Remote sensing of tropospheric methane and isotopes of atmospheric carbon dioxide using Fourier Transform Spectrometry

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Abstract

Due to the warming effect of atmospheric trace gases, such as CH$_4$ and CO$_2$, it is important to monitor their variations and understand their sources and sinks. While an increasing trend in atmospheric concentrations of CH$_4$ and CO$_2$ is confirmed by many measurements, the sources and sinks are not completely understood. As one of the methods determining sinks and sources of traces gases, inverse modeling, its accuracy depends on assimilated observation and the simulation ability of atmospheric motion. For CH$_4$ measurements, a method has been developed to determine tropospheric column-averaged mole fractions of CH$_4$ from total columns of CH$_4$ and N$_2$O measured by solar absorption Fourier transform spectrometer (FTS). The motivation of this work is that tropospheric CH$_4$ is more directly related to its sources and sinks compared to the total columns, which contain variabilities of stratospheric CH$_4$ mostly originating from dynamic processes. Another reason is that the chemical transport model, in its current state, represents the troposphere better than the stratosphere.

The method is applied to most of the FTS sites within the Total Carbon Column Observing Network. The measured tropospheric and stratospheric column-average CH$_4$ are used to assess performances of three European CH$_4$ models in the troposphere and stratosphere separately. In addition, the isentropic mixing processes and evolutions of the polar vortex in the models are evaluated using equivalent length. It is found the southern surf zone is not developed to a real extent. Together with the southern surf zone, a region with both vertically and horizontally uniform CH$_4$ occur between 450 and 850 K (~18 and 30 km) in surf zone latitudes, which is absent in the models. The modeled polar vortex breaks too fast compared to the measurements.

Measuring different isotopes of one species is another approach to improve knowledge on the sources and sinks of traces gases. This is explored for CO$_2$ using ground-based solar FTS spectra, specifically the ratio $^{13}$C/$^{12}$C in atmospheric CO$_2$. Retrieval from the FTS spectra is almost entirely determined by assumed molecular spectroscopy. The existing databases can not fulfill requirements for CO$_2$ isotopes retrieval. An algorithm that inverts molecular spectroscopy from the ground-based spectra is developed. This algorithm is applied to H$_2$O, CO$_2$ and solar lines indicating its feasibility. While the inverted spectroscopy improves the accuracy of the column and profile retrieval of CO$_2$ and H$_2$O, the retrieved ratio $^{13}$C/$^{12}$C is still beyond the required accuracy at a FTS site Bialystok.
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1. Introduction

1.1 Sources and sinks of atmospheric CH$_4$

CH$_4$ is the second most important anthropogenic greenhouse gas in the atmosphere and one of the concerns of this thesis. CH$_4$ is produced in several processes, including both natural and anthropogenic processes. The geographic distribution and strength of each source differ from the others, and could change with time depending on human activities (e.g. industry, agriculture) or climate conditions (e.g. temperature, humidity and flood). They are showed in Fig. 1.1 and described in the following.

**Natural wetlands:** Natural wetlands are the largest natural sources of CH$_4$. According to oxygen condition wetland ecosystems can be classified into an aerobic zone and an anaerobic zone below it. Organic carbon in the soil is broken down to simple substrates through microbial processes at first. Then the end products of these preparing steps are used by methanogen communities to produce CH$_4$ in the anaerobic zone. There are three paths, named diffusion, ebullition and plant-mediated transport for CH$_4$ produced in the anaerobic zone to leave into the atmosphere. There usually exists a gradient of CH$_4$ concentration from the anaerobic zone to the soil surface, which can result in an upward diffusion of CH$_4$. The diffusion path passes the aerobic zone where a lot of CH$_4$ is consumed by methanotrophic communities. In the ebullition process CH$_4$ is taken out of the wetland in the form of gas bubbles, which avoids the oxidation of CH$_4$ in the aerobic zone. The transport of CH$_4$ from the wetland to the atmosphere by the ventilation system of plants bypasses the aerobic zone as well. Among the three paths the diffusion contributes least to the CH$_4$ emission from wetlands.

The estimated wetland CH$_4$ emissions range from 80 to 280 Tg CH$_4$ yr$^{-1}$, have a median value of 164 Tg CH$_4$ yr$^{-1}$ (Bridgham et al., 2013). The global area of wetlands ranges from 7.1 to 26.9 × 10$^6$ km$^2$ for model simulations, and from 4.3 to 12.9 × 10$^6$ km$^2$ for observations (Melton et. al., 2013). The zonal sum of wetlands area simulated by models peaks in the tropics and around 60°N. For zonally summed CH$_4$ emissions, both models and observations reveal two peaks in the tropics and around 60°N as well, and the former is much larger (Spahni et. al., 2011; Melton et. al., 2013). The strong emissions of CH$_4$ in the tropics are mainly attributed to South American, and the one around 60°N to northern peatlands. The CH$_4$ emissions from wetlands depend on ecosystem hydrology, soil and vegetation characteristics, and they are believed to be sensitive to climate conditions. For example, it is stated that wetland emissions dominated the substantial interannual variability of CH$_4$ sources between 1984 and 2003 (Bousquet et. al., 2006). In a model study, a large fraction of the global and tropical variability in wetland CH$_4$ emissions can be attributed to El Niño/Southern Oscillation (ENSO) between 1950 and 2005.

**Fresh water:** Fresh waters include lakes, rivers and reservoirs, and have similar CH$_4$ production mechanisms and emission pathways except for reservoirs, for which there are additional pathways (downstream dam emissions). The estimated CH$_4$ emission from fresh water is about 93 Tg CH$_4$ yr$^{-1}$
resulted by ebullition and diffusive flux. Among these fluxes lakes, reservoirs and rivers contribute about 71.6, 20.0 and 1.5 Tg CH$_4$ yr$^{-1}$, respectively (Bastviken et al., 2011). In addition, there is about 10 Tg CH$_4$ yr$^{-1}$ flux from plant-mediated transport.

**Biomass burning:** The fires of savanna, woodland, deforestation, forest, agriculture and peat release the chemical compounds of burning vegetation. Most of the emissions contain carbon in the form of CO$_2$ and CO (about 90%). The rest of the carbon is emitted in the form of CH$_4$, other gases, and smoke particles. These chemical gases and particles have import influence on tropospheric chemistry and climate. The strength of emissions depends on area burnt, potentially burnable vegetation, emission factor and burning efficiency. The emission factor relates the emission of a particular species to the amount of fuel burned, and depends on the type of biomass burning and species. For CH$_4$ the emission factor is largest for peat fires, agriculture waste burning and tropical forest fires (Werf et al., 2010; Andreae and Merlet, 2001). Burning efficiency describes the combusted fraction of burnable vegetation, and depends on the type of ecosystem and season. Fire carbon emissions are about 2000 Tg C yr$^{-1}$, in which grasslands, savannas and woodlands contribute 60%. The geographic distribution of carbon emission has maxima in Africa where savannas dominate, the northern part of South America and Equatorial Asia where deforestations dominate (Werf et al., 2010). The CH$_4$ emissions mainly come from Africa (36%), Southeast and Equatorial Asia (32%), Tropical America (16%) and Boreal (10%). The total emissions of CH$_4$ are estimated to be 11-53 Tg CH$_4$ yr$^{-1}$ (Crutzen and Andreae, 1990).

**Termites:** The emissions of CH$_4$ from termites is a balance between the production in the colony of termites and oxidation by bacteria during emission into the atmosphere. The estimated amount of CH$_4$ emissions are 1.5-7.4 Tg CH$_4$ yr$^{-1}$ (Sugimoto and Inoue, 1998).

