is unknown, or if the sensitivity of the RT forward model  $\mathbf{F}$  to  $\mathbf{b}$  (i.e.,  $\mathbf{K_b} = \frac{\partial \mathbf{F}}{\partial \mathbf{b}}$ ) is non linear (e.g., if  $\mathbf{b}$  is the  $\mathcal{E}_{\mathcal{M}}$  profile). The  $\epsilon_{frw}$  can in fact be understood as a light path miscalculation and, as shown in the following sections, should not be neglected when simplifying a 3-D (plus time) atmosphere into 1-D. Indeed, as recently argued in *Leitão et al.* (2010) and *Vlemmix et al.* (2010), the trace gas retrieval can be improved (its error decreased) if the uncertainty of each forward model parameter is minimized.

## 8.2.2 Application

In this section the different retrieval steps summarized in Fig. 8.8 are applied for measurements performed during the aircraft ascent indicated with a box in Fig. 8.9 (starting at 14:30 UT). That particular ascent started at around 14:30 UT, while flying over sea ice at  $\sim 81^{\circ}$ N and 7°E, with northwesterly ground winds of 6 m/s. During the approximately 30 minutes of the ascent, the aircraft climbed from around 50 m of altitude up to 10.5 km. Figure 8.10 schematizes the scattering events that may affect the RT on the scattered skylight aircraft-borne limb measurements presented in this work.

Herein, the radiance and  $O_4$  measurements gathered during that ascent are used (Fig. 8.9). In this case, the skylight radiances are measured at 349 nm (peak cross-section of BrO absorption



Figure 8.9: Measurement flight on 8 April 2007. Panel (a) shows the  $O_3$  vmr measured in situ with an UV absorption photometer (DLR). Flight sections within the Arctic BL with ODEs are indicated by arrows. Panels (b), (c) and (d) show, resp., the radiances at different wavelengths, the BrO dSCDs and the  $O_4$  d $\tau$  measured with the UV channel of the mini-DOAS instrument. The tropospheric vertical profiles of the aerosols  $\mathcal{E}_{\mathcal{M}}$  and of the trace gases presented in this work are retrieved from data measured during the aircraft ascent starting at around 14:30 UT (box).

band), at 360.8 nm (peak cross-section of  $O_4$  absorption band), and at 353 nm (negligible  $O_4$  and BrO absorption) aiming at the aerosol retrieval (see later in the text). Throughout this work, the aerosol retrieval is performed at 353 nm including also the rather small wavelength dependency (around 5%) in the spectral range of 349–360.8 nm.

In this section limitations and error sources of the algorithm are analyzed. First, the error contribution of different forward parameters **b** to the RT model are studied. Then, the aerosol  $\mathcal{E}_{\mathcal{M}}$  profile retrieval is performed. Once an effective aerosol  $\mathcal{E}_{\mathcal{M}}$  vertical profile is inferred and included in the RT model, the trace gas profile inversion is validated by comparison of regularized and calculated O<sub>4</sub>.



Figure 8.10: Scheme of the scattering events that may affect the RT on scattered skylight aircraftborne limb measurements. Once the solar radiation enters the pseudo-TOA with a certain Solar Zenith Angle (SZA), not only air molecules but also the ground (G), ice crystals, cloud and aerosol particles may act as scattering centers. The scattered light eventually gets in the line-ofsight of the instrument (L-O-S), defined by the roll angle of the aircraft ( $\alpha$ ). In the right side, the altitude gradients of the radiances  $I(\lambda)$  and  $O_4$  are drawn. BL, FT, LS and US stand for the boundary layer, free troposphere, low stratosphere and upper stratosphere, resp.

## Analysis of the forward parameters for the radiative transfer modeling

Optical remote sensing of atmospheric parameters is often hindered by the complexity of the RT in the troposphere. In fact, one of the reasons for selecting the particular aircraft ascent for a more detailed study is the fact that it appears as the simplest RT scenario from the whole flight.

Noteworthy is that, since RT input data may largely suffer from the improper knowledge of their 3-D distribution, here the RT modeling and the inferred quantities (relative radiances and  $d\tau$ ) are regarded as an approximation for a more complex reality. Since no further means are available to reconstruct the latter, sensitivity studies are undertaken in order to learn more how uncertainties of the assumptions may propagate into the final result.

In this work some of the important parameters for the RT modeling are (a) taken from in situ instruments deployed on the aircraft, (b) estimated, and (c) inferred from our measurements (i.e., aerosols extinction coefficient  $\mathcal{E}_{\mathcal{M}}$ ). This section details (a) and (b) RT forward parameters, while (c) and the aerosol optical properties affecting the RT are addressed later in the text.

(a) Physical properties of the atmosphere such as the temperature, pressure, humidity are taken from data collected by the Falcon aircraft basic instrumentation.  $O_3$  mixing ratios were in situ measured by the UV absorption photometer (DLR) also on board the Falcon aircraft. Since in the considered wavelength range  $O_3$  is only weakly absorbing, spatial variations of the  $O_3$  concentration may only weakly influence the RT and thus are not further considered.

(b) The aircraft ascent here considered began at  $81^{\circ}$ N,  $7^{\circ}$ E (14:30 UT), when flying over sea ice. Sensitivity studies (see Fig. 8.11, left) indicate that uncertainties of the ground albedo can lead to a rather large relative error (~30%) in the RT forward model. However, in this work the ground albedo is inferred with the assistance of an albedometer measurement platform, and of a digital camera installed on the Falcon cabin looking in the direction of the flight. The albedometer was aboard the AWI Dornier-228 Polar 2 aircraft that was also deployed during the ASTAR 2007 campaign, and performed measurements of the albedo of sea ice, snow and open water (*Ehrlich*, 2009). Measurements from the albedometer reported a sea ice albedo of 79% in the UV-A spectral range. In addition, visual inspection of the recorded movie assisted us to improve our knowledge of the (radiative) ground conditions. During the 30 minutes of the aircraft ascent, the Falcon aircraft flew over closed sea ice, some leads covered by thin ice, and snow covered glacier. Hence, for the RT model of this passage a surface albedo of 79% with an uncertainty of 20% is considered.

#### Study of the vertical profile retrieval of the aerosol extinction coefficient

Key parameters for the tropospheric RT are the abundance of aerosol and cloud particles. In general, images from the camera confirmed the (radiative) complexity of the atmosphere during the ASTAR 2007 campaign. Large horizontal surface albedo gradients and/or heterogeneous cloud and particle layers were present during most of the campaign, thus, potentially introducing large uncertainties into the RT. In fact, sensitivity studies show that, for the particular passage of the  $8^{th}$  April deployment herein studied, the aerosol  $\mathcal{E}_{\mathcal{M}}$  uncertainty could contribute with more than 40% of the total forward error (see Fig. 8.11, right). Accordingly, most challenging parameter to define for the RT model of each case study appears to be the aerosol and cloud particles.

A summary of the aerosol number densities in situ measured in the course of the 8 April 2007 sortie is presented in Fig. 8.12. During that flight, haze was not dense in the Arctic atmosphere. However, different aerosol layers were sampled. In situ measurements showed that some pollution (particles and  $SO_2$ ) was contained in the BL which, in general, was characterized by relatively high relative humidity (causing some haze particles, and occasionally some clouds). Another thin pollution layer was observed at 4.5 km altitude, but only during



Figure 8.11: Influence of forward parameters in the RT model of a known trace gas  $(O_4)$ . Left: influence of the ground albedo, comparing the forward modeled  $O_4 d\tau$  if a ground albedo of 5% (ocean) and 90% (snow) are considered in the forward RT model. Right: influence of the  $\mathcal{E}_{\mathcal{M}}$ vertical profile, comparing a Rayleigh atmosphere with a rather strong haze situation ( $\mathcal{E}_{\mathcal{M}} = 0.1$ km<sup>-1</sup>) throughout the whole troposphere.

part of the flight segment just before the ascent sequence started. In the UT/LS, enhanced aerosol concentrations were also observed (at around 15:15 UT). This layer appeared during aircraft ascent and descent at different altitudes (8 and 9.5 km), suggesting its spatial heterogeneity.

The video of the selected passage of the 8<sup>th</sup> April sortie shows an overall cloud free atmosphere, and a fairly good visibility. However, some aerosol layers were crossed as reported by two aerosol spectrometer probes deployed by DLR on the Falcon aircraft. These probes were a Passive Cavity Aerosol Spectrometer Probe (PCASP-100X which detected aerosols in a size range of ~0.15-1  $\mu$ m), and a Forward Scattering Spectrometer Probe (FSSP-300, which monitored the aerosols and cloud particle in a the size range ~0.4-20  $\mu$ m).

The aerosol optical properties affecting the RT at a given wavelength are the phase function (characterized by an asymmetry parameter g), the single scattering albedo ( $\varpi_0$ ) and the extinction coefficient ( $\mathcal{E}_{\mathcal{M}}$ ). Aiming for a qualitative comparison, a vertical profile of the  $\mathcal{E}_{\mathcal{M}}$  is inferred from (1) our optical remote sensing measurements (referred to as IUP-HD  $\mathcal{E}_{\mathcal{M}}$ ), and (2) the in situ measured aerosol data (referred to as DLR  $\mathcal{E}_{\mathcal{M}}$ ). Details for each retrieval case are



Figure 8.12: Vertical profile of coarse mode aerosol number densities (for different particles) measured in situ during the entire 8 April 2007 flight excluding the first and last 20 minutes of flight close to Longyearbyen airport.

as follows:

- 1. Proceeding as detailed in Sect. 8.2.1, IUP-HD  $\mathcal{E}_{\mathcal{M}}$  is inferred from the (relative) radiances at 353 nm measured during the ascent starting at 14:30 UT. Aerosol optical parameters considered for that retrieval are the phase function, herein simplified as Henyey-Greenstein's with g=0.7, and  $\varpi_0=99\%$ . These assumptions are based on measurements of microphysical and radiative aerosol properties performed during the ASTAR 2007 (e.g., *Ehrlich et al.*, 2008; *Lampert et al.*, 2009).
- 2. The DLR  $\mathcal{E}_{\mathcal{M}}$  from the PCASP-100X and FSSP-300 measurements is determined during a number of constant level flight legs (e.g., *Weinzierl et al.*, 2009). For this, averaged particle size distributions are derived assuming a refractive index of an aged ammonium sulfate type of aerosol. In addition, absorption by particles in the tropospheric aerosol column is assumed to be negligible (i.e., 1.54+0.0i). The scattering (extinction) coefficient is then determined using a Mie model assuming spherical particles. A complete time series (or vertical profile) of scattering/extinction coefficients along the flight is constructed from the aerosol surface area concentrations following from the DLR probes measurements, using the average ratio of scattering coefficient and surface area density in the constant

altitude flight legs. Three vertical profile scenarios are obtained then: (a) a clean case scenario representing the lowest concentrations per altitude bin over the entire flight, (b) a case for the particular ascent profile flown at around 14:30 UT, and (c) a case scenario representing the few pollution layers found during the flight. In the DLR  $\mathcal{E}_{\mathcal{M}}$  retrieval major uncertainties are introduced with the assumptions of refractive index and particle sphericity, which are probably smaller than the variability of atmospheric conditions during the flight. These uncertainties are not further discussed since this exercise only aims for a qualitative comparison of IUP-HD  $\mathcal{E}_{\mathcal{M}}$  and DLR  $\mathcal{E}_{\mathcal{M}}$ .

Inferred  $\mathcal{E}_{\mathcal{M}}$  vertical profiles (1) and (2 a, b, c) are compared in Fig. 8.13, where the vertical resolution of the in situ data has been adopted to the rather coarse resolution of the RT model. As seen in Fig. 8.13, IUP-HD  $\mathcal{E}_{\mathcal{M}}$  tends to a rather clean scenario above the first 500 m up to the UT/LS. In fact, below 6 km altitude, IUP-HD  $\mathcal{E}_{\mathcal{M}}$  points to an aerosol load even lower than the "cleanest" in situ measured values.



Figure 8.13: Vertical profiles of remotely sensed and in situ measured aerosol extinction coefficients  $\mathcal{E}_{\mathcal{M}}$  (8 April 2007 sortie). In red, the IUP-HD  $\mathcal{E}_{\mathcal{M}}$  retrieved at 353 nm from measurements performed during the ascent at 14:30 UT is presented (79% ground albedo, g=0.7). The pink shadow covers wavelength (349–360.8 nm) and ground albedo uncertainties of IUP-HD  $\mathcal{E}_{\mathcal{M}}$ . The profiles derived (at 349 nm) from the in situ data correspond to the ascent at 14:30 UT (dark blue), and to a clean (cyan) and aerosol loaded case scenario (dashed line) measured during the 8 April 2007 flight.