**Geological:** Geological sources of CH$_4$ include emissions from ocean and lithosphere. The ocean contributes about 0.6-1.2 Tg CH$_4$ yr$^{-1}$ (Rhee et al., 2009). The CH$_4$ in the lithosphere is produced through several processes, microbial CH$_4$ production, thermogenic CH$_4$ production and gas hydrates. After the production, they can bypass the water column in the ocean in the form of bubbles and enter the atmosphere, dissolve in ocean, or be released into the atmosphere by volcanoes. The amount of CH$_4$ entering the atmosphere produced in the lithosphere is 42-64 Tg CH$_4$ yr$^{-1}$ (Etiope et al., 2008).

**Agriculture and waste:** The agriculture sources of CH$_4$ include enteric fermentation, rice cultivation, manure management and agriculture soils. The waste sources of CH$_4$ include landfilling of solid waste, wastewater and some other processes. The emissions by these CH$_4$ sources are 187-224 Tg CH$_4$ yr$^{-1}$ (Kirschke et al., 2013).

**Fossil fuels:** This category relates to the energy need of humankind. It includes natural gas and oil system, coal mining activities, stationary and mobile combination and other processes. The strength is 85-105 Tg CH$_4$ yr$^{-1}$ (Kirschke et al., 2013).

Atmospheric CH$_4$ is destructed in the troposphere by oxidation with OH, which constructs the sinks of atmospheric CH$_4$ together with loss to the stratosphere, soils and tropospheric Cl. These
processes are described in the following.

**Tropospheric OH:** Atmospheric OH radical is produced by two steps, the production of O(\(^1\)D) (the O atom in an excited singlet state) through photolysis of O\(_3\) by ultraviolet solar radiation, the produced O(\(^1\)D) reacts with H\(_2\)O molecule and produces OH. The concentration of OH depends on the strength of ultraviolet radiation, the concentration of O\(_3\) and H\(_2\)O. CH\(_4\) reacts with OH in the manner:

\[
CH_4 + OH (+O_2) \rightarrow CH_3O_2 + H_2O. \tag{1.1}
\]

There are several reactions following (1.1), and final products are CO\(_2\), H\(_2\)O, O\(_3\), OH and HO\(_2\). There is plenty of ultraviolet radiation in the stratosphere, and much of ultraviolet radiation is absorbed by stratospheric O\(_3\). On the other hand, almost all of atmospheric H\(_2\)O stay in the troposphere. The global averaged vertical distribution of OH peaks in the range of 500-700 hPa, with an order of 10\(^6\) molecules cm\(^{-3}\). The latitude distribution of OH presents a maximum between 30\(^\circ\)S and 30\(^\circ\)N, which changes following the seasonal shift of maximum solar radiation. The maximum of OH concentration in lower tropical troposphere results from high H\(_2\)O concentration, strong solar radiation and low O\(_3\) column overhead there. The amount of CH\(_4\) consumed by tropospheric OH is 430-587 Tg CH\(_4\) yr\(^{-1}\) from models study (Naik et. al., 2013).

Figure 1.1. Sources and sinks of atmospheric CH\(_4\) with errorbar indicating spread of the reported values. There are not uncertainties given for the fresh water and Cl in marine BL because their measurements are rare.
Stratospheric consumption: CH₄ can be transported up to the stratosphere and consumed by OH, Cl atoms and O(1D). The reaction of CH₄ with OH is an important source of stratospheric H₂O. The stratospheric sink of CH₄ is commonly assumed to be about 40 Tg CH₄ yr⁻¹.

Soil: Except for chemical destruction of CH₄ in the atmosphere, soil can uptake CH₄ as well. Uptake of CH₄ in soil occurs via oxidation by specialized aerobic bacteria. The magnitude of soil sink derived from model is about 28 Tg CH₄ yr⁻¹ (Curry, 2007), and 22-44 Tg CH₄ yr⁻¹ from measurements (Dutaur and Verchot, 2007).

Cl in the marine boundary layer: According to the model simulation (Allan et. al., 2007) Cl atoms in the marine boundary have a concentration of 18 × 10³ atoms cm⁻³, and oxidize 25 (range 13-37) Tg CH₄ yr⁻¹.

1.2 Atmospheric properties and CH₄ transport

The earth-atmosphere system receives its energy from solar radiation. The atmosphere is a thin layer of gas constrained to earth surface by gravity. The spectrum of solar radiation can be described well by a flux distribution function for a blackbody with a temperature of 5800 K. Solar radiation distributes mainly between 0.2 and 3 μm and has maximum at about 0.5 μm. Part of this incoming radiation is reflected back to space by the earth's surface and atmosphere, and the residual is absorbed and reemitted by the earth-atmosphere system.

The atmosphere is mainly composed of N₂, O₂ and Ar, these three gases contribute 99.93% totally in dry air (Jacob, 1999, p. 2). Besides these gases the atmosphere contains trace gases, e.g. CO₂, Ne, O₃, He, CH₄, Kr, H₂, N₂O, H₂O, CO, hydrocarbons and chlorofluorocarbons (CFCs). A molecule absorbs or emits radiation through changing its internal state, which includes electronic, vibrational and rotational states. The state of a molecule is quantized and therefore its absorption or emission is selective. The energy associated with the change in molecular states decreases for electronic, vibrational and rotational states sequentially. They correspond to ultraviolet, near-infrared and far-infrared regions respectively. The change in the molecular state can occur independently for each type or in a combination of them. The symmetries of N₂, O₂, and Ar molecules forbid a radiation-induced change in their vibrational and rotational states (Goody and Yung, 1989, p. 74). As a result, there is no absorption in the near-infrared region from them. In the ultraviolet region O₂ has important absorption, as well as O₃. All the minor constituents of the atmosphere absorb in the near-infrared region and H₂O dominates the absorption in the far-infrared region (Goody and Yung, 1989, p. 68).

The capture of the energy associated with solar radiation is accomplished through interaction between the earth surface and the atmosphere. About 46% of incoming solar radiation is absorbed directly by the earth surface and 19% by the gases O₃, H₂O, O₂, and CO₂ (Mitchell, 1989). If the earth-atmosphere system is taken as a blackbody then such amount of input energy flux will give an effective emission temperature of 255 K (the effective emission temperature is a temperature under
which the Stefan-Boltzmann law predicts an amount of emission radiation same as absorbed one). This low-temperature earth-atmosphere system emits radiation having wavelengths longer than 4 \( \mu \text{m} \). In a stable earth-atmosphere system, the incoming solar radiation is balanced by the sum of reflected solar radiation and thermal radiation from the earth-atmosphere system at the top of the atmosphere. The effective emission temperature of the earth-atmosphere system is much lower than observed temperature at the earth surface. The earth surface absorbs solar radiation and then emits thermal radiation. The minor constituents of the atmosphere, \( \text{H}_2\text{O}, \text{CO}_2, \text{O}_3, \text{N}_2\text{O}, \text{CH}_4 \) and CFCs, have significant absorption in the infrared region. A fraction of the thermal radiation from the earth surface is absorbed by these minor constituents. The atmosphere emits thermal radiation up to space and down to the earth surface. The earth surface is nearly a blackbody in the infrared region, and absorbs almost all of the downward radiation from the atmosphere. As a result, the earth surface receive more radiation than directly absorbed solar radiation and has a higher temperature than the effective emission temperature of 255 K. This effect of the atmosphere is known as the greenhouse effect. The atmospheric gases that contribute to this effect are called greenhouse gases (GHGs). Different gases have different strength for the greenhouse effect. The strength is determined by the absorption wavelengths, the strength of the absorption line, the concentrations and absorption efficiency of other gases in the same wavelengths. In the current state of the atmosphere, important GHGs are \( \text{H}_2\text{O}, \text{CO}_2, \text{CH}_4, \text{N}_2\text{O}, \text{O}_3 \) and CFCs, their contributions decreases in turn (Mitchell, 1989). The increases in the concentrations of GHGs will warm the earth surface, therefore there is much concern about the increasing GHGs in the atmosphere.

The atmosphere is adhered to the earth surface by gravity. In vertical direction the atmospheric density decreases exponentially, and about 99.9% of its mass locates below 50 km (comparing to the earth radius of 6371 km). According to the thermal structure of the atmosphere in vertical direction, the atmosphere is usually classified into four layers, troposphere, stratosphere, mesosphere and thermosphere (Fleagle and Businger, 1980, p. 79-84). The troposphere extends from the surface to 8-18 km depending on latitude and season. About 80% of the atmospheric mass is located in the troposphere. Temperature decreases with altitude in this layer at a typical rate of 6.5 K/km. The atmosphere is statically unstable in most cases in the troposphere, and convection occurs to adjust the vertical distribution of its temperature. The stratosphere extends from the top of the troposphere to about 50 km. Atmospheric temperature increases in the stratosphere, and the atmosphere is statically stable. Consequently, the atmospheric motions are mainly in horizontal direction in the stratosphere. In the mesosphere from 50 km to about 85 km, the temperature decreases with altitude similar to the troposphere. Above the mesosphere is the thermosphere, and the temperature increases until about 250 km and then becomes almost constant with altitude. The constant temperature has large variability from 1000 to 2000 K, which is related to solar activities.

The thermal structure of the atmosphere as described above can be understood approximately in term of radiative equilibrium and radiative-convective models (Goody and Yung, 1989, p. 388-420). In the radiative equilibrium model it is assumed that solar heating rates are equal to the thermal cooling rate at each height level. Solar radiation downward to the atmosphere is equal to thermal
radiation upward to space at the top of the atmosphere. At the earth surface the sum of solar and thermal radiation downward to ground is equal to that upward through the atmosphere. Assuming the absorption of solar radiation by the atmosphere is homogeneous, atmospheric temperature calculated based on the assumption of radiative equilibrium decreases monotonically with altitude. If taking the absorption of solar radiation by atmospheric gases into account, which varies with altitude, the calculated atmospheric temperature increases above 10 km for an average condition at 40°N. This feature corresponds to the vertical distribution of temperature in the troposphere and the stratosphere. Another difference from accounting for the gas's absorption is that the temperature decreases faster with height near to ground. When dividing absorption and emission of solar and thermal radiation into contributions from various gases, it shows that the increase of atmospheric temperature in the stratosphere is caused by absorbing solar radiation by O₃. In the troposphere, especially lower troposphere, the absorption of solar radiation by H₂O heats atmosphere as well. The heating of O₃ and H₂O is balanced by thermal cooling of H₂O and CO₂. The lapse rate of the temperature from the radiative equilibrium model is too large in the troposphere to be statically stable. Convection must develop to adjust the vertical distribution of tropospheric temperature until the atmosphere is statically stable. In a simple radiative-convective model, the upward heat flux can be related to the difference of the lapse rate given by radiative equilibrium and a prescribed neutral lapse rate (It is 6.5 K/km based on observation).

CH₄ is emitted at the earth surface and mixed upward into the atmospheric boundary layer (It usually extends from ground to 1-2 Km) through turbulence in 1 day, or several hours under condition with strong convection driven by solar heating at ground. The transport of CH₄ into middle and upper troposphere is accomplished by convective motions caused by the instability in the troposphere. The convective motion is stronger over the continents than over oceans because of the larger heat capacity of water, therefore the vertical mixing of CH₄ is more efficient over the continents. The vertical motion can be driven by horizontal motion as well. For example, the upward branch of the Hardley cell is driven by horizontal convergence at tropics. The vertical transport of CH₄ in the free troposphere occurs at much larger spatial scales compared to the turbulence in the atmospheric boundary layer. The temporal scale associated with the vertical transport in the free troposphere is about one month (Jacob, 1999, p. 67). The efficiency of horizontal transport of CH₄ in the free troposphere is different for different directions. The latitudinal transport of CH₄ is much faster than meridional transport in the same hemisphere. Temporal scale is about 2 weeks for the latitudinal transport and 1-2 months for the meridional transport in each hemisphere. There is a strong barrier for the meridional transport at the intertropical convergence zone (ITCZ). The ITCZ is a persistent convergence belt near the equator formed by the southward branch of the northern Hardley cell and northward branch of the southern Hardley cell (Holton, 2004, p. 371-374). There is a strong ascending motion at the ITCZ throughout the year and divergence in the upper troposphere. The position of the ITCZ varies seasonally and along longitude, and is located at a latitude with a maximum temperature of the earth surface in meridional direction. Generally the ITCZ is in the warmer part of two hemispheres. Meridional motion in the troposphere is basically driven by latitudinal gradients of the earth surface.
temperature. Around the ITCZ such gradients are absent and then motion crossing the ITCZ is weak. The typical time is about 1 year for air to exchange between northern and southern hemisphere. The ITCZ is a realistic boundary separating the air of the two hemispheres. The lifetime of CH$_4$ in the troposphere is about 10 years, much longer compared to the temporal scales of the tropospheric transport in each hemisphere. It can be expected that CH$_4$ is well-mixed in the troposphere of each hemisphere.

As described earlier, the atmospheric temperature decreases with altitude in the troposphere and arrives at a local minimum at the tropopause. In the stratosphere located just above the tropopause the atmospheric temperature increases with altitude. The strong static stability of the stratosphere prevents convective motions originating in the troposphere from continuing into the stratosphere. The transport from the troposphere to the stratosphere is mainly accomplished by ascending motions in the tropics. The typical time for air to ascend into the stratosphere is 5-10 years. The air ascending into the stratosphere is taken toward the poles and subsides back into the troposphere at mid to high latitudes. The circulation is called stratospheric residual circulation, which is driven by eddy-induced zonal force in the stratosphere (Holton 2004, p. 407-421), in contrast to the thermally driven tropospheric circulation. CH$_4$, as well as other long lived species such as N$_2$O, are distributed mainly by the transport, and present similar patterns in the stratosphere. It takes 1-2 years for air to move back into the troposphere. Because of the slow transport from the troposphere to the stratosphere and the destruction in the stratosphere, the concentration of CH$_4$ is much lower in the stratosphere than in the troposphere and decreases with altitude above the tropopause with height owing to increased oxidations by radicals.