In order to investigate likely causes for these differences and their consequences for the 14:30

UT  $\mathcal{E}_{\mathcal{M}}$  inferred profiles (see Fig. 8.13), sensitivity tests are performed for different parameters.

The most sensitive parameter for the RT in the BL appears to be the ground albedo. By analyzing Fig. 8.13, if a 20% uncertainty of the ground albedo is assumed, the inferred IUP-HD  $\mathcal{E}_{\mathcal{M}}$  vertical profile shows an averaged 200% relative error in the very first layers of the BL (see pink shadow). Nevertheless, as seen in the figure, uncertainties in the ground albedo do not cover the differences between both  $\mathcal{E}_{\mathcal{M}}$  profiles.

Sensitivity studies indicate also that, for the selected spectral range, the inferred  $\mathcal{E}_{\mathcal{M}}$  may only weakly depend on wavelength (by less than 5%).

Assumptions regarding optical properties of the aerosol particles may also cause the differences. The IUP-HD  $\mathcal{E}_{\mathcal{M}}$  represents an effective extinction coefficient profile constrained to one single type of aerosol (optically described by g = 0.7 and  $\varpi_0 = 99\%$ ). Conversely, the in situ probes collect data from (optically) different aerosol types that likely coexist in the atmosphere. The single scattering albedo considered in both approaches differs in only 1%. Thus  $\varpi_0$  is not considered the optical parameter directing the differences between IUP-HD and DLR  $\mathcal{E}_{\mathcal{M}}$ . On the other hand, sensitivity studies (Fig. 8.14) indicate that modeling the relative radiances considering DLR  $\mathcal{E}_{\mathcal{M}}$  in the RT model, leads to a better agreement with measurements if different values for the asymmetry parameter are allowed at different altitudes.

Bearing all these considerations in mind, a quantitative comparison of the  $\mathcal{E}_{\mathcal{M}}$  profiles inferred from both approaches should be regarded with caution. Furthermore, the uncertainties afore mentioned may also indicate the restriction of our aerosol inversion. If the retrieval was not limited by the information content of the measurements, a more detailed remote sensed characterization of the aerosol optical properties could be performed, e.g., by an aerosol  $\mathcal{E}_{\mathcal{M}}$  inversion not constrained to one type of aerosol, by taking into account possible 3-D effects, by analyzing the rotational Raman scattering (Ring effect, e.g., *Landgraf et al.*, 2004; *Wagner et al.*, 2009), and by including the polarization of light in the algorithm (e.g., *Emde et al.*, 2010). Moreover, the retrieval of aerosols from measured relative radiances may also be combined with O<sub>4</sub> d $\tau$ measurements to gather more information content limits the retrieval and, therefore, such a detailed characterization of aerosols is out of the scope of this work.

Since a self-consistent treatment of the RT is required throughout each of the steps of the retrieval algorithm, Fig. 8.14 also indicates the limitation of using DLR  $\mathcal{E}_{\mathcal{M}}$  as a RT forward parameter for the inversion of the trace gas profiles (see also Fig. 8.16, center). Hence, the inferred IUP-HD  $\mathcal{E}_{\mathcal{M}}$  profile (constrained to a constant g and  $\varpi_0$ ) should be regarded as an effective 1-D



Figure 8.14: (Left) Sun normalized radiances measured and modeled during the 14:30 UT ascent. Measured radiances (at 353 nm) are shown in black. At 353 nm and 79% ground albedo, radiances are modeled considering different  $\mathcal{E}_{\mathcal{M}}$  (refer to Fig. 8.13) and asymmetry parameter scenarios. Red: IUP-HD  $\mathcal{E}_{\mathcal{M}}$  with g=0.7. Blue: DLR  $\mathcal{E}_{\mathcal{M}}$  with g=0.7. Green: DLR  $\mathcal{E}_{\mathcal{M}}$  with variable g. Error bars of all modeled radiances include their wavelength dependency (349-360.8 nm). In addition, a ground albedo uncertainty of 20% is considered for the DLR radiances. (Right) Profiles of the aerosol asymmetry parameter considered for the RT studies (g within the range of 0.6-0.85 as reported for the Arctic, e.g., Lampert et al., 2009).

aerosol extinction profile describing the Mie scattering processes in the 1-D atmosphere. The characterization of the RT with this approach is validated in the following section.

## 8.2.3 Validation of the retrieval of the tropospheric trace gas vertical profile: $O_4$ regularization

One of the first steps in the trace gas retrieval method is to choose an atmospheric vertical grid that fits the information content of the measurements. Considering the speed of the aircraft and the integration time of our spectra during the aircraft ascent of interest (see Fig. 8.9), diverse studies on the altitude grid and the information content of the measurements suggest that a finer grid than the one used in this work (11 layers) does not improve the retrieval but might, however, result in misinterpretation of the measured data at a given layer (depending also on the regularization strength  $\alpha$ ).

Following Eq. (8.6) and using the L-curve criterion to define the regularization parameter  $\alpha$ 



Figure 8.15: L-curve for defining the regularization parameter for the regularization of  $O_4$ .

(Fig. 8.15), the inversion of the O<sub>4</sub> vertical profile constrained by the inferred IUP-HD  $\mathcal{E}_{\mathcal{M}}$  vertical profile (Fig. 8.13) is performed. Figure 8.16 characterizes the O<sub>4</sub> profile retrieval at 360.8 nm. As shown by its kernel matrix **A** (Fig. 8.16, left), in the retrieval of  $\mathbf{x}_{reg}$  roughly 8 degrees of freedom are obtained. Since **A** gives the sensitivity of the retrieved profile to the true state, an averaging kernel smaller than unity indicates the limitation of the measurements to provide fully independent information of the true state **x**. Therefore, the effective null-space contribution is not negligible. Since  $\mathbf{x}_{reg} = \mathbf{A}\mathbf{x} + error$  and the true O<sub>4</sub> state (**x**) is given by Eq. (6.25), the retrieval error can be estimated.

Figure 8.16 (center) shows  $\mathbf{x}$  (blue),  $\mathbf{A}\mathbf{x}$  (red) and  $\mathbf{x}_{reg}$  (and covariance, black) for the retrieval of the O<sub>4</sub> extinction coefficient profile using the aerosol IUP-HD  $\mathcal{E}_{\mathcal{M}}$  as a forward parameter in the RT model. For comparative purposes, Fig. 8.16 (center) also shows (in green) the regularized O<sub>4</sub> profile constrained by the  $\mathcal{E}_{\mathcal{M}}$  profile as inferred from aerosol concentrations in situ measured (in dark blue in Fig. 8.13). Figure 8.16 (right) illustrates the relative error of the O<sub>4</sub> retrieval (constrained by IUP-HD  $\mathcal{E}_{\mathcal{M}}$  profile). In the troposphere (up to 8.5 km), the retrieval of the O<sub>4</sub> vertical profile shows a good agreement with the true state, with a maximum relative error of 20%. This error is mostly dominated by the error in the forward RT model (i.e., coupling of ground albedo and aerosol load uncertainties), which can be understood as a miscalculation of the light path in a given layer. On the other hand, in regions where trace gas concentrations are close to the detection limit of the instrument (e.g., O<sub>4</sub> in the UT/LS), the retrieval noise (the measurement error) dominates the total error of the retrieval.



Figure 8.16: Retrieval of the  $O_4$  vertical distribution. Left: Averaging kernels showing ~8 degrees of freedom. Center: The  $O_4$  true state is shown in blue (considering 10% error).  $\mathbf{x}_{IUP-HD reg}$  (in black) is the regularized  $O_4$  profile if the IUP-HD  $\mathcal{E}_M$  profile (see Fig. 8.13) is included in the RT model (the error bars include the retrieval noise and the effect of uncertainties of the ground albedo and the aerosol load). The contribution of the true state to the row space (IUP-HD reg) is shown in red. For comparison purposes,  $\mathbf{x}_{DLR reg}$  (in green) corresponds to the regularized  $O_4$ profile if DLR  $\mathcal{E}_M$  (b) profile (in dark blue in Fig. 8.13) is included in the RT model. Right: Relative error of the (IUP-HD)  $O_4$  retrieval.

## 154 CHAPTER 8. RETRIEVAL OF TROPOSPHERIC TRACE GAS ABUNDANCES

# Chapter 9

# Bromine monoxide in the Arctic troposphere

Once the theoretical background for the spectral retrieval of tropospheric trace gases and for their mathematical inversion into concentration or vmr have been set, those techniques are applied in this chapter for characterizing the presence of bromine monoxide in the Arctic troposphere.

Section 9.1 presents the retrieval of BrO vmr vertical profiles from measurements performed during the ASTAR 2007 campaign. After assessing the sensitivity of the measurements, the inferred BrO vmr vertical profiles are compared to other trace gases ( $O_3$ , CO), and to total BrO column densities (VCD) measured by satellite.

Once the inferred BrO vmr are characterized, Sect. 9.2 assesses its sources, photochemistry pathways and transport processes. This assessment is performed first in the UT/LS region, analyzing the effect that tropopause folds may have in the sensed BrO vmr. Then, the studies focus on the BrO within the polar boundary layer, and the related ozone depletion events. In that sense, the BrO in the BL above the High Arctic sea ice is analyzed from a vertical distribution perspective. Moreover, based on measurements performed during 115 km horizontal aircraft passage 60 m above the sea ice, a cross-section of the bromine monoxide above the sea ice is provided. The presence of the measured BrO is related to the measurements of  $O_3$  vmr and aerosol surface area concentration (DLR) and, furthermore, to meteorological conditions and to the properties of the surrounding sea ice.

## 9.1 Tropospheric vertical profile of BrO volume mixing ratios

Since in Sect. 8.2 the robustness and consistency of the algorithm for the profile retrieval of tropospheric trace gases is validated in inter-comparison with the  $O_4$  vertical profile, confidence is gained in the novel method to retrieve vertical profile distribution of trace gases in the troposphere. Here the vertical tropospheric profile of BrO vmr in the Arctic spring for the same aircraft ascent analyzed in Sect. 8.2, is presented in Fig. 9.1.



Figure 9.1: Retrieval of the BrO vmr vertical profile. Left: averaging kernel profile indicating 10 degrees of freedom. Right: BrO vmr vertical profile. The black error bars include the retrieval noise and the uncertainty in forward RT model parameters such as the aerosol load and the ground albedo. The cyan error bars include biases in the error estimation if BrO horizontal gradients within each modeled atmospheric layer were present during the time of the measurements.

Overall, the inferred BrO profile appears to be C-shaped, having three distinct regions: the BL with high BrO mixing ratios (around 15 ppt), the free troposphere with BrO vmr close the detection limit ( $\sim 1.5$  ppt), and the UT/LS where the BrO vmr increase with altitude. As indicated by the averaging kernels (Fig. 9.1, left panel), the inferred BrO tropospheric profile has roughly 10 degrees of freedom with an altitude resolution of about 1 km.

Before the discussion can address further details of the inferred BrO profile and inter-

comparisons with other studies can be made, specific aspects of our technique and potential implications for the inferred BrO need to be discussed.

Since there is a very small contribution of the true state to the null-space (averaging kernels very close to unity throughout the whole profile, Fig. 9.1, left), the regularized BrO profile presented in black in Fig. 9.1 (right) is a reasonably good but smoothed approximation of the BrO true state. In the first 1.5 km of the BrO profile (see Fig. 9.1, right), the forward model RT error is estimated as 80% of the total (black) error, and for the altitudes above, the measurement error dominates (70%) the total BrO retrieval error. Also, the limited height resolution of this aircraft-borne limb technique for trace gas detection - as indicated by the full width at half maximum of the averaging kernels - suggests that details of the BrO profile shape within the first 500 m of the BL are somewhat uncertain. This statement is particularly supported by the scattering due to particles that tend to radiatively smooth the profile shape in that region (Fig. 8.13).

Furthermore, since the aircraft ascent from near the ground into the UT/LS took roughly 30 minutes and covered a latitude-longitude distance corresponding to 250 km, the profile retrieval inherently condenses information gained from a 3-D plus time measurement into a 1-D effective profile. Consequently, sensitivity studies are performed aiming to estimate the horizontal sensing distance of the limb measurements during the aircraft ascent (i.e., *horizontal sensitivity*). For these studies a stratified atmosphere is considered and, thus, the retrieved aerosols (IUP-HD  $\mathcal{E}_{\mathcal{M}}$ ) are supposed to have a homogeneous horizontal distribution. This assumption is believed to be valid for the passage over the High Arctic sea ice herein studied where, in the viewing direction of the mini-DOAS instrument, no open water (possible convection) was encountered. In the following, these sensitivity studies are detailed.

#### Horizontal sensitivity of the measurements

In order to estimate the horizontal sensing distance of the measurements presented in this work, the sum of the *n* scattering events (*se*) affecting the radiative transfer is simplified in these studies as a single scattering center or *sensing center*  $SC^1$ . This simplification addresses the idea of *single scattering approximation* (e.g., *Platt and Stutz*, 2008) and is depicted in Fig. 9.2. The concept relies on the probability or weighting factor that a scattering event  $se_n$  has of affecting the RT of the measurements. As explained in Sect. 2.3.1, that probability depends on the phase function of the scattering event  $\wp(\mu_n)$ , where  $\mu_n := \cos(\vartheta_n)$  ( $\vartheta_n$  is the angle of scattering after  $se_n$ ). Thus, the weighting function may be described as a radiance given as:

$$I = \left\langle \sum_{n=0}^{\infty} \exp(-\tau_n) \cdot \wp(\mu_n) \right\rangle = \left\langle \sum_{n=0}^{\infty} \omega_n \right\rangle, \tag{9.1}$$

<sup>1</sup>T. Deutschmann is gratefully acknowledged for contributing to the development of these studies

where  $\tau_n$  is the optical density between the  $se_n$  and the Sun. Each scattering event n is characterized by its spatial location  $\mathbf{r}_n$ , given by its spatial coordinates (e.g., geocordinates), and by its distance toward the next scattering event  $l_n$  (refer to Fig. 9.2(a)). Hence, the *location of the effective sensing center* can be described as

$$\mathbf{r}_{SC} = \frac{\left\langle \sum_{n=0}^{\infty} \omega_n \cdot \mathbf{r}_n \right\rangle}{\left\langle \sum_{n=0}^{\infty} \omega_n \right\rangle} \tag{9.2}$$



(a) Scattering event  $(se_n)$  and scattering length  $(l_n)$ 



(b) Sensing Center (SC), and sensing length (sl)

Figure 9.2: Scheme of the concept of the horizontal sensitivity of a measurement. (a) All the scattering events se of associated light path length l may be regarded as (b) an effective center of scattering or sensing center SC. The horizontal sensitivity is given by the projection of the sensing length sl into the xy-plane.

Therefore, the effective distance between that SC and the detector yields the *effective sensing* distance or sensing length of the measurements:

$$sl_{SC} = \frac{\left\langle \sum_{n=0}^{\infty} \omega_n l_n \right\rangle}{\left\langle \sum_{n=0}^{\infty} \omega_n \right\rangle}.$$
(9.3)

Hence, the aimed horizontal sensing or *horizontal sensitivity* of the measurements can be understood as the projection of  $sl_{SC}$  into the xy-plane. Since the classic definition of boxAMFs as given by Eq. (6.24) provides the sensitivity of the measurement to a given layer and is used to quantify the light path length, considering the above  $sl_{SC}$  should be similar to the classic 1-D boxAMF. More detailed studies may be performed by 3-D boxAMF, but such a detailed analysis is out of the scope of this thesis, and this may be considered a consistent approximation of an effective horizontal sensitivity. Furthermore, these simple calculations may be used as a measurement flight planning tool in future campaigns. The application for the particular aircraft ascent case study is shown in Fig. 9.3.

The sensing length altitude dependency given in Fig. 9.3, understood by means of vertical profile of the air density and of the retrieved aerosol  $\mathcal{E}_{\mathcal{M}}$  profile from Fig. 8.13 (IUP-HD), is also depicted in Fig. 9.4. As expected for measurements in the UV range and in a rather clean atmosphere, during the whole measurement passage, the Rayleigh scattering dominates the RT processes affecting the light path. However, Mie scattering is also relevant in the boundary layer (with higher aerosol load). Overall and as already reported for other airborne scattered skylight measurements performed in limb geometry (e.g., *Weidner*, 2005), the probability of the light to be scattered into the line-of-sight of the instrument is higher for the layer where the instrument is located in.

The main outputs from the above described sensitivity studies shown in Fig. 9.3 and Fig. 9.4 are: (1) the mini-DOAS instrument collected scattered skylight from a volume of air that (horizontally) extended 10 to 40 km from left side of the aircraft, (2) the Rayleigh scattering by air molecules dominates over particle scattering when the aircraft ascended from the BL up to the UT/LS, (3) most of the information gathered comes from the line-of-sight of the instrument. Some implications of these three findings are given below.

• Finding (1) indicates a horizontal sensitivity of the limb measurements of 10-40 km (increasing with altitude). Thus, any small scale variability of the targeted trace gas existing within that distance from the aircraft (depending on the altitude), is in fact averaged in our observations. This averaging may not limit the BrO profile retrieval in the free and upper troposphere where a horizontal homogeneity is probably justified. Conversely, strong BrO horizontal gradients may exist in the BL. In order to study possible BrO horizontal gradients within the horizontal instrument sensitivity range, forward RT analyses are performed. These analyses suggest that, within the first 600 m, the BrO vmr allowing to (independently) reproduce the measured BrO dSCD may be as large as 20 pptv (in cyan in Fig. 9.1). More insight into the horizontal variability of boundary layer BrO vmr is given in Sect. 9.2.

Following with the forward RT analyses to study possible BrO horizontal gradients above the BL, between 1.2–3 km, the BrO dSCDs measured may also be consistent with BrO



(b) Vertical profile of the measurements' horizontal sensitivity

(c) Vertical profile of 1-D boxAMF

Figure 9.3: Horizontal sensing distance. (a) Aerial view of the Sensing Centers SCs (in green). Their distance to the instrument, which location is given by the red flight trajectory, provide the sensing length of the measurements. Figure courtesy of T. Deutschmann, (b) Vertical profile of the measurements horizontal sensitivity during the aircraft ascent, (c) Vertical profile of the 1-D boxAMF of the measurements.



Figure 9.4: Scattering events and sensing length vs. detector altitude (in the left). Red dots symbolize Rayleigh scattering and ground events are shown in yellow. Scatter events due to cloud and aerosol particles are given by the green dots. Also added are absorption events (blue dots). Figure courtesy of T. Deutschmann.

vmr of up to 2.5 ppt. Nevertheless, above 3 km, the measurements were not reproducible within the error margins if a steady BrO vmr larger than 3 ppt would be considered in the free troposphere. Moreover, GOME-2/MetOp-A satellite observations indicate that, at the beginning of the aircraft ascent, an area of high BrO vertical column density (VCD) was crossed (see also Table 9.1). Thus, the retrieved BL part of the profile shown in Fig. 9.1 may only be representative for the first part of the ascent.

- Finding (2) suggests that the BrO profile retrieved in the UT/LS is independent from the assumption of the horizontal stratification of the aerosols' optical parameters.
- Another critical aspect of the retrieved BrO profiles in the UT/LS (and also of the retrieved IUP-HD  $\mathcal{E}_{\mathcal{M}}$  profile from Fig. 8.13) addresses a possible contamination of the measured BrO absorption by photons back-reflected from or near the ground, thus carrying to the location of detection some BrO absorption from the BrO cloud in the BL (refer to Fig. 9.5). However, result (3) suggests e.g. that the BrO profile retrieved in the upper troposphere is not an artifact from BrO enhanced in the BL. This is also confirmed by forward modeling studies which show that the BrO dSCDs measured in the UT/LS can be explained (within the error bars) if no enhanced BrO is considered in the BL. Moreover, the retrieved BrO vmr in the lowermost stratosphere compare well with expectations based on atmospheric BrO profile measurements performed during a large suite of balloon deployments into the lower and middle atmosphere from low, mid and high-latitudes during the past 15 years (e.g., *Weidner et al.*, 2005; *Dorf et al.*, 2006). Also, since the BrO averaging kernels are very close to unity throughout the whole vertical profile (see Fig. 9.1), the mentioned BrO surface contamination may be in general ruled out (although the width of the averaging kernel is also to be considered).

## 9.1.1 BrO vmr vertical profile in context with other trace gases

Next the inferred BrO profiles are put in the context of other in situ measured trace gases (O<sub>3</sub> and CO in Fig. 9.6). Such an investigation may also assist to test even further the consistency of the retrieved BrO profile. Figure 9.6 indicates (in red) that the slightly enhanced BrO found in the upper troposphere could be due to the transport of air masses from the lowermost stratosphere deriving from a tropopause fold (see Sect. 3.2.3). Hence, this would lead simultaneously to enhanced O<sub>3</sub> and BrO and to depleted CO. In fact, such transport events are known to occur frequently during the Arctic spring season and are studied in detail in Sect. 9.2. These arguments enforce us to confirm that the BrO vmr inferred in the UT/LS region represent a fairly accurate description of real physical quantities, and are not merely artifacts of the retrieval technique.



Figure 9.5: Radiative transfer estimations of the ground scattering events. Left: Probability of light scattering ground events reaching the detector as the aircraft ascended (79% ground albedo). Right: Elevation angle of the telescopes as given by the roll angle of the Falcon aircraft. Note the change into logarithmic scale after 1°.

More difficult to discuss are the BrO vmr inferred in the free troposphere. Indeed, there are reports of some ppt of BrO vmr detected in the free troposphere during similar conditions (e.g., *Fitzenberger et al.*, 2000). In addition, the averaging kernels of our BrO retrieval (Fig. 9.1, left) indicate the independence of the information inferred. Nevertheless, the small BrO vmr close to or at the detection limit found for the free troposphere ( $\leq 0.9$  ppt, Sect. 8.1.1) renders it difficult to quantify whether some BrO is actually present. One recent study reports on reactive bromine measurements (HOBr, Br<sub>2</sub> and BrO) present in the BL and free troposphere during the Arctic spring of 2008 (*Neuman et al.*, 2010). In *Neuman et al.* (2010) the amount of reactive bromine in the free troposphere was found to be low ( $\leq 1$  pptv and typically close to detection limit). Photochemical arguments put forward by the authors (also valid for our conditions) suggest that most (if not all) of the detected reactive bromine was actually HOBr (reservoir) rather than BrO. Since these arguments may also apply for the present observations, it can be concluded that BrO was not unequivocally detected in the free troposphere during the ASTAR 2007 campaign.

Next the BrO detected within the BL of the Arctic troposphere during spring 2007 is considered based on Fig 9.6, right (see also Sect. 9.2). Overall, the near surface BrO vmr show strong heterogeneities (with values between 8-30 ppt) with a general trend of decreasing BrO with



Figure 9.6: Aircraft-borne measurements performed by the DLR ( $O_3$  and CO) and the IUP-HD group (BrO) on April 1<sup>st</sup> (green) and 8<sup>th</sup> (cyan, red, blue) during the ASTAR 2007 campaign. Note that the maximum altitude in the cyan profiles (descent at 13:00 UT, 8 April) is around 4 km. The tropopause height for April 1<sup>st</sup> (green) and 8<sup>th</sup> (blue) are indicated with arrows in the left panel.

height. This finding is well in agreement with previous observations of near surface BrO vmr typically high ( $\geq 10$  ppt) during the polar spring ODEs (e.g., *Hausmann and Platt*, 1994; *Saiz-Lopez et al.*, 2007). However, even though in *Neuman et al.* (2010) BrO is found within this vmr range, their measurements together with photochemical arguments indicate that most of the reactive bromine was actually HOBr (and possibly Br<sub>2</sub>), rather than BrO. Since herein BrO is selectively detected with the DOAS method, their finding of BrO playing a minor role in the total reactive bromine during ODEs somehow contrasts with the overall finding of this work, at least in situations where enough ozone is still available to oxidize the Br atoms formed either from Br<sub>2</sub> or BrCl photolysis (see also Sect. 9.2).

Another aspect of the bromine detection may address the variability of BrO in the BL due to the proximity to the open sea, broken sea ice (leads) or closed sea ice. In order to investigate potential source regions of reactive bromine, particular aircraft trajectories were planned aiming at flying over these potential sources. As an example, different ascents and descents on April 8<sup>th</sup> probed the atmosphere over (a) closed or broken sea ice (green, cyan and red profiles in Fig. 9.6), and over (b) open ocean and scattered sea ice (blue profile in Fig. 9.6). Worth mentioning is that sensitivity studies indicate that heterogeneities in the forward model parameters may affect in unique ways the forward model error (and therefore the total error) for the inferred BrO tropospheric profiles presented in Fig. 9.6 (right). For instance, the error of the BrO profile at 14:30 UT (in red) is found to be largely determined by the aerosol load. On the other hand, the ground albedo variability dominates the error of the BrO profile at 15:20 UT (in blue). A first inspection of the measured  $O_3$ , CO and BrO profiles (Fig. 9.6) reveals that the largest BrO vmr (up to 30 ppt) was found during the descent over (b) on April 8<sup>th</sup> (in blue), while the lowest ozone - very close to the detection limit of 3 ppb - was detected during the ascent on April 8<sup>th</sup> over (a) (in red). Transport and photochemical processes, as well as heterogeneous reactions may interact in a complicated manner for concluding the source region for reactive bromine as (a) or (b). These aspects are addressed in detail in Sect. 9.2.