The geographic distribution of atmospheric CH$_4$ is a combination effect of atmospheric transport, sources and sinks. Satellites are a useful tool to visualize the global distribution of CH$_4$, as being shown in Fig. 1.2. Higher CH$_4$ concentration in northern hemisphere compared to southern hemisphere is a result of most of CH$_4$ sources locate in the northern hemisphere, slow transport between two hemispheres and rapid mixing in each hemisphere relative to the long lifetime of CH$_4$. The boundary between high and low CH$_4$ concentrations approximately denotes the mean position of the ITCZ. Several regions present higher CH$_4$ concentrations relative to the surrounding, for example, South America, middle Africa, East Asia and Russian. Some important CH$_4$ sources exist in these regions, which are wetlands, biomass burning, rice cultivation and boreal wetland, respectively. The long-term trend and seasonal variation of CH$_4$ depend on a balance between and seasonal cycles of its sources and sinks. Fig. 1.3 presents zonally averaged CH$_4$ over time and latitude, derived from in situ measurements at the earth surface (mostly in marine boundary layer). Regions in mid- to high-southern latitudes are far from any strong sources, and then present a well mixed CH$_4$ field. The seasonal cycles there are really regular compared to significant interannual variability in northern hemisphere. The reasons are that the seasonal variation of OH dominates the seasonal cycle of CH$_4$ in southern hemisphere, but more factors (transport, sources and sinks) influence northern CH$_4$ cycle.
Figure 1.2. Satellite measurements of column-averaged CH$_4$ concentration for 2003-2005. [Courtesy of M. Buchwitz, IUP, University of Bremen.]

Figure 1.3. Zonally averaged representation of the global distribution of CH$_4$ at the earth surface (mostly in the marine boundary layer). [Courtesy of NOAA/ESRL.]
Although the categories of CH$_4$ sources and sinks are known quite well, but their magnitudes are poorly known up to now. The large uncertainties of sources and sinks limit the ability of model to predict CH$_4$ variation in the future.

### 1.3 Ground-based observation of greenhouse gases by TCCON

It is important to monitor the temporal and spatial variation of greenhouse gases because of their climate effects. The Total Carbon Column Observation Network (TCCON) is a network of ground-based Fourier Transform Spectrometers (FTS) measuring atmospheric trace gases. The ground-based FTS records solar spectra at ground level in the near-infrared spectral region, where H$_2$O, CO$_2$ and CH$_4$ have significant absorption features, and CO, N$_2$O and HF absorb solar radiation as well. According to their absorption features the column-averaged concentrations of these species can be derived. The aimed precision of TCCON measurements is 0.1%, which can be achieved under clear sky condition. The high precision measurements can be used to validate measurements of satellite and model simulations.

The global sources and sinks of greenhouse gases are usually derived from top-down and bottom-up approaches. The top-down approach determines optimal surface fluxes that agree with measurements best. The surface fluxes are transformed to atmospheric concentrations of greenhouse gases using a chemical transport model. The bottom-up approach is a process-based model, which determines surface fluxes through directly describing various mechanisms influencing fluxes. The performance of the top-down approach depends on measurement quantity and simulating ability of chemical transport model. TCCON measurements can act as an independent validation for the top-down approach, or validate surface flux from the bottom-up approaches using chemical transport model.

The first part of this thesis describes the derivation of tropospheric column-averaged CH$_4$ concentration using TCCON column data of CH$_4$ and N$_2$O. There is much lower CH$_4$ concentration in the stratosphere compared to the troposphere. The variabilities of the tropopause and stratospheric CH$_4$ cause variabilities of the column-averaged CH$_4$ concentrations. Currently numerical models have difficulties in simulating tropopause variabilities and some stratospheric processes, for example the polar vortex. If the tropospheric column-averaged CH$_4$ is used, such difficulties can be avoided.

The second part of this thesis is about the retrieval of the $\delta^{13}C$ in atmospheric CO$_2$ from TCCON spectra. One difficulty of the top-down approach to estimate sources and sinks of greenhouse gases is the attribution to different categories. Taking isotopes measurements of greenhouse gases into account is a way to improve it. For example, CO$_2$ produce by fossil fuel burning contain higher $^{13}C$ than by biosphere.
2. Methods

2.1. Fourier transform spectrometry

The Fourier transform infrared spectrometry (FTS) records the interference pattern of incident light. The incident light is split into two beams and then combined together. The intensity of the combined light depends on the difference of the paths from splitting to combination of two beams, and the spectrum of the incident light. The FTS records the variation of the intensity of the combined light along the difference of the paths, namely interferogram. The spectrum can be recovered from the interferogram.

![Diagram of Fourier transform infrared spectrometry](image)

Figure 2.1. Diagram sketch of a Fourier transform infrared spectrometry. $r$ and $t$ represent reflection and transmission coefficients, their subscripts denote corresponding object. $x_1$ and $x_2$ are paths of two beams.

The working principle of the FTIR can be described by Fig. 2.1. Assuming incident light is monochromatic and can be described as $e^{iwt}$, then the balanced output $A$ can be described as,

$$A = e^{iwt} (t_s r_{c_1} e^{-i2\pi \sigma x_1} + r_s r_{c_1} t_c e^{-i2\pi \sigma x_2}),$$

where, $\sigma$ is an inverse of the wavelength. If ignoring the differences of reflection and transmission coefficient between different objects, the intensity of the balanced output is,
\[ E = A^* A = 2 r^2 t^2 (1 + \cos 2\pi \sigma x), \] (2.1)

where \( r \) and \( t \) represent reflection and transmission coefficients, and \( x = x_2 - x_1 \). Since the constant term in the bracket of Eq. 2.1 is not important, the intensity of the balanced output is basically proportional to the cosine of the path difference. When the incident light contains various frequencies and has a spectrum \( B(\sigma) \), the intensity of the balanced output, the interferogram, is,

\[ I(x) = \int_{0}^{\infty} B(\sigma) \cos 2\pi \sigma x d\sigma. \]

The multiplier and constant term in Eq. 2.1 has been left out during deriving above equation. So the interferogram recorded by the FTS is a cosine transform of the spectrum. The spectrum can be recovered by taking the interferogram’s cosine transform. Usually the equation above is written as,

\[ I(x) = \int_{-\infty}^{\infty} B_e(\sigma) \cos 2\pi \sigma x d\sigma ; \quad B_e(\sigma) = \frac{1}{2} (B(\sigma) + B(-\sigma)). \] (2.2)

Conversely, for an ideal interferogram there is,

\[ B_e(\sigma) = \int_{-\infty}^{\infty} I(x) \cos 2\pi \sigma x dx. \]

The reason for extending to minus frequency is an easier mathematical manipulation of Eq. 2.2 in analysis of a non-ideal interferogram.

While the relation between a spectrum and an interferogram is clear, there are several limitations in the real observation. The path difference is limited for a real FTS. It is equivalent to multiply \( I(x) \) by a rectangle function with a width of twice the maximum path difference. In spectrum domain, it means a convolution of \( B_e(\sigma) \) with a sinc function. The width of the sinc function is inversely proportional to the maximum path difference, and is an indication of the resolution in the spectrum. Moreover, a FTS has a finite aperture. The path difference of the combined beams varies with the distance of hitting point on the aperture off the center. The recorded \( I(x) \) at a specific path difference actually contains contributions from other path differences. The effect on a spectrum is a convolution by a rectangle function of width proportional to wavenumber and the aperture size. These effects of physical limitations of the FTS on the spectrum is combined into a convolution function, namely the instrumental line shape function (ILS). The ILS characterizes how a real spectrum is smeared into an observed one.

The performance of a FTS can not be ideal, and suffers various deficiencies. One common error is inaccurate knowledge on the position of the moving mirror in Fig. 2.1. Its effects on the spectrum depend on its distribution along the path difference. For example, a periodic error in \( x \) will result in false lines locating off from the true line. Other examples are that the response of instrument to signal intensity changes with path difference (usually decreases with path difference) and the aperture is not centered on the optical axis. As a result, the real ILS differs from the nominal one.
accounting for the limited path difference and aperture only. Additional measurements have to be taken to determine what it is.