## 9.1.2 Satellite validation

Herein, presented BrO abundance data are inter-compared with simultaneous satellite-borne BrO observations. The satellite data, derived from GOME-2/MetOp-A measurements, consist of total, stratospheric and tropospheric BrO vertical column densities (VCD) retrieved using two different algorithms developed by the Max-Planck-Institute for Chemistry (MPIC), and by the BIRA-IASB/TEMIS groups. The satellite retrievals of both groups are based on a residual technique that combines measured total BrO slant columns and estimates of the BrO absorption in the stratosphere. Furthermore, stratospheric and tropospheric airmass factors are applied in order to account for changes in measurement sensitivity in both stratospheric and tropospheric layers. The BIRA-IASB team applies a stratospheric correction based on the BrO climatology described by (Theys et al., 2009) which uses estimates of the tropopause height (derived from ECMWF data<sup>2</sup>), as well as  $O_3$  and  $NO_2$  vertical columns simultaneously retrieved by GOME-2 (more details can be found in *Theys*, 2010a; *Theys*, 2010b). The total, stratospheric and tropospheric BrO VCD as derived by this group are shown in Fig. 9.7. The MPIC team uses a slightly different stratospheric correction by applying a statistical approach which considers  $O_3$  as a tracer for stratospheric air masses and assumes a linear relationship between measured  $O_3$  and stratospheric BrO slant columns. The remaining BrO SCD is considered to be located in the boundary layer. In contrast to the BIRA algorithm, background BrO in the troposphere is implicitly accounted for in the stratospheric columns and not in the tropospheric estimates (indicated as \* in Table 9.1).

In order to compare the satellite columns with the airborne results, only satellite pixels with

<sup>&</sup>lt;sup>2</sup>ECMWF: European Centre for Medium range Weather Forecasts



Figure 9.7: Total (upper panels), stratospheric (middle panels) and tropospheric (low panels) BrO VCD for the  $1_{st}$  and  $8_{st}$  April, 2007 (left and right column, resp.). Inferred by the BIRA-IASB team (courtesy of N. Theys). The island of Spitsbergen is marked with a black cross.

overpasses 30 minutes before and after the duration of the passages are considered. In addition to the satellite pixels intercepting the Falcon flight track, pixels falling roughly 20 km on the left side of the track (in the mini-DOAS viewing direction) are also taken into account. Adding those pixels parallel to the flight track aim at considering an averaged horizontal sensitivity of the limb measurements throughout the aircraft ascent. Finally, only the satellite pixels displaying the highest sensitivity to surface BrO have been kept for the comparison.

Table 9.1 provides an overview of the inter-comparison exercise. Shown are the tropospheric BrO columns inferred from the flights on April  $1^{st}$  and  $8^{th}$  during the ASTAR 2007 campaign (see also Fig. 9.6, right) and integrated over the BL, the free troposphere and the entire troposphere. In addition, estimates of stratospheric BrO columns, inferred from balloon measurements *Dorf et al.*, 2006, are provided after adapting them for similar tropopause height. The airborne data (IUP-HD) are compared to the satellite columns (MPIC and BIRA). Note that no satellite data are given for the 13:00 and 15:20 UT profiles on 8 April 2007, due to the small number of satellite pixels meeting our selection criterion.

As shown in Table 9.1, within the limits of the experimental errors, the integrated BrO column amounts using the airborne and the satellite approaches compare reasonably well. Differences between the three groups may be due to different wavelength range chosen for the BrO spectral retrieval (airborne retrieval: 346–359 nm, BIRA: 332–359 nm and MPIC: 336–360 nm), although the possibility that different air masses were sampled cannot be ruled out. On the other hand, deviations between the two satellite retrievals may be attributed to a different choice of the VCD retrieval algorithm (MPIC applies a normalization following the method published by Richter et al. (2002) while the BIRA product does not apply any normalization procedure). Since the ground albedo significantly alters the sensitivity for the satellite detection of trace gases close to the surface, the ground albedo may also play a role in those differences. In these studies, the MPIC group uses the same surface albedo than the mean value used by the IUP-HD one (79%). On the other hand the BIRA group uses variable surface albedo values per pixels, with mean values of 75% (1<sup>st</sup> April) and 68% (8<sup>th</sup> April) based on (Koelemeijer et al., 2003) climatology. Overall, worth mentioning is also that compared to airborne values, the satellite retrieval does not systematically underestimate BrO, a behavior one would expect if the satellite detection of near surface BrO would be systematically obscured in the Arctic, e.g., by scattering due to aerosol and cloud particles.

## 9.2 Sources, photochemistry and transport processes

In the previous section the algorithm for retrieving BrO vmr vertical profiles has been applied, characterized and validated for measurements gathered during different aircraft passages. Here

		1 Ap	8 April 2007						
		Airborne	Satellite		Airborne			Satellite	
		IUP-HD	MPIC	BIRA	IUP-HD		MPIC	BIRA	
		$(10^{13}molec/cm^2)$	$(10^{13}molec/cm^2)$		$(10^{13}molec/cm^2)$			$(10^{13}molec/cm^2)$	
				13:00 UT 14:30 UT 15:20		15:20  UT	14:30 UT		
$VCD_{trop}$	BL	$2.0{\pm}0.6$	$2.5{\pm}1.0^{*}$	-	$3.9{\pm}2.0$	$3.8{\pm}1.2$	$5.8{\pm}1.8$	$2.8{\pm}1.0^{*}$	-
	Free	$1.0{\pm}1.0$	-	-	$\geq (0.7 \pm 2.5)$	$1.6{\pm}1.3$	$1.5{\pm}1.1$	-	-
	TOTAL	$3.0{\pm}1.2$	-	$4.0{\pm}1.5$	$\geq (4.6 \pm 3.2)$	$5.4{\pm}1.8$	$7.3 \pm 2.1$	-	$5.3 {\pm} 1.5$
$\mathrm{VCD}_{strat}$		$3.9{\pm}0.3$	$4.2{\pm}0.6^*$	$3.9{\pm}0.8$		$3.7{\pm}0.3$		$4.2{\pm}0.7^*$	$3.7{\pm}0.8$
$VCD_{TOTAL}$		$6.9{\pm}1.2$	$6.7 {\pm} 1.9$	$7.9{\pm}2.3$	$\geq (8.3 \pm 3.2)$	$9.1{\pm}1.8$	$11.0 \pm 2.1$	$7.0{\pm}2.0$	$9.0{\pm}2.3$

Table 9.1: BrO VCD comparison between airborne and satellite measurements during the Arctic spring (2007). Details given in the text.

an analysis of the photochemistry and transport processes related to bromine monoxide during the Arctic spring is performed for the particular 8 April 2007 case study.

Based on in situ measured  $O_3$  and CO vmr (DLR), the first part of this section characterizes the location of the tropopause for the 14:30 UT aircraft ascent, and the consecutive 15:20 UT descent. The UT/LS exchange layer is then delimited, and the sensed BrO is analyzed toward the mixing layer vertical extent. Additionally, one mini-DOAS deployment during the GRACE 2008 campaign is chosen for a brief analysis of the BrO and  $O_3$  abundances within the tropopause inversion layer (*TIL*) addressed in Sect. 3.2.3.

The second part of this section focuses on bromine related ozone depletion events in the lowermost troposphere. First, the dynamical and chemical vertical structure of the boundary layer over the sea ice is studied. Then, the possible sources of bromine species are characterized. Finally the boundary layer BrO lifetime and the ozone loss rate are estimated from measurements performed during a 115 km horizontal aircraft passage, only 65 m above the High Arctic sea ice (8 April 2007).

## 9.2.1 BrO and the dynamical tropopause

As detailed in Chap. 3, the tropopause may be defined from different points-of-view. The concept of *chemopause* is applied in this section for characterizing the extent of the UT/LS mixing layer during the 8 April 2007 sortie, for the 14:30 UT aircraft ascent and the consecutive 15:20 UT descent. The temperature and wind speed during these two cruises are given in Fig. 9.8.

In general the UT/LS transition layer or mixing layer can be estimated by the chemical L-curve method described in Sect. 3.2.3. In the stratospheric-tropospheric tracer space, the UT/LStransition layer lays between purely stratospheric air masses with very high O<sub>3</sub> vmr and very low CO vmr (i.e., vertical branch of the O<sub>3</sub>-CO space), and purely tropospheric air masses with high CO vmr and low O<sub>3</sub> vmr (i.e., horizontal branch of the O<sub>3</sub>-CO space). Figure 9.9, shows the O<sub>3</sub>-CO space during the 14:30 UT aircraft ascent, and the consecutive 15:20 UT descent. Additionally, Fig. 9.10 (upper panels) presents the inferred BrO vmr for those passages, aiming at analyzing the effect of the mixing layer extent on the retrieved BrO vmr in the UT/LS region. For comparison, the lower panels of Fig. 9.10 show the in situ measured O<sub>3</sub> vmr (DLR).

As shown in Fig. 9.10 and reported by e.g. *Pan et al.* (2004), the transition layer or chemopause oscillates around the thermal tropopause. However, while the upper limit of such layer appears at similar altitude in both passages, measurements performed during the ascent indicate



Figure 9.8: Left: Flight profile and temperature. Right: Flight profile and wind speed (northwesterly). Note the peak of wind in the 15:30 UT tropopause (data provided by the DLR). The time of the flight when the thermal tropopause was crossed is marked with the yellow boxes. The lowers limit of the thermal tropopause is given by the gray horizontal line (TP). The horizontal distance between the TP in the ascent and descent is roughly 70 km.

that the mixing layer reaches lower altitudes into the troposphere. In order to address this from a trace gas perspective, one should bear in mind that the BrO vmr inferred from mini-DOAS measurements should be regarded as an averaged value of a volume of air that extends as far as 30 km away from the aircraft, while the CO and  $O_3$  are in situ measured. Figure 9.10 shows that, during the ascent, the BrO vmr in the UT/LS is clearly enhanced as compared to the descent. This correlates with the wider mixing layer during the ascent, that reaches 2.5 km below the thermal tropopause lowest limit. Similarly, the  $O_3$  vmr in the ascent shows some enhancement just below the tropopause, and a decrease just above it (compare to the descent passage). Therefore one may conclude that, in that passage, the BrO vmr is enhanced in the trough of the fold and the stratospheric air intrusion reaches down to ~7 km. In general, these studies indicate the relevance of an accurate definition of the tropopause altitude for inferring e.g. the tropospheric VCD of important trace gases such as BrO.

The sensitivity of the mini-DOAS measurements to the dynamic processes in the UT/LS region is also checked for one sortie during the summer GRACE 2008 campaign. In this case the studies presented address the definition of the static stability of the environment (squared



(a)  $O_3$ -CO space, 14:30 UT ascent

(b) O<sub>3</sub>-CO space, 15:20 UT descent

Figure 9.9: The chemopause during the 8 April 2007 sortie. Data provided by H. Schlager (DLR). The color-code indicates the altitude where the measurements were performed.

buoyancy frequency  $N^2$ ), given in Sect. 3.2.3.

As mention in Sect. 7.3.2, during the GRACE 2008 campaign (sortie 15<sup>th</sup> July, 2008), the Falcon aircraft flew from Kangerlussuaq toward Spitsbergen. Studies performed by the group of Jülich based on meteorological data from ECMWF (Kunz, 2010), show that most of that flight took place within a highly stratified low stratosphere (very high  $N^2$ ). Additionally, analyses of the O<sub>3</sub>-CO space shown in that work establish the coincidence of the Tropopause Inversion Layer (TIL) with the UT/LS mixing layer. This is summarized in Fig. 9.11(a). Additionally, Fig. 9.11(b) presents the in situ measured O<sub>3</sub> vmr from H. Schlager's group (DLR), and the BrO dSCDs remotely sensed with the mini-DOAS instrument during the same flight. As shown in the figure, within the steady horizontal passage inside the mixing layer, the in situ measured  $O_3$  vmr (cyan low panel) presents strong variations indicating the dynamics of the tropopause fold and the stratosphere-troposphere exchange. Similarly, the measured BrO dSCDs show a variability of  $8 \cdot 10^{13}$  molec/cm<sup>2</sup> for the steady altitude (approx. 1 pptv). This BrO variability supports the idea that not only the BrO vmr is affected by the stratosphere-troposphere exchange dynamics, but that the effect is actually captured by the mini-DOAS measurements. Since in this horizontal passage the BrO dSCD measurements show approx. 3 degrees of freedom, a vertical vmr profile retrieval is not addressed herein. However, these analyses already show the potential of these sort of aircraft-borne limb measurements.