2.2. Retrieval theory and methods

Retrieval is a process of deriving the quantities which are interested for us from indirect measurements. There are usually more than one solution which predict comparable measurements within the measurement error. The reason is that any physical measurement has error, and some components of the quantity interested might have none or little effect on the measurement. The components of the quantity interested which do not exit in the measurement must be obtained from other sources. Even for the components existing in the measurement it is usually better to apply some constraints since the measurement error always come and could distort a solution seriously. Knowledge about the quantity that is independent from the measurement is called a priori. With the measurement and a priori on the hand, approaches are needed to combine information presenting in the measurement and a priori. The principle of such approaches should be minimizing the influence of the measurement error and extracting as much as possible information from the measurement.

Bayes’s theorem provides a useful conceptual frame for retrieval problems. It can be expressed as,

$$P(x|y) = \frac{P(y|x)P(x)}{P(y)}, \quad (2.3)$$

where $x$ and $y$ represent a state (quantities interested) and measurement, respectively. $P$ means probability density function (pdf). $P(x)$, $P(y)$ are a prior pdf of the state and measurement. $P(y|x)$ is the pdf of the measurement when the state takes the value of $x$. $P(x|y)$ is the pdf of the state when the measurement has the value of $y$, called a posterior pdf of the state. The Bayes theorem gives an explicit expression on how does knowledge on the state change with the measurement available. Assuming both the measurement error and the state have a Gaussian distribution, and ignoring the term $P(y)$ since it is just a scale factor then Eq. 2.3 can be written as,

$$-2\ln P(x|y) = (y-f(x))^T S^{-1}_e (y-f(x)) + (x-x_a)^T S^{-1}_a (x-x_a) + c, \quad (2.4)$$

where, both $x$ and $y$ are vectors that represent the state and measurement. $f(x)$ is a forward function which describes how the state is related to the measurement. The superscript $T$ means transpose. $S_e$ and $S_a$ are the measurement error covariance and a priori covariance of the state, respectively. $x_a$ is a prior value of the state, $c$ is a constant. It is clear that the a posterior pdf of the state contains contributions from both the measurement and a prior knowledge. Knowing the a posterior pdf of the state, a criterion is needed to select one solution from all states. One reasonable selection is the most probable state. Another could be the expected value of the a posterior pdf. The former criterion is used here and applied in most of this thesis.

A numerical procedure should be used to search a solution $x$ minimizing Eq. 2.4 since usually the forward function is a nonlinear and complicated function of the state and the equation can not be
dealt with analytically. At the maximum probability state the derivative of Eq. 2.4 with respect to
the state is zero. The Gauss-Newton method is commonly used to obtain the state which zeros the
derivative of Eq 2.4. It is an iterative method (Rodgers et al., 2000),
\[
x_{i+1} = x_i + \left( S_a^{-1} + k_i^T S_e^{-1} k_i \right)^{-1} k_i^T S_e^{-1} \left( y - f (x_i) \right) - S_a^{-1} (x_i - x_a),
\]
where the subscript \(i\) denotes the \(i\)th step in the iteration. \(k_i\) is a matrix that contains the derivatives
of the forward function to the state, with elements \(k_{ij} = \partial f / \partial x_j\), the subscripts here mean the \(i\) and \(j\)
th elements of vector \(x\) and vector-valued function \(f\). When the iteration converges to a state \(\hat{x}\) the
Eq. 2.5 can be written as,
\[
\hat{x} = x_a + \hat{G} \left[ y - f (\hat{x}) + \hat{k} (\hat{x} - x_a) \right], \quad \hat{G} = (S_a^{-1} + \hat{k} S_e \hat{k})^{-1} \hat{k}^T S_e^{-1}.
\]
Except for obtaining a solution, it is even more important to characterize this solution. For example,
how far is the solution from the true state, how sensitive is the solution to the measurement error.
Especially for remote sensing the solution usually is some function of the true state, such relation
needs to be determined as well. Since the solution contains information from both the measurement
and the a prior it is necessary to know how much information is taken from the measurement.
Assuming the forward function is linear in a region around \(\hat{x}\), within which the true value of the
state \(x\) locates. It means \(y = f (\hat{x}) + \hat{k} (x - \hat{x}) + \epsilon\), \(\epsilon\) is the measurement error. The expression for the
solution Eq. 2.6 can be written as,
\[
\hat{x} = x_a + \hat{G} \left[ \hat{k} (x - x_a) + \epsilon \right].
\]
According to Rodgers (2000), the expected value of the first terms in Eq. 2.4 at the solution is
declared as degrees of freedom for signal, that of the second term as degrees of freedom for noise.
\[
d_s = E \left[ (\hat{x} - x_a)^T S_a^{-1} (\hat{x} - x_a) \right] = tr (\hat{G} \hat{k})
\]
\[
d_n = E \left[ (\hat{k} (x - \hat{x}) + \epsilon)^T S_e^{-1} (\hat{k} (x - \hat{x}) + \epsilon) \right] = tr \left( [\hat{k}^T S_e^{-1} \hat{k} + S_a^{-1}]^{-1} S_a^{-1} \right),
\]
where, \(E\) means calculating an expected value and \(tr\) means calculating a trace of a matrix. The sum
of \(d_s\) and \(d_n\) is equal to the dimension of the state vector. When a prior constraint, described by \(S_a\),
is tight the solution will approach the a prior value of the state and \(d_s\) will decrease. At the same
time the degrees of freedom for noise will increase, which means the measurement mainly provides
noise information.
Except for the state, a forward function is determined by many other parameters. For example, in
the case of retrieving CO2 profiles from a ground-based FTS measured spectra the CO2 profiles will
be the state. But other parameters impact spectra as well, like atmospheric temperature, pressure
and water profiles, solar position, instrument parameters, spectroscopy parameter of all molecules
contributing to absorption in a used spectral region. It is also possible that some factors are still not
recognized and not included in the forward function. The knowledge on the recognized parameters
of the forward function can not be completely correct in practice. The forward function must be
replaced by a likely imperfect forward model $F$, which could have not completely correct model parameters. Its relation to the forward function is,

$$f(x, b, b') = F(x, \hat{b}) + K_b(b - \hat{b}) + \Delta f(x, b, b'), \quad (2.9)$$

where, $b$ collects recognized model parameters and $b'$ includes unknown parameters. $K_b$ is the derivative of $F(x, b)$ to the model parameters at their estimated value $\hat{b}$. $\Delta f$ is the error in the forward model caused by the unknown parameters. As a result, the $f$ and $k$ in Eq. 2.5 and 2.6 must be replaced by $F(x, \hat{b})$ and its derivatives to the state $K$, respectively, in practice. The solution obtained when using the forward model $F$ has properties different from that described in Eq. 2.7 and 2.8. They are explained as follows, use a relation $y = f(x, b, b') + \epsilon$ and rewrite Eq. 2.6 in terms of $F$ and $K$,

$$\hat{x} = x_a + \hat{G} [F(x, b, b') - F(\hat{x}, \hat{b}) + \hat{K} (\hat{x} - x_a)] + \epsilon. \quad (2.10)$$

Compared to Eq. 2.7, there are two additional terms contributing to the solution in Eq. 2.10. They are the solution errors caused by the error in the forward model parameters and parameters not included in the forward model. Only the last three terms in Eq. 2.10 are called error term. But the error related to unknown model parameters is not possible to evaluate. The covariances of other two error terms can be derived from the statistical properties of forward model parameters and the measurement error. The first two terms together describe how the solution is related to the true value and a priori value of the state. Especially important is the term $\hat{A} = \hat{G} \hat{K}$, called averaging kernel. The rows of an averaging kernel matrix expand a space, which is a subspace of the state vector space. Only these states locating in the subspace can contribute to the solution, or can be measured. The state outside the subspace is orthogonal to all rows of the averaged kernel matrix and then its product with the matrix is a zero vector.