(c)  $O_3$  vmr, 14:30 UT ascent

(d)  $O_3$  vmr, 15:20 UT descent

Figure 9.10: The Arctic tropopause from a trace gas perspective. Upper panels: The transition or mixing layer estimated in Fig. 9.9 is overlaid on the BrO vmr vertical profile (red horizontal lines). The color code used gives the altitude of the  $O_3$ -CO measurements presented above. Lower panels: The O3 vmr is situ measured by H. Schalger (DLR). In all panels the lowest limit of the thermal tropopause is indicated with the dashed gray line and the boundaries of the transition layer are given by the red horizontal lines.
#### 9.2.2 BrO in the polar marine boundary layer

After having addressed the BrO abundance in the UT/LS, here BrO and the related ODE are studied in the polar marine boundary layer. Before focusing on the distribution, sources and photochemistry of BrO in the BL, the  $O_3$ -CO space used in Sect. 9.2.1 for defining the chemopause in the 14:30 UT ascent and 15:20 UT descent, is here applied for gaining an overview of the vertical extent of the ODE in both passages. As shown in Fig. 9.12(a), the O<sub>3</sub>-CO correlation presents two main branches resulting from the strong stratification of the polar troposphere. First, there is a vertical branch where CO vmr is rather constant while  $O_3$  vmr increases steadily with altitude ("ODE branch"). Above roughly 2.5 km, the  $O_3$  vmr data are scattered versus CO vmr, indicating that the air masses probably belong to the free troposphere. The  $O_3$ -CO space in the low troposphere during the 15:20 UT descent shows similar behavior. As shown in Fig. 9.12(b), despite the pollution layer (increased CO) in the BL nearby the Longyearbyen airport, CO vmr remains constant with height until about 1.2 km, where the O<sub>3</sub>-CO correlation is scattered (air from the free troposphere). Based on both figures, the threshold of the background or free tropospheric ozone in this sortie is then to 45 ppbv, with a vertical extent of 1.2–2.5 km. This vertical extent of the ODEs agrees with the altitudes of up to 4 km measured in the Norwegian Arctic by e.g. Solberg et al. (1996). In their study, and based on long term studies accounting for the seasonality of the background (free) tropospheric ozone, 25 ppbv is set as the  $O_3$  vmr threshold for an ODE. However, their springtime  $O_3$  vmr measurements gathered in a non-ODE situation are similar to the 45 ppb  $O_3$  vmr threshold given in this work.

#### BrO and the vertical structure of the polar boundary layer

The studies here presented focus on the vertical structure of the BL above the sea ice as inferred from measurements performed during the 14:30 UT ascent. Similarly to the tropopause, the boundary layer structure and dynamics may be described from a meteorological point of view, and from a chemical perspective (e.g., Anderson and Neff, 2008). Here both approaches are addressed. Since the measurements are performed during the aircraft ascent, the collected data may comprise local information of the BL, and also information of advected air masses. Hence, the vertical structure of the BL presented in the following may be regarded with some caution. Moreover, there are no data available for the very first 60 m above the sea ice. Keeping these limitations in mind, and in order to establish a mixing depth for a chemical analysis, Fig. 9.13(a) presents the in situ measured temperatures (T and  $\theta$ ), as well as the water mixing ratio and relative humidity. As shown in the figure, the BL over the flat sea ice in the given sunny and low (5–6 m/s) wind conditions, presents a rather complicated structure. Overall, the BL



(a) Vertical cross section of  $N^2$ . Adopted from Kunz (2010)



(b)  $O_3$  vmr and BrO dSCDs

Figure 9.11: (a) Vertical cross section of  $N^2$  along the (black) flight track on 15 July 2008 ( $N^2 \propto \frac{d\theta}{dz}$ ). The cyan colored section corresponds to the part of the flight within the mixing layer (based on  $O_3$ -CO studies shown in Kunz, 2010). The thermal tropopause is marked in gray. The PV isolines are given in red dashed lines, and the isentropes (K) in white lines. The black box is the passage selected for a closer look to  $O_3$  and BrO in the lower panel. Figure adapted from Kunz (2010). (b)  $O_3$  vmr (cyan) and BrO dSCDs (color-coded) in the mixing layer. The color-code corresponds to the elevation angle of the mini-DOAS instrument's telescopes. The  $O_3$  data are kindly provided by H. Schlager (DLR).



(a)  $O_3$ -CO space in the BL, 14:30 UT ascent (b)  $O_3$ -CO space in the BL, 15:20 UT descent

Figure 9.12:  $O_3$ -CO space in the polar boundary layer. (a) Boundary layer above the sea ice. (b) Boundary layer (mostly) above ocean, and approaching the Longyearbyen airport. The  $O_3$  vmr detection limit is 3 ppb. The color-code provides the altitude of the measurements. Data provided by H. Schlager (DLR).

seems to be moderately stable up to 2.5 km, coinciding with the altitude threshold for the ODE inferred from Fig. 9.12(a). An attemptive description of this BL may be as follows. A surface layer up to  $\sim 100$  m height (although complicated to confirm without the first 60 m) where heat, momentum and moisture are exchanged with the sea ice. A stable, and rather mixed layer based on e.g. the relative humidity, of 800 m height lays below an entrainment layer of unsaturated moist air (*entrainment zone*). In this case, the top of the boundary layer is defined as the mid-depth of that entrainment zone.

Additionally, Fig. 9.13(b) shows a summary of the trace species measured within this BL. In the context of bromine monoxide measurements, the in situ measured O<sub>3</sub>, CO and NO<sub>y</sub> are degraded to the coarser vertical resolution of the mini-DOAS measurements. Detection limits of the trace gases presented in the figure are 1.5 pptv (BrO), 3 ppbv (O<sub>3</sub>), 5 pptv (NO<sub>y</sub>) and 2 ppbv (CO). As shown in the figure, the background (free troposphere) O<sub>3</sub> shows a very strong gradient within the defined entrainment zone, supporting the idea that exchange processes take place at that altitude with a flux of free tropospheric ozone into the BL of  $4.6 \cdot 10^{10} \frac{molec}{cm^2 s}$ . In the right panel of the figure, the clear anti-correlation of the BrO-O<sub>3</sub> vmr is demonstrated, with a calculated ozone loss of ~1 ppbv/day within the 1.7 km of the entrainment zone.

Regarding the first 500 m of the BrO vmr in Fig. 9.13(b), as explained before and based on the averaging kernels, details should be treated with caution. Above that altitude, the BrO vmr decreases exponentially with height with a scale height of about 750 m. Despite the rather coarse vertical resolution of these particular BrO measurements, the BrO scale height of this passage agrees with the other BrO vmr vertical profiles inferred within this work (Fig. 9.6). Since these BrO vmr vertical profiles are retrieved from measurements performed above different surfaces with unique properties regarding bromine emission, (i.e., close sea ice, leads, scattered sea ice, and open ocean), the given BrO scale height may involve not only vertical, but also horizontal transport processes.

#### BrO horizontal cross-section over the sea ice

This section analyses the measurements gathered during the horizontal passage between 14:10–14:35 UT, i.e., the passage just before the ascent described in the previous section (refer to Fig. 7.3.1 for an overview of the flight). During that horizontal leg, the aircraft flew 60–100 m above the sea ice, covering a horizontal distance of approx. 115 km under clear sky conditions and 5 m/s wind speed.

Since in this case all the BrO dSCDs were gathered within the boundary layer, the  $O_4$  method described in Sect. 6.3 is used herein for inferring the boxAMF and the BrO abundances (vrm and VCD), assuming a well mixed layer of 1 km height. In this passage the spatial resolution of the mini-DOAS measurements is 2–16 km in the direction of the flight as given by the integration time (time resolution), and approx. 15–25 km to the left side of the aircraft (given by the horizontal sensitivity of the measurements). Thus, each measurement gathered by the mini-DOAS instrument comprises information related to an area of approx. 8x20 km<sup>2</sup>.

Here, the inferred BrO abundances are put in context with in situ measured trace gases and aerosols (DLR). Then, the boundary layer BrO VCD inferred from the mini-DOAS measurements (i.e. BrO IUP-HD) are compared to the boundary layer BrO VCD retrieved by the MPIC group from the satellite GOME-2/MetOp-A (for the MPIC retrieval of BrO VCD refer to Sect. 9.1). Moreover, the retrieved BrO abundances (IUP-HD) are then related to the properties of the underlying sea ice, aiming at assessing the possible bromine sources. For a better understanding, data presented in this section are accompanied with sea ice satellite images as given by different instruments aboard the ESA's Envisat satellite (Medium Resolution Imaging Spectrometer *MERIS*, and the Advanced Synthetic Aperture Radar ASAR), and the NASA Earth Orbiting System satellite (Moderate Resolution Imaging Spectrometer *MODIS*, and the Advanced Microwave Scanning Radiometer AMSR-E). All the sea ice satellite images presented here are provided by ESA's PolarView project, via L.T. Pedersen (Center for Ocean and Ice of the Danish Meteorological Institute (DMI), Pedersen, 2010).

Figure 9.14 presents the aerial view of the selected horizontal flight passage over the sea ice. The aircraft entered the sea ice area at 100 m altitude, and descended to approx. 60 m, where it flew for  $\sim 20$  min. Then the aircraft started ascending slowly up to 100 m, and turned east. From the passage shown in Fig. 9.14, different locations are chosen for the analysis of the



(b) Vertical vmr distribution of trace gases in the BL over the sea ice

Figure 9.13: Boundary layer vertical structure and distribution of trace gases. Note the semilogarithmic scales. (a) In situ measured temperatures (T and potential temperature  $\theta$ ), water mixing ratio and relative humidity (data provided by the DLR). The boundary layer vertical structure is indicated at the right side of the figure. Top of BL indicates the top of the boundary layer. (b) Vertical vmr distribution of trace gases as measured in the boundary layer. The in situ measured CO, O<sub>3</sub> and NO<sub>y</sub>, provided by H. Schlager (DLR), are degraded to the mini-DOAS vertical resolution.

backward trajectories provided by A. Stohl (FLEXPART model, *Stohl et al.*, 1998). A detailed study from the A to F locations given in Fig. 9.14 showed no major differences between air masses reaching different measurement points. Hence, only two chosen locations (A and E) are shown for an overview of the history of the air masses probed during the passage (Fig. 9.15 and Fig. 9.16). As shown by the retroplume summaries (Fig. 9.15(a) and Fig. 9.16(a)), air masses coming from the North were crossed at the beginning of the passage, while later the air masses arrived from the North-West (Fig. 9.16(a)). For measurements at A and E, the air masses traveled very close to the ground from Siberia, over the North Pole, to the measurement point within about 5 days. Hence, for that period, air masses were in contact with the High Arctic sea ice.

The trace gas and aerosol data gathered during the passage are presented in Fig. 9.17 and summarized in Table 9.2. Trace gas vmr presented in the figure are BrO (remote sensed, IUP-HD), and  $O_3$ ,  $NO_y$ ,  $HNO_3$ , CO (in situ, H. Schlager, DLR). The aerosol surface area concentration shown herein are inferred from the in situ measured particle number densities and size distribution (A. Minikin, DLR). The in situ data are provided here at the time resolution of the BrO measurements. Since  $HNO_3$  vmr measurements are below or within the instrumental detection limit range of 30–50 ppt, they are not further considered.

Table 9.2: Mean values and detection limits of the trace gases vmr measured during 115 km of flight 60–100 m above the High Arctic sea ice (8 April 2007, SZA= 78°). O<sub>3</sub>, CO, NO<sub>y</sub> vmr are provided by H. Schlager (DLR). The mean aerosol surface area concentration in this passage is  $39 \ \mu m^2/cm^3$  (A. Minikin, DLR).

Species	Mean vmr	Det. limit
BrO	12  ppt	1.5  ppt
IO	$\leq 2 \text{ ppt}$	2  ppt
$O_3$	$\leq 3 \text{ ppb}$	$3 \mathrm{\ ppt}$
$NO_y$	600  ppt	$5 \mathrm{ppt}$
$HNO_2$	$\leq 0.2 \text{ ppb}$	0.2  ppb
$CH_2O$	$\leq 5 \text{ ppb}$	5  ppb
CO	166  ppb	2  ppb

As shown in Fig. 9.17, the BrO vmr exhibits an positive gradient along the passage above the sea ice. On the other hand, despite measurements performed nearby the turn of the aircraft, the  $O_3$  vmr is below 3 ppb during most of the passage (approx. 100 km). As expected in a pristine atmosphere, NO<sub>y</sub> and CO vmr are rather low. The aerosol surface area concentration shows no major change during the passage. However, noteworthy is the higher surface area concentration detected at the edge of the sea ice (right bottom values), corresponding to in situ measured



Figure 9.14: Upper panel: The flight track over the sea ice. The horizontal passage selected for the study is given in red. The sea ice MERIS satellite image (8 April 2007) is provided by Pedersen (2010). The yellow shadow represents the horizontal sensitivity of the mini-DOAS instrument. Lower panels: The left panel provides in red the wind direction (red) along the flight trajectory (in black). The wind speed was 5 m/s. The selected locations for backward trajectory analyses are indicated by A-F. The right panel provides the color-coded box air mass factors (boxAMF) used for the retrieval of BrO abundances. Additionally, the flight direction and the viewing direction (VD) of the mini-DOAS instrument are indicated.