The derivation of the definition of the degrees of freedom for signal and noise in Eq. 2.8 is based on the solution expression of Eq. 2.7. When using a likely imperfect forward model in practice, the solution expression needs to be replaced by Eq. 2.10. The expected value of the second term in Eq. 2.4 at the solution contains more terms than $tr(\hat{G} \hat{K})$, but only this term is treated as the degrees of freedom for signal $d_s$. The expression of $d_n$ in Eq. 2.8 needs to be changed as well in this case, but not important in the thesis. So the number of independent pieces of information from the measurement is equal to the trace of the averaging kernel matrix.

To obtain a maximum a posterior solution (that minimize Eq. 2.4) the a priori covariance is needed. A priori covariance can be derived from the direct measurements of the state or constructed through some approximate methods. There is another method to construct a prior constraint, namely
Tikhonov-Phillips regularization, which selects a solution with the most similarity with a prior in
the absolute value or difference between the elements of a state vector. These constrains do not have
probability-related meaning, result in a solution which is not necessarily most probable. In
Tikhonov-Phillips regularization method, usually a function as follows is minimized,

\[
(y - F(x))^T S_{e}^{-1}(y - F(x)) + (x - x_{a})^T (y^2 B^T B)(x - x_{a}),
\]  

(2.11)

where \( B \) is a matrix to apply regularization constraints and \( y^2 \) is a scale factor, and for convenience
other parameters of \( F \) than the state \( x \) are omitted. Compared to Eq. 2.4 the inverse a prior
covariance is replaced by \( y^2 B^T B \), which however is not a measure for probability distribution of
the state. The derived properties, e.g. the degrees of freedom for signal and error characteristic, for
the maximum a posterior solution is also suitable to this case. The matrix \( B \) can be any linear
combination of following matrices,

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix},
\begin{pmatrix}
1 & -1 & 0 \\
0 & 1 & -1 \\
0 & 0 & 0
\end{pmatrix},
\begin{pmatrix}
1 & -2 & 1 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}.
\]  

(2.12)

The example matrices are given in a dimension of 3×3, but their row and column dimensions
should be equal to the dimension of the state vector in practice. The first matrix constraint the
absolute value of the state toward the a prior value. The second and third matrix make sure the first
and second order differences of the state is close to the differences of the a prior state. The scale
factor determines how strong the constraint applied by the matrix \( B \) is.

In this thesis, two retrieval codes are applied to get the information of atmospheric greenhouse
gases from ground-based FTS measured spectra, namely GFIT and PROFFIT. GFIT is a nonlinear
least-squares spectral fitting algorithm (Wunch et al., 2011), which only retrieves the total columns
of interested gases. For atmospheric application, a set of a prior profiles of all atmospheric species
which have observable absorption feature is prepared. The temperature, water and pressure of the
atmosphere is obtained from some additional sources (measurements, reanalysis meteorological
data etc.). Spectroscopy parameters of molecule are from HITRAN (Rothman et al., 2010) and
some other sources. The forward model in GFIT is a line-by-line calculation of absorption of
atmospheric species but ignoring scattering effect of molecule. The absorption line shape of
molecule is described by the Voigt function. The retrieval process of GFIT is a minimization of a
function having the format of Eq. 2.4, however, only the scale factors to the a prior profiles of
atmospheric species is retrieved. PROFFIT is a more flexible inversion code, which allows both
scaling the a prior profiles and retrieving profiles of atmospheric species (Hase et al., 2004). The a
prior constraint can be the a prior covariance, and the Tikhonov-Phillips regularization matrix. The
physical contents in the forward model are generally similar to GFIT. But PROFFIT includes more
selections for absorption line shape of molecule, and atmospheric self-emission if needed.
3. Retrieval of tropospheric CH$_4$ from solar absorption FTS spectra

The atmospheric mole fraction of CH$_4$ has increased from about 700 ppb to the current atmospheric background of about 1800 ppb since 1770. Despite this dramatic increase, the observed global mean atmospheric abundance was nearly constant from 1999 to 2006, before it began to increase again in 2007 (Rigby et al., 2008; Dlugokencky et al., 2009). This behavior is a subject of open scientific discussion (Bousquet et al., 2011; Pison et al., 2013). Several explanations exist due to large uncertainties in our knowledge on the sources and sinks of CH$_4$. Usually surface CH$_4$ and total column-averaged mole fractions of CH$_4$ (referred to total xCH$_4$ hereafter) are used in the top-down estimation of the sources and sinks of CH$_4$. Tropospheric column-averaged mole fractions of CH$_4$ (referred to tropospheric xCH$_4$ hereafter) could provide a better constraint in retrieving drivers of CH$_4$ variations, since the tropospheric xCH$_4$ is free from influences of stratospheric CH$_4$.

The tropospheric xCH$_4$ can be derived using methods such as: (i) a posterior correction to the total column using a proxy for variations in the stratospheric contribution, such as the HF total column as an estimator for the stratospheric CH$_4$ contribution (Washenfelder et al., 2003; Warneke et al., 2006), as well as (ii) a direct determination of the tropospheric mole fraction of CH$_4$ via a retrieval of CH$_4$ profiles (Sepúlveda et al., 2012). Currently the second method is only applied to the Network for the Detection of Atmospheric Composition Change (NDACC) high resolution mid-infrared solar absorption spectra, not to the near-infrared TCCON spectra. The first method is based on the fact that a linear relationship exists in the stratosphere between the mole fractions of CH$_4$ and HF and that the tropospheric mole fraction of HF exhibits little variabilities, and is indeed approximately zero. The stratospheric column of CH$_4$ can therefore be inferred from the total column of HF via this linear relationship, and then subtracted from the total column of CH$_4$ to yield the tropospheric CH$_4$ column. Variations in the CH$_4$ column due to changes in surface pressure are determined from the O$_2$ column. Using this method, the tropospheric xCH$_4$ can be determined with a precision of 0.5 % (Washenfelder et al., 2003). In this chapter, a new method based on a posterior correction is proposed and tested. The tropospheric xCH$_4$ using the algorithm developed by Sepúlveda (2012) is also presented as a comparison.

3.1. A posteriori correction method

In the stratosphere, a compact correlation exists between species of sufficiently long lifetime (Plumb et al., 1992). Species whose local lifetimes are longer than quasi-horizontal transport time scales share surfaces of constant mixing ratio, and a scatter plot of the mixing ratio of one versus that results in a compact curve. These correlations have been demonstrated by data sets from both chemical transport models and in situ measurements, such as observations taken from an aircraft platform (Avallone et al., 1997), Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) observations (Michelson et al., 1998) and balloon observations (Herman et al., 1998). This is true in the case of CH$_4$ and N$_2$O in the stratosphere. Hence, using N$_2$O to infer the stratospheric contribution of the total column of the CH$_4$ is an alternative approach. This approach is, however, complicated by the fact that N$_2$O is also present in the troposphere. In this work, we describe a
method to derive the tropospheric $x\text{CH}_4$ in which the stratospheric $\text{N}_2\text{O}$ column is used to estimate the stratospheric column of the $\text{CH}_4$. We apply the method to TCCON spectra at four sites, one tropical, two extra-tropical and one polar, and compare it with the results derived with the method using HF.