Figure 9.15: Backward trajectory of the the airmass at measurement point A. Meteorological data from ECMWF (FLEXPART, Stohl et al., 1998). (a) Retroplume summary (color code: m height). The purple line indicates the backward trajectory of the airmass. (b) Foot-print emission sensitivity related to the residence time of the airmass over a unit area, averaged to the lowest 100 m (color code: ns/kg). Mean value 9.4 ns/kg. The numbers superimposed in the plume give an approximate indication of where the plume was at what time. (c) Time series (in days) of the mean altitude of the retroplume (Alt.), as well as the fraction of particles in the boundary layer (BL), and in the stratosphere (ST).



Figure 9.16: Backward trajectory of the the airmass at measurement point *E*. Meteorological data from ECMWF (FLEXPART, Stohl et al., 1998). (a) Retroplume summary (color code: m height). The purple line indicates the backward trajectory of the airmass. (b) Foot-print emission sensitivity related to the residence time of the airmass over a unit area, averaged to the lowest 100 m (color code: ns/kg). Mean value 9.8 ns/kg. The numbers superimposed in the plume give an approximate indication of where the plume was at what time. (c) Time series (in days) of the mean altitude of the retroplume (Alt.), as well as the fraction of particles in the boundary layer (BL), and in the stratosphere (ST).



Figure 9.17: Geolocated summary of the vmr of BrO,  $O_3$ ,  $NO_y$ , CO,  $HNO_3$  (H. Schalger, DLR), together with the aerosol surface area concentration (A. Minikin, DLR). Gray areas represent measurements below instrumental detection limit. Data are presented at the mini-DOAS instrument time resolution.

coarse particles (probably sea spray). Moreover, nearby the turn of the aircraft the surface area concentration decreases following a decrease on the coarse particles number density and the slightly higher amount of fine particles in situ measured (that may correspond to secondary aerosols). In order to investigate the sustainability of such amount of BrO vmr despite the very low ozone, the role of heterogeneous reactions is addressed. Figure 9.18 shows the role of the measured aerosol surface area concentration, in the  $BrO-O_3$  ratio. As shown in the figure, the higher increase of BrO vmr (vertical branch) occurs when  $O_3$  vmr is below 3 ppb (0–3 ppb). In these measurements, the aerosol surface area available for heterogeneous reactions (possible recycling bromine species), is higher compared to the measurements with ozone above 3 ppb, and less (and finer) particles. From this study one may conclude that bromine activation is supported by aerosol particles. However, despite the aerosol surfaces, bromine monoxide may still be produced under very low  $O_3$  vmr circumstances. Hausmann and Platt (1994) reported 1 ppb as the ozone vmr threshold for the formation of BrO via the  $Br + O_3$  reaction. In addition, based on a 1-D chemical and transport model, Lehrer et al. (2004) estimated that O<sub>3</sub> threshold as 2 ppb. Since the ozone detection limit in this case is 3 ppb, the production of BrO from oxidation of Br with ozone cannot be ruled out (see later in the text). In addition, and unlike the in situ measurements, the BrO vmr reported in this work are an average value of the BrO contained in a volume of air with a surface area of approx.  $8 \times 20 \text{ km}^2$ . Moreover, meteorological conditions suggest that at least two different air masses where crossed by the aircraft. Hence, further conclusions regarding the role of heterogeneous reactions in the bromine activation would require additional information such as, e.g., the chemical composition of the sampled aerosols.

Aiming at a better understanding of the BrO abundances in the boundary layer, the inferred data from the mini-DOAS measurements (i.e. BrO IUP-HD) are compared to BrO VCD retrieved from the satellite the MPIC group (for the MPIC satellite retrieval of BrO VCD refer to Sect. 9.1). As shown in the upper panel of Fig. 9.19, satellite and aircraft-borne measurements detect a clear BrO gradient between  $80-82^{\circ}N$ , with slightly higher values reported by the MPIC group (although within the estimated error margin of  $\pm 1 \cdot 10^{13}$  molec/cm<sup>2</sup>). The BrO VCD satellite retrieval shows a region of strongly enhanced BrO (a "hot spot") covering part of the aircraft passage, and extending to the North-Northwest direction. In order to investigate possible sources of this BrO "hot spot", the sea ice properties are analyzed in the following.

The lower panel of Fig. 9.19 shows the boundary layer BrO vmr (IUP-HD) overlaid on a MERIS sea ice satellite image (*Pedersen*, 2010). As shown in the figure, the sea ice exhibits different leads in the vicinity of the flight track, including a rather long one (approx. 33 km long) crossed just before the aircraft turned to the East. Figure 9.20 shows a photograph of that lead, as recorded by the video camera on board the cabin of the Falcon aircraft. As seen in the photograph, that



Figure 9.18: Role of the aerosol particles in the BrO-O<sub>3</sub> ratio. The color-code provides the aerosol surface area concentration for the corresponding measurement. The time resolution of the in situ measured O<sub>3</sub> and aerosol is degraded to the BrO vmr resolution (i.e., 8 km in the direction of the flight). For the calculation, all measurements gathered with O<sub>3</sub> below detection limit are regarded as zero ozone. Hence, the vertical branch represents all measurements where  $0 < O_3^{vmr} < 3ppb$ . The horizontal branch comprises two sectors. A left one given by measurements with O<sub>3</sub> below detection limit, combined with measurements with O<sub>3</sub> > 3 ppb ("mixed"). And a right hand sector comprising measurements all with O<sub>3</sub> above 3 ppb.

section of the lead was not open but covered by young ice.

Since young and first-year sea ice are possible sources of bromine, the sea ice concentration is studied in Fig. 9.21. As given in the figure, the concentration of sea ice also shows a gradient coinciding with the beginning of the passage (sea ice edge). As for the multi-year sea ice concentration analysis, a younger sea ice region seems to be located around 80.5°N, 15°E. However, the coarse resolution of these images hinders small sea ice features clearly detected by e.g. the MERIS satellite (Fig. 9.19).

A further step is given in the study of possible bromine sources, addressing now images from the Moderate Resolution Imaging Spectrometer (MODIS) and from the Advanced Synthetic Aperture Radar (ASAR). As explained in Sect. 5.1.3, a close look to the radar images may assist to define small sea ice structures like leads or even frost flowers. Since there is no available ASAR image for that region on 8 April 2007, an ASAR image from 9 April 2007 12UT is corrected for sea ice drift by L.T. Pedersen (DMI), to reproduce the 8 April 2007 sea ice situation (e.g. Sandven et al., 2007). The images, together with the BrO vmr along the flight track are shown in Fig. 9.22. The left panel shows a visible image of the sea ice situation during the flight, exhibiting several leads within the horizontal viewing range of the mini-DOAS instrument, and an airmass moving from the East. A closer look to the image also shows growing ice in many of the leads along the flight track. Such is the case of the lead crossed by



Figure 9.19: Boundary layer BrO vertical column density inferred from satellite (MPIC) and aircraft (IUP-HD) measurements (8 April 2007). Top: Satellite BrO boundary layer column density inferred by the MPIC group  $(10^{13} \text{ molec/cm}^2, \text{ courtesy of H. Sihler})$ . Additionally, the boundary layer BrO VCD retrieved in this work is overlaid (with the corresponding color-code given in the bottom panel). Bottom: Boundary layer BrO retrieved in this work, given in vmr (ppt) and VCD ( $10^{13} \text{ molec/cm}^2$ , assuming a 1 km well-mixed BL). The MERIS satellite image of the sea ice for that day is provided by Pedersen, 2010.



Figure 9.20: Lead with young ice underneath the Falcon aircraft (8 April 2007).

the aircraft just before the turn (see also Fig. 9.20). Since the BrO vmr increases when the aircraft approaches this lead, one may conclude that the lead is a possible source of bromine. Nevertheless, the radar image in right panel shows young (growing ice) and also first-year sea



Figure 9.21: Sea ice concentration (%). AMSR-E satellite images for 8 April 2007, provided by Pedersen (2010). The selected passage is given in white.

ice not only within the range covered by the mini-DOAS instrument, but also upwind of the measurements. These studies suggest that the probed air masses comprise BrO transported from neighboring leads upwind (also suggested by the "hot spot" found with the BrO VCD satellite retrieval), and BrO locally emitted from frost flowers in the growing sea ice, or activated by heterogeneous reactions in aerosols from the snow, frost flowers, or brine forming in the leads.



(a) BrO and MODIS image

(b) BrO and ASAR image

Figure 9.22: BrO and sea ice properties. (a) MODIS satellite image for 8 April 2007. A section of the horizontal passage (just before the turn) and the retrieved BrO are superimposed (not geolocated). Note the convergence of NW and N air masses above the ocean (see low left corner of the image). (b) ASAR satellite image for 9 April 2007 12UT, sea ice drift corrected for the 8 April 2007 (Pedersen, 2010). The horizontal passage and the color coded retrieved BrO abundances are geolocated in the image (VCD and vmr). As suggested by the overall gray color, most of the sea ice in the image corresponds to multi-year sea ice. However, young sea ice (on growing sea ice) and first-year sea ice (FY) are also present in the viewing direction or upwind of the mini-DOAS instrument. The (5 m/s) wind direction is indicated by the black arrows on top of the aircraft trajectory. In both images, kindly provided by Pedersen (2010), the approximated horizontal sensitivity of the color-coded BrO abundances is delimited by a continuous yellow line.

In order to analyze the possible effect of the particular crossed lead on the BrO vmr and the ODE, a closer look is now given to the measured trace gases. This is shown in Fig. 9.23. For the

period when the aircraft flew steadily at approx. 65 m above the sea ice just before the turn to the East, the upper panel of the figure shows the combination of in situ measured potential temperature (DLR), and visual information gathered from the video of the flight (location of the lead). As suggested by the potential temperature in the figure (and indicated also by the above satellite images), the aircraft crossed two main airmasses. A warmer Northerly airmass (higher), and then a colder Northwesterly airmass (lower). Based on the location of the lead and the wind direction, the Northerly airmass (N in the figure) reaching the aircraft may arise from turbulences due to the heat and moisture released from the lead ahead. Additionally, the lower panel of Fig. 9.23 shows the remotely sensed BrO vmr, and the in situ measured ozone vmr and aerosol surface area concentration (DLR). The concentration of aerosol surface area varies between  $32-44 \ \mu m/cm^3$  and, in the proximity of the lead, the rather smaller surface area concentration ( $32-35 \ \mu m/cm^3$ ) follows the finer aerosol particles detected, suggesting the presence of secondary aerosols and heterogeneous reactions. However, as mentioned before, additional aerosol information would be needed for further the discussion of the heterogeneous chemistry.

As given in Fig. 9.23, the BrO vmr shows a clear gradient downwind, while the ozone vmr is below the detection limit (<3 ppb). However, just before the lead (and downwind from it), the ozone vmr presents a peak. Above and after the lead, both BrO and  $O_3$  vmr show a clear drop and later recovery. Reasons leading to that complex structure of the trace gases are hard to address due to the different measurement techniques. Nevertheless, a possible reason may be the micrometeorology and/or recycling processes related to the particular lead and to neighboring ones (e.g., *Piot and von Glasow*, 2008).

In order to estimate the ozone loss rate and chemical lifetimes in this scenario (Fig. 9.23), the following reactions are analyzed for the higher and lower BrO concentrations withing this passage, i.e.,  $[BrO_{high}] = 3.6 \cdot 10^8 \text{ molec/cm}^3$  (14 pptv), with  $[O_3] = 13 \cdot 10^{10} \text{ molec/cm}^3$  (5 ppbv), and  $[BrO_{low}] = 1.7 \cdot 10^8 \text{ molec/cm}^3$  (6.5 pptv), with  $[O_3] = 9.1 \cdot 10^{10} \text{ molec/cm}^3$  (3.5 ppbv).

$$Br + O_3 \longrightarrow BrO + O_2$$
 (9.4)

$$BrO + BrO \longrightarrow 2Br + O_2$$
 (9.5)

$$\operatorname{BrO} \xrightarrow{n\nu} \operatorname{Br}$$
(9.6)

$$BrO + HO_2 \longrightarrow HOBr + O_2$$
 (9.7)

$$HOBr \xrightarrow{n\nu} Br + OH \tag{9.8}$$

$$HOBr \xrightarrow{uplake} HOBr(aq) \tag{9.9}$$



Figure 9.23: Horizontal cross-section of the sea ice boundary layer. (a) The potential temperature indicates two air masses crossed, indicated with the N and NW direction in black. The location of the lead and the wind direction (5 m/s) are indicated with cyan arrows in both figures. (b) Chemistry above the sea ice. The in situ measured  $O_3$  vmr with detection limit of 3 ppb is provided by H. Schlager (DLR), and the aerosol surface area concentration by A. Minikin (DLR, in situ). Both in situ data are degraded to the mini-DOAS horizontal resolution.

For these studies, the average aerosol surface area concentration measured in this passage is  $39 \ \mu m^2/cm^3$  (DLR) is accounted for, and a mass accommodation coefficient of 0.2 (refer to Eq.(4.128)) is considered for the HOBr uptake on NaCl aerosols (*Abbatt and Waschewsky*, 1998). Hence, assuming a steady state for HOBr, its concentration is given by

$$[HOBr] = \frac{k_{(BrO+HO_2)}}{J_{HOBr} + k_{uptake}} [HO_2] [BrO].$$
(9.10)

Additionally, if a steady state for BrO is considered, the concentration of Br is given by

$$[Br] = \frac{\left(2k_{(BrO+BrO)}\left[BrO\right] + J_{BrO} + k_{(BrO+HO_2)}\left[HO_2\right]\right)}{k_{(Br+O_3)}} \cdot \frac{[BrO]}{[O_3]}$$
(9.11)

and the ozone loss rate as

$$\frac{d[O_3]}{dt} = k_{(Br+O_3)} [Br] [O_3].$$
(9.12)

Therefore, assuming a concentration of  $HO_2 = 10^8 \text{ molec/cm}^3$  based on *Mao et al.* (2010), and considering the reaction rates given in Table 5.4, the estimated times for the reactions (9.4)–(9.9) are shown in Fig. 9.24.



Figure 9.24: Simplified photochemistry scheme of an ODE over the Arctic sea ice (8 April 2007). Calculations are performed for  $[BrO_{high}] = 3.6 \cdot 10^8 \text{ molec/cm}^3$ , with  $[O_3] = 13 \cdot 10^{10} \text{ molec/cm}^3$  (in red), and  $[BrO_{low}] = 1.7 \cdot 10^8 \text{ molec/cm}^3$ , with  $[O_3] = 9.1 \cdot 10^{10} \text{ molec/cm}^3$  (in blue). The aerosol uptake (in gray) is estimated based on Eq. (4.128) at T = 260 K, assuming a mass accommodation coefficient of HOBr on NaCl of 0.2 (Abbatt and Waschewsky, 1998). If, on the other hand, the particles consists on deliquescent NaBr aerosols, the mass accommodation of HOBr is 0.6 (Wachsmuth et al., 2002), and thus the aerosol uptake would require ~45 minutes.

Hence,  $\frac{[BrO_{high}]}{[Br]} = 6$  and  $\frac{[BrO_{high}]}{[HOBr]} = 1.6$ , with an ozone loss rate of 0.9 ppbv/h. This O<sub>3</sub> loss rate yields a lifetime of the remaining ozone of roughly 5h30min, and suggests that the removal of ozone in that airmass started 2 days prior the measurement (considering the background ozone vmr of 45 ppb). If, on the other hand, the lower BrO concentration of the passage shown in Fig. 9.23 is considered, then  $\frac{[BrO_{low}]}{[Br]} = 4.6$ , and the ozone loss rate of 9 ppbv/day. This implies an ozone lifetime of 9 h, and an ODE initiated 4.5 days before the measurement. Therefore, based on the ratios  $\frac{[BrO]}{[Br]}$  and  $\frac{[BrO]}{[HOBr]}$  here given, and unlike results presented by Neuman et al. (2010), in the probed ozone-depleted air masses most of the bromine is contained

190

in the reactive form of BrO.

Observations and model studies suggest that the majority of the ozone (~90%) is depleted within the first 5 days of the ODE, with the maximum ozone loss rates of 2.4 ppb/h to 7.6 ppb/day occurring at the begining and at the end of the event (e.g., *Platt*, 1997; *Lehrer et al.*, 2004; *Piot and von Glasow*, 2008). The above estimated ozone loss rates agree with the models, and suggest that the measuremets are gathered in two different airmasses with the ODE initiated between 2 and 4.5 days prior the measurement. However, the above calculations neglect additional processes that may contribute to the activation and/or loss of BrO<sub>x</sub> and O<sub>3</sub> (refer to Sect. 4.4.1). Moreover, the in situ measured sudden increase of O<sub>3</sub> vmr, together with the differences in the lifetimes and ozone loss rates given (22–9 ppbv/day) may result from, e.g., lead-related turbulences that could allow ozone from the free troposphere to enter the BrO enriched boundary layer and, thus, prolonging the lifetime of BrO (e.g. *Piot and von Glasow*, 2008). Therefore, these studies may only provide an order of magnitude for the lifetime of BrO and Br in the presence of very low O<sub>3</sub>. Additional measurements of e.g. Br<sub>2</sub>, HOBr, and aerosol composition would have been very useful for assesing further photochemical and transport studies.

Data here presented indicate that, from a given source (e.g., brine aerosols),  $BrO_x$  may be activated and sustained in an ozone depleted airmass through heterogeneous reactions, photolysis and self reactions (if enough  $O_3$ ), and also through filaments of free tropospheric ozone entering the BrO enriched boundary layer. Therefore, over a sea ice region with several potential bromine sources such as brine, frost flowers, halide snow, ocean in the open leads, young ice within the leads or first year sea ice, plumes of high BrO may travel long distances supported also by weather patterns and sea ice micrometeorology. Once a BrO plume leaves the sea ice region, it may still be fed by e.g. sea salt bromide. Eventually reactive bromine may transform into reservoirs, and be transported with the aerosol particles. The possibility of those bromine enriched aerosols to reach lower latitudes may be higher just after the polar sunrise, when the polar dome disappears and airmass displacements are stronger.

### Chapter 10

### Conclusion

The present work reports on recent developments of aircraft-borne DOAS (Differential Optical Absorption Spectroscopy) UV/vis measurements of scattered skylight performed in limb viewing geometry. The data discussed here were obtained with the UV channel of a lightweight mini-DOAS instrument during its first deployments on the DLR-Falcon aircraft. Research flights were conducted around Svalbard and Greenland during the spring 2007 and summer 2008, respectively. The ultimate goals of those deployments were to investigate the performance of the mini-DOAS instrument, and to prove the capabilities of the limb geometry measurement technique. Both objectives were herein achieved by characterizing the vertical and horizontal distribution of a weak absorber such as bromine monoxide in the springtime Arctic troposphere.

#### Instrument performance

Overall, the mini-DOAS instrument demonstrated a good performance throughout the campaigns, with optically stable spectrometers and good signal-to-noise ratio  $(N/S = 10^{-4}/10^{-3}$  for the UV/vis channels at 80% saturation).

This work focuses on measurements performed with the UV spectrometer. Studies established the instrumental detection limit for BrO vmr at 0.6 ppt in the lower stratosphere, at 0.9 ppt in the free troposphere, and at 3.2 ppt in the boundary layer. Additionally, instrumental detection limits for boundary layer HNO<sub>2</sub> and CH<sub>2</sub>O vmr were estimated at 0.2 ppb and 5 ppb, respectively, and at 0.5 ppt for OCIO in the lower stratosphere (10 km).

For the instrument operated in fix-mode viewing geometry with the telescopes possitoned parallel to the ground, the measurements showed to be highly sensitive toward the detection of absorbers located at the same atmospheric layer as the instrument. In this work vertical profiles concentrations of BrO were inferred from measurements gathered during the aircraft ascent/descent, while a horizontal cross-section of the bromine monoxide abundance in the boundary layer could be derived from measurements performed during a steady horizontal aircraft passage.

#### Vertical profile retrieval of tropospheric BrO

As a consequence of the spatial and temporal variability of the cloud and aerosol particles and of the ground albedo, the main challenge in the interpretation of the collected optical data during the Arctic campaigns arose with the retrieval of BrO vmr vertical profiles due to complex radiative transfer situation at the time of the measurements.

Here, a two-step process for the vertical profile retrieval of trace gases from the aircraft-borne measurements of scattered skylight in limb viewing geometry was proposed. First, an effective vertical profile of the aerosol extinction coefficient was inferred from measured Sun normalized radiances. This retrieved aerosol profile was then included as an input parameter in the forward radiative transfer model, which is needed for the mathematical inversion of the trace gas vertical profile concentration. To overcome the lack of a priori knowledge of the targeted trace gas, a regularization approach was suggested for its mathematical inversion. The consistency and limitations of the retrieval algorithm were tested with an absorber of known tropospheric profile  $O_4$  (e.g., *Pfeilsticker et al.*, 2001).

The retrieval method was then applied for inferring vertical profiles of tropospheric BrO during the polar spring of 2007. Typically, the retrieved profiles from the boundary layer up to the lowermost stratosphere showed 10 degrees of freedom. Sensitivity studies indicated that the error of the inferred BrO vertical profiles was dominated by the forward modeling error in the boundary layer (due to radiative transfer uncertainties), and by the instrumental detection limit at higher altitudes. The BrO vmr detection limit was established at 1.5 ppt (averaged in altitude). The retrieved BrO profiles exhibited 1 km vertical resolution, with an altitude dependent horizontal sensitivity of 10–40 km.

#### BrO in the Arctic troposphere

• Vertical distribution

The inferred BrO profiles generally showed large and heterogeneous mixing ratios within the BL (8–30 ppt), small mixing ratios within the free troposphere ( $\leq 1.5$  ppt), and variable mixing ratios (1–4 ppt) in the upper troposphere and lowermost stratosphere, increasing with height. The latter two findings could be explained by the known atmospheric photochemistry of bromine and by the transport of stratospheric air masses into tropospheric altitudes (as seen by simultaneous O<sub>3</sub> and CO measurements). On the other hand, the former finding pointed to halogen activation within air masses of so-called ozone depletion events (ODE), linked to salt halides aerosols (e.g., Br<sup>-</sup>) resulting from the sea ice formation. The estimated ozone loss varies from 1 ppbv/day in the entrainment zone of the boundary layer, to an average ozone loss of 15 ppbv/day in the first 100 m of the boundary layer. The inferred total column amounts of tropospheric BrO were inter-compared with collocated GOME-2/MetOp-A satellite measurements. The comparison showed reasonably good agreement within the given errors of both methods, thus providing confidence that neither the airborne profile measurements nor the satellite ones were systematically biased.

• Horizontal distribution

The capabilities of the mini-DOAS observations were further exploited by characterizing thea bundance of BrO in the polar marine boundary layer. A horizontal aircraft passage 60–100 m above the sea ice was chosen for this purpose.

The inferred BrO abundances for that passage ranged between 4–15 ppt, values in agreement with former measurements in ozone depletion situation (*Hausmann and Platt*, 1994). Results were inter-compared with BrO column densities inferred from collocated GOME-2/MetOp-A satellite measurements. The comparison showed reasonably good agreement within the given errors of both methods, and indicated a strong enhancement of BrO in the measurement region and neighboring area.

The inferred BrO vmr from the aircraft-borne measurements were further analyzed toward  $O_3$  vmr, CO vmr, aerosol surface area concentration, meteorological data and sea ice properties. Profiting from this multi instrumental approach, results on the bromine-related ozone depletion event in the passage indicated ozone depleted air masses up to 1.2–2.5 km of altitude. In addition, over 100 km, the BrO vmr increased while  $O_3$  was below (or close to) instrumental detection limit (3 ppb). The measured BrO vmr gradient was related to two different air masses, with possible heterogeneous activation of bromine in the proximity of sea ice leads, turbulences and transport processes above the sea ice, and oxidation of bromine with remaining  $O_3$  over a wide area.

Estimations neglecting micrometeorological conditions above the sea ice, and accounting for BrO photolysis, self and HO<sub>2</sub>-reaction, as well as HOBr uptake into aerosol particles, yielded a BrO lifetime toward self-reaction in the order of 50–70 min (depending on the probed air mass), and an ozone loss rate of 22–9 ppbv/day, in agreement with chemical and transport models (e.g., *Platt*, 1997; *Lehrer et al.*, 2004; *Piot and von Glasow*, 2008). Moreover, studies indicated that most of the bromine atoms within the the probed ozonedepleted air masses were contained as bromine monoxide.