### 3.1.1. FTS measurements

Here we use solar absorption FTS measurements at four TCCON stations: Ny-Ålesund (78.9°N, 11.9°E) at Spitsbergen (Palm et al., 2010), Orléans, France (47.97°N, 2.113°E), Bialystok, Poland (53.23°N, 23.025°E) (Messerschmidt et al., 2010, 2012), and Darwin, Australia (12.424°S, 130.892°E) (Deutscher et al., 2010). The near-infrared observations cover the spectral range between 4000 cm$^{-1}$ and 10 000 cm$^{-1}$ and were carried out with a CaF$_2$ beam splitter and a room-temperature InGaAs photodiode. The spectra were analyzed using the retrieval code GFIT. Atmospheric absorption coefficients are calculated line-by-line for each gas in a chosen spectral window, and for each retrieval level using the assumed temperature, pressure and a priori profile in the forward model. All these absorption coefficients together produce the atmospheric transmittance spectrum. The temperature, pressure and water vapor profiles are obtained from National Centers for Environmental Prediction (NCEP) reanalysis data provided by the NOAA/ESRL Physical Sciences Division (Kalnay et al., 1996), and interpolated in time and space from six-hourly data to local solar noon and site latitude/longitude. The simulated spectrum is compared with the measured spectrum and a prior profiles iteratively scaled to minimize the least-squares differences between the calculated and measured spectra. The spectral regions used in this study are the TCCON-standard regions given in Wunch et al. (2010).

### 3.1.2. In situ measurements

The spatial and temporal variations of tropospheric $\text{N}_2\text{O}$ need to be known to derive the tropospheric $x\text{CH}_4$ in the posterior correction proposed here. The combined Nitrous Oxide data from the NOAA/ESRL Global Monitoring Division, which is sampled at a set of atmospheric background air sites, is used to derive the global distribution, seasonal cycle and long-term trend of tropospheric $\text{N}_2\text{O}$.

To validate the tropospheric $x\text{CH}_4$ derived from FTS measurements, in situ data from several sources is used. At Ny-Ålesund (78.9°N, 11.9°E) in situ $\text{CH}_4$ data is the NOAA surface flask measurements (Dlugokencky et al., 2012) sampled at Zeppelin mountain, which has an elevation of 474 masl compared to the TCCON site's elevation of 20 masl. The relatively high elevation and absence of strong local sources means that these measurements could approximately represent the free troposphere, and are used here in the absence of other more appropriate validation data. Low altitude aircraft flight data is available at Orléans, taken twice per month since 1998 up to 3 km, corresponding to approximately 700 hpa in the pressure coordinate. Over Bialystok there has been regular profiling with semi-monthly to monthly observations using flask sampling at multiple levels up to 3 km for $\text{CO}_2$, $\text{CH}_4$, $\text{N}_2\text{O}$ and other tracers since 2002. These measurements are extended through the entire atmosphere via a linear interpolation between 3.0 km and the tropopause altitude.
and assuming the GFIT a priori above that. The tropospheric xCH$_4$ obtained from the extended low altitude aircraft measurements are used to check the seasonal behavior of the FTS-derived tropospheric xCH$_4$.

In addition, data from the HIAPER Pole-to-Pole Observations (HIPPO) of Carbon Cycle and Greenhouse Gases Study and Infrastructure for the Measurement of the Europe Carbon Cycle (IMECC) aircraft campaigns is used to calibrate the derived tropospheric xCH$_4$. HIPPO of Carbon Cycle and Greenhouse Gases Study measured cross sections of atmospheric concentrations of greenhouse gases approximately pole-to-pole, from the surface to the tropopause (Wofsy et al., 2011). A comprehensive suite of atmospheric trace gases pertinent to understanding the Carbon Cycle were measured. The measurements were taken using the High- performance instrumented Airborne Platform for Environmental Research. In this work, the measurements near the TCCON site at Darwin are used. The IMECC project aimed to build the infrastructure for a coordinated, calibrated, integrated and accessible data set for characterizing the carbon balance of the European. The aircraft campaign conducted within the IMECC project was organized by the Max Planck Institute for Biogeochemistry. A Learjet 35 aircraft was equipped with a cavity ring-down spectroscopy instrument (Picarro Inc.) for measuring CO$_2$ and CH$_4$ mixing ratios and with a vacuum UV fluorescence analyzer for CO. Profiles were taken from 300 m to 12 000 m over the European TCCON stations, including Bialystok and Orléans, during September and October of 2009 (Geibel et al., 2012).

3.1.3. Theory description

For both HF and N$_2$O, assuming there is a linear relationship in the stratosphere between their mole fractions, $f$, and that of CH$_4$, then

\[ f_{CH_4}(z) = a + bf_y(z), \]  

(3.1)

where, $y$ represents HF or N$_2$O. Figure 3.1 presents the correlation of the stratospheric mole fractions of HF (left) and N$_2$O (right) with CH$_4$ based on retrievals from the ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer) satellite (Bernath et al., 2005). The deviation of the N$_2$O-CH$_4$ relationship from the global fit occurs only when N$_2$O mole fractions are lower than 50 ppb, and represents a small contribution to the column. For the derivation of $a$ and $b$, the retrieved stratospheric profiles of HF, N$_2$O and CH$_4$ are separated into several 20 degrees wide latitude bands. In case of HF, the latitudinal variation of the slope $b$ ranges from 740 to 870 ppb ppb$^{-1}$, and from 3.6 to 4.4 ppb ppb$^{-1}$ for N$_2$O. Between 2004 and 2010 no discernible time-dependency could be detected. At the four TCCON sites: Ny-Ålesund, Bialystok, Orléans and Darwin the slopes, $b$, corresponding to their latitude bands are 4.34, 4.39, 4.39 and 3.53 ppb ppb$^{-1}$, respectively, for N$_2$O, and $-749.05$, $-751.21$, $-751.21$ and $-876.03$ ppb ppb$^{-1}$ for HF. Multiplying both sides of Eq. 3.1 with air density and integrating through the stratosphere yields,

\[ V C_{CH_4}^{strat} = aV C_{air}^{strat} + bV C_{y}^{strat}, \]  

(3.2)
where \( \text{VC} \) denotes the vertical column. The stratospheric column of \( y \) can be obtained by subtracting the tropospheric column from the total column, so Eq. 3.2 can be rewritten as follows,

\[
\text{VC}_{\text{CH}_4}^{\text{strat}} = a\text{VC}_{\text{air}}^{\text{strat}} + b(\text{VC}_y^{\text{strat}} - \text{VC}_y^{\text{trop}}).
\] (3.3)

The tropospheric \( x_{\text{CH}_4} \) is then calculated as,

\[
x_{\text{CH}_4}^{\text{trop}} = \frac{\text{VC}_{\text{CH}_4} - \text{VC}_{\text{CH}_4}^{\text{strat}}}{\text{VC}_{\text{air}}^{\text{trop}}}. \] \] (3.4)

In Eq. 3.3 the tropospheric column of HF is zero. The abundance of \( \text{N}_2\text{O} \) is well-mixed in the troposphere because of its long lifetime (120 years) and the major sink is destruction in the stratosphere. The mole fraction of \( \text{N}_2\text{O} \) is almost constant with respect to altitude in the troposphere. The horizontal distribution of \( \text{N}_2\text{O} \) is fairly uniform with small variability (3-5 ppb) (Kort et al., 2011). In the calculation of the tropospheric column of \( \text{N}_2\text{O} \), only horizontal and time variations are considered. The NOAA \( \text{N}_2\text{O} \) measurements contain a set of globally distributed sites influenced mainly by atmospheric background air. We approximately separate measured \( \text{N}_2\text{O} \) concentration into three terms: global means of each year, a mean over all years of residual meridional variations relative to the global mean, and means over all years of residual monthly variations relative to yearly mean at a specific latitude. The second and third components are shown in Fig. 3.2. At a specific station and time, the corresponding three components are obtained from interpolations in time and latitudes. Then the tropospheric \( \text{N}_2\text{O} \) concentration is calculated as their sum. With the predicted concentration, the tropospheric column of \( \text{N}_2\text{O} \) is just calculated as its product with the dry air column in the troposphere.