#### Outlook

Although the UV spectrometer exhibited a good signal-to-noise ratio, the detection limit of weak absorbers was governed by the Ring effect in the DOAS retrieval. The sensitivity toward relevant trace gases such as BrO, OCIO or IO may be improved by an accurate modeling of the Ring cross-section.

In the case of an aircraft-deployment, the combination of the high speed of the measurement platform and the time required for each measurement (i.e., integration time per spectrum × number of co-added spectra), resulted in a complex combination of viewing geometries intrinsic to each measurement. This not only complicated the radiative transfer modeling needed for the retrieval of trace gas concentrations, but also may have caused loss of information contained in the measurements. Therefore, the option of measuring independent spectrum (not co-added) should be implemented. In addition, with the DOASIS software used in this work for the measurement routine, the two stepper-motors (directed by a single controller), failed to operate simultaneously. Recently the independent spectrum and the stepper-motor issues have been solved by implementing the MS-DOAS software from U. Frieß.

Based on the experience gained during the ASTAR 2007 campaign and in order to facilitate and complement the radiative transfer studies, a web cam (with known viewing direction related to the telescopes) is strongly suggested. This was already accounted for during the mini-DOAS deployment on the Geophysica 2010 campaign. Accordingly, the design of the mini-DOAS version for the novel HALO aircraft already includes an integrated camera.

For future airborne deployments, additional ground base and/or ship base measurements would be very useful for assessing possible local sources and sinks of the targeted trace gas to retrieve, as well as for the synoptic characterization of the surface layer (relevant in the case of e.g. low altitude flights). Moreover, for long and steady horizontal aircraft passages with the mini-DOAS instrument operating in limb scanning mode, the combination of radiative transfer analysis with a time dependent vertical profile retrieval of the targeted trace gas (e.g., *Kritten et al.*, 2010) could provide interesting insight in e.g. the activation of chlorine species in the polar vortex, and the characterization of stratosphere-troposphere exchanges in the tropopause folds. Also photochemical and transport models would improve the understanding of the gathered data.

Results presented herein showed the potential of a multi instrumental approach toward the atmospheric research. Future deployments should accordingly profit of merging optical and chemical measurements of different substances, and of combining in situ and remote sensing techniques aboard the same aircraft. However, since the in situ measurements capture the local atmospheric conditions (chemistry, aerosol and transport processes), and the mini-DOAS instrument averages information of an atmospheric region extending several kilometers away from the aircraft (10–40 km in this work), the interpretation of the whole data set should be handle with care. The synergy of in situ and remote sensing techniques may be exploited by measuring the same trace gas (e.g.,  $O_3$  from UV absorption and mini-DOAS), and also by measuring chemically related trace gases (e.g.,  $Br_2$  from a chemical ionization mass spectrometer, and BrO from DOAS instrument).

The BrO satellite inter-comparison exercises performed in this work showed the relevance of properly accounting for not only the ground albedo, but also the dynamic processes that may alter the definition of the tropopause and of the top of the boundary layer. A miscalculation of both boundaries in the retrieval of BrO stratospheric and tropospheric column densities, may result on an overestimation or underestimation of e.g. the BrO abundance in the free troposphere. In this work the analysis of the  $O_3$ -CO correlation assisted for that definition.

Regarding the bromine-related ODEs in the polar spring, the impact that the recent switch of the Arctic sea ice type from multiyear to first-year sea ice may have on the atmospheric chemistry is uncertain. Further field campaigns would assist for a better understanding of the possible effects by addressing, e.g., the snow, sea ice and aerosol bromine recycling processes (including the evolution of their bromide partitioning in the winter season), the surface layer fluxes of trace gases (e.g.  $Br_2$ , BrCl, HONO), the investigation of the photochemistry and radiative transfer within the snow, and the chemical composition of aerosols (HOBr, sulfate-depleted aerosols).

Future applications of the aircraft-borne limb technique are wide-spread, such as measurements of atmospheric halogen radical profiles (BrO, IO, OClO, ...) above oceanic waters of large biological activity (e.g., along the shores of large tides, the tropical Atlantic, the tropical Eastern and Western Pacific), in polar regions, within plumes of volcanic emissions, over salt lakes, or even in the free troposphere and lowermost stratosphere. Other applications of the technique may focus on studies where other gases, also accessible with UV/vis/near-IR DOAS technique ( $O_3$ ,  $NO_2$ , HONO,  $CH_2O$ ,  $C_2H_2O_2$ , all three phases of water, etc.), are important. Such investigations are planned within future deployments of the novel research aircraft DLR-HALO. In addition, the retrieval of aerosol and cloud particle optical properties simultaneously measured - such as the extinction coefficient profile - can not only improve the accuracy of the key trace gas retrievals, but also represents a research field with great potential for, e.g., radiative forcing and climate feedback investigations.

CHAPTER 10. CONCLUSION

## Publications

Parts of this work have been published in:

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Contributions have been made to the following articles:

- Butz, A., Bsch, H., Camy-Peyret, C., Chipperfield, M. P., Dorf, M., Kreycy, S., Kritten, L., Prados-Roman, C., Schwärzle, J., and Pfeilsticker, K.: Constraints on inorganic gaseous iodine in the tropical upper troposphere and stratosphere inferred from balloon-borne solar occultation observations, *Atmos. Chem. Phys.*, 9, 7229-7242, doi:10.5194/acp-9-7229-2009, 2009.
- Kritten, L. and Butz, A. and Dorf, M. and Deutschmann, T. and Kühl, S. and Prados-Roman, C. and Pukīte, J. and Rozanov, A. and Schofield, R. and Pfeilsticker, K.: Time dependent profile retrieval of UV/vis absorbing radicals from balloon-borne limb measurements a case study on NO<sub>2</sub> and O<sub>3</sub>, *Atmos. Meas. Tech.*, **3**, 933-946, doi:10.5194/amt-3-933-2010, 2010.

CHAPTER 10. CONCLUSION

# List of Figures

2.1	Quantized transitions within a diatomic molecule	7
2.2	Radiometric quantities	3
2.3	Fraunhofer lines	)
2.4	Solar flux spectrum centered at 500 nm	)
2.5	Earth-atmosphere global radiation and energy balance	)
2.6	Terrestrial radiation spectrum	
2.7	Energy level diagram for scattering processes 12	)
2.8	Rayleigh phase function for unpolarized light 14	F
2.9	Mie phase	;
2.10	Energy diagram for absorption and emission processes	7
3.1	Vertical structure of the Earth's atmosphere	2
3.2	Aurora australis	3
3.3	Poleward atmospheric energy transports	ý
3.4	Tropospheric circulation	;
3.5	Horizontal transport times	7
3.6	Atmospheric circulation	7
3.7	Quasi-Biennial Oscillation	3
3.8	Vertical transport times	3
3.9	Dynamical stratosphere-troposphere exchange	L
3.10	Tropopause fold	2
3.11	The "chemopause" concept 33	3
4.1	Atmospheric lifetimes	;
4.2	Solar actinic flux (UV) vs. altitude	3
4.3	Stratospheric $O_x$ loss	)
4.4	$O_3$ during the polar sunrise $\ldots \ldots \ldots$	)
4.5	Correlation OH vs $O_3$ 43	3
4.6	Diurnal variation of NO <sub>2</sub> , NO, and reservoirs $\ldots \ldots \ldots$	;

4.7	Tropospheric production rate of $O_3 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 47$
4.8	RHS 49
4.9	Halocarbons as greenhouse gases
4.10	The bubble-burst mechanism
4.11	Chlorine activation
4.12	MBL IO and BrO
4.13	Scheme of gas an aqueous phase halogen reactions
4.14	VSLS 61
4.15	SGs of Cl and Br in the stratosphere
4.16	Halogen species in the stratosphere
4.17	Evolution of chlorine and bromine
4.18	$\operatorname{Br}_y$ diurnal cycle
4.19	Aerosol modes
4.20	Uptake of HCl and $N_2O_5$ on aerosol particles $\ldots \ldots \ldots$
5.1	Definition of the Arctic
5.2	The Arctic Ocean
5.3	Brine and sea ice
5.4	Salt content in brine
5.5	Sea ice properties
5.6	Pathways of the sea ice formation
5.7	Lead with young sea ice
5.8	Satellite retrieval of sea ice properties
5.9	Air chemistry in the Canadian arctic
5.10	Pollution into the Arctic
5.11	PSCs, chlorines species in the Arctic vortex
5.12	Monthly mean total ozone columns over the poles
5.13	Stratospheric ozone hole: Arctic vs. Antarctic
5.14	First report of bromine correlation with Ozone Deplation Events
5.15	Simplified scheme of the bromine explosions
5.16	Bromine and mercury in the polar regions
5.17	Ionic concentration of snow on top of sea ice
5.18	Daily evolution of $O_3$ , $Br_2$ and $BrCl$ above snow $\ldots \ldots $ 92
5.19	Modeled evolution of halogen species vs. ozone concentration
5.20	The Arctic amplification
5.21	Arctic sea ice extent
5.22	Arctic sea ice extent minimum
5.23	Sea ice trend of the Arctic Ocean in winter (2004–2008)

6.1	DOAS principle
6.2	BrO absorption cross-section
6.3	Temperature dependence of the BrO absorption cross-section
6.4	Experimental DOAS measurement setups
6.5	Balloon-borne mini-DOAS viewing geometry
7.1	Sketch of the mini-DOAS housing
7.2	The mini-DOAS instrument on board the Falcon aircraft
7.3	1 April 2007 sortie
7.4	8 April 2007 sortie
7.5	15 July 2008 sortie
8.1	UV spectra of the absorption cross-sections used in this work
8.2	Absorption cross-sections for the BrO spectral retrieval
8.3	BrO DOAS evaluation
8.4	BrO spectral retrieval and the Ring effect
8.5	BrO dSCDs vs Temperature
8.6	OCIO DOAS evaluation
8.7	$O_4$ DOAS evaluation
8.8	Retrieval method in a two-step process
8.9	Measurement flight on 8 April 2007
8.10	Scattering events affecting the RT in aircraft-borne measurements
8.11	Influence of forward parameters in the RT model
8.12	Vertical profile of coarse mode aerosol number densities
8.13	Vertical profiles of remotely and in situ measured aerosol $\mathcal{E}_{\mathcal{M}}$
8.14	Sun normalized radiances and asymmetry parameter
8.15	L-curve for $O_4$
8.16	Retrieval of the $O_4$ vertical distribution $\ldots \ldots \ldots$
9.1	Retrieval of the BrO vertical profile
9.2	Concept of the horizontal sensitivity of a measurement
9.3	Horizontal sensing distance
9.4	Scattering events vs. detector altitude
9.5	Ground scattering events
9.6	Aircraft-borne measurements of $O_3$ , CO and BrO
9.7	BrO VCD inferred by the BIRA-IASB team
9.8	Flight profile, temperature and wind speed
9.9	Chemopause on the 8 April 2007 sortie
9.10	BrO in the chemopause on 8 April 2007 172

9.11	BrO and the tropopause inversion layer
9.12	O <sub>3</sub> -CO space in the polar BL $\ldots$
9.13	Boundary layer meteorology
9.14	Horizontal passage
9.15	Backward trajectory $A$
9.16	Backward trajectories $E$
9.17	Summary of vmr measured in the horizontal passage
9.18	Role of the aerosol particles in the BrO-O <sub>3</sub> ratio. $\ldots$ $\ldots$ $\ldots$ $\ldots$ $184$
9.19	Boundary layer BrO VCD satellite comparison
9.20	Lead with young ice underneath the Falcon aircraft
9.21	AMSR-E satellite images for 8 April 2007
9.22	BrO and sea ice properties
9.23	Cross-section of the sea ice boundary layer
9.24	Photochemistry of an ODE over the sea ice

## List of Tables

2.1	Electromagnetic spectrum and associated phenomena
4.1	Halocarbons atmospheric lifetime and mixing ratios
4.2	Sea water ionic composition
4.3	Tropospheric aerosol particles
5.1	Composition of frozen sea water
5.2	Brine composition
5.3	Salinity of new ice
5.4	ODEs-related reaction rates
6.1	RTM vertical grid
7.1	Technical details of the mini-DOAS spectrometers
7.2	Noise contribution for the UV/vis channels of the mini-DOAS instrument $\ldots$ 117
7.3	ASTAR 2007 campaign, Falcon deployment
7.4	Overview of the mini-DOAS deployments during ASTAR 2007
7.5	GRACE 2008 campaign, Falcon deployment
7.6	Overview of the mini-DOAS deployments during GRACE 2008
8.1	List of trace gases considered for the DOAS retrieval
9.1	BrO VCD: airborne and satellite comparison
9.2	Mean values of trace gases above the sea ice

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