Figure 3.1. Correlations between the stratospheric mole fractions of \( \text{N}_2\text{O} \) (right) and HF (left) with \( \text{CH}_4 \) on a global scale. Correlation coefficient, slope and intercept are indicated in the legend. The data are from the ACE-FTS satellite.
While Eq. 3.3 and 3.4 are straightforward, the tropopause position is necessary for calculating tropospheric air column. It could cause potential problems since knowledge of tropopause position might be not accurate enough. There is a way to bypass it, as described in the following. In the case of the HF, when approaching the tropopause, the HF concentration approaches zero and so the constant $a$ in Eq. 3.1 represents the CH$_4$ concentration in the troposphere. Washenfelder et al. (2003) treated $a$ as the tropospheric xCH$_4$, and use O$_2$ columns to infer the dry air column. Under these conditions, inserting Eq. 3.3 into Eq. 3.4 yields the equation used by them,

$$X_{\text{CH}_4}^{\text{trop}} = a = \frac{0.2095 (VC_{\text{CH}_4} - b VC_{\text{HF}})}{VC_{O_2}}.$$  (3.5)

This method can be used in the N$_2$O correction approach as well. Since the N$_2$O mole fraction is almost constant in the troposphere and its value can be quite well predicted, we then subtract the tropospheric N$_2$O mole fraction from its mole fraction profile in the whole atmosphere. Such a derived “species” is also present completely in the stratosphere, and a linear relationship between the derived “species” and CH$_4$ mole fractions exits in the stratosphere. But the constant $a$ in Eq. 3.1 is replaced by a value equal to $a$ plus the tropospheric N$_2$O mole fraction multiplied by the slope $b$. When the new constant is treated as the tropospheric xCH$_4$, we get an expression,

$$X_{\text{CH}_4}^{\text{trop}} = \frac{VC_{\text{CH}_4} - b (VC_y - X_y^{\text{trop}} VC_{\text{air}})}{VC_{\text{air}}},$$  (3.6)
where, $X_{y}^{trop}$ is replaced by $X_{N_2O}^{trop}$ when using N$_2$O, or set to zero for HF case.

Due to the effect of the averaging kernels the straightforward equation Eq. 3.6 needs to be modified. The total column retrieved by GFIT is a weighted sum of partial columns at retrieval levels. The weights are represented by the averaging kernel, which is a function of the altitude and solar zenith angle, and usually differ from unit. Figure 3.3 presents the averaging kernels of HF, N$_2$O and CH$_4$ retrieval at Bialystok from all spectra during 2010. It should be noted that GFIT just scales a prior in the retrieval so the rows of its averaging kernel have the same shape. The showed are the column averaging kernel vector (Connor 2009) instead of the full averaging kernel matrix, which basically is a weighted average of all rows. The shape of the column averaging kernel depends largely on the solar zenith angle. The N$_2$O averaging kernel has a large weight in stratosphere and small weight in troposphere, so true variations in the stratospheric column of N$_2$O are amplified in the retrieved total column, and true tropospheric variations are dampened. The CH$_4$ averaging kernel is close to unity at all altitudes, so the effect of the averaging kernel is small.

Figure 3.3. The averaging kernels of HF, N$_2$O and CH$_4$ at Bialystok for all spectra from 2010. the colors indicate the solar zenith angle (SZA) of the corresponding measurements.

To see how an averaging kernel influences retrieval, using Eq. 2.10 and ignoring last three error terms, replacing the state notation $x$ by the mole fraction profile $f$, and omitting the hat notation, then we have,

$$f_r = f_a + A(f_t - f_a),$$

(3.7)

where, the $f_r$, $f_t$ and $f_a$ are retrieved, true and a prior mole fraction profiles, respectively. $A$ is the averaging kernel. Integrating Eq. 3.7 and rearranging yield,
\[
\int_{0}^{P_s} f_r \frac{dp}{mg} = \int_{0}^{P_s} (I - A) f_a \frac{dp}{mg} + \int_{0}^{P_s} A f_t \frac{dp}{mg},
\]

(3.8)

where \( m \) is the molecular mass of moist air \((m=(1-X_{H_2O})m_{dry}+X_{H_2O}m_{H_2O})\), \( g \) is the gravitational acceleration, \( I \) is an identity matrix, and \( P_s \) is surface pressure. Since GFIT performs a profile scaling retrieval, Eq. 3.8 should be written in the form of the column averaging kernel,

\[
\int_{0}^{P_s} f_r \frac{dp}{mg} = \int_{0}^{P_s} (1-a(p)) f_a \frac{dp}{mg} + \int_{0}^{P_s} a(p) f_t \frac{dp}{mg},
\]

(3.9)

where, \( a(p) \) is the column averaging kernel vector, which is a function of pressure (altitude). From the equation above, it can be seen that the retrieved total column includes contributions from a prior and true profiles, whose weights are determined by the column averaging kernel magnitude.

After taking the averaging kernel effect into account Eq. 3.6 is changed to following equations,

\[
X_{CH_4}^{trop} = \frac{VC_{CH_4}^r - \gamma_{CH_4} - b \mu_y (VC_{y}^r - \gamma_{y} - \varphi_{y} X_{y}^{trop} VC_{air})}{\varphi_{CH_4}^r VC_{air}},
\]

(3.10)

where, \( y \) represents \( N_2O \), \( HF \) or \( CH_4 \), and \( VC^r \) is the retrieved total column including a prior and averaging effect as described by Eq. 3.9, being distinguished from the true column \( VC \). Considering the calculation of the coefficients \( \varphi \) and \( \mu \), the true mole fraction profiles of \( N_2O \) or \( HF \) are needed. Because of the long lifetime of \( N_2O \) and \( HF \), and then small variabilities of their profiles, the GFIT a prior profiles should be a reasonable approximation. However, the GFIT a prior does not account for the influence of the polar vortex, within which air is subsided strongly and the profiles of atmospheric species deform as well. According to Toon et al. (1992) this deformation can approximately be described by one parameter, the degree of subsidence. Here the degree of subsidence is derived through compressing a reference \( N_2O \) profile to fit the FTS measured total column-averaged \( N_2O \) mole fraction. The reference profile has same shape as the \( N_2O \) a prior profile, but its tropospheric mole fraction has the same value as that predicted by the mentioned method (a sum of three terms). The subsidence is achieved through a relation

\[
f_{N_2O}^{sub}(z) = f_{N_2O}^{ref}[z(1+dos)],
\]

\( dos \) is the degree of subsidence. The subsided profile is integrated, accounting for the a prior and averaging kernel according to Eq. 3.9, to give a predicted total column-averaged mole fraction of \( N_2O \). The \( dos \) is changed until the prediction and measurement of
total column-averaged \( N_2O \) mole fractions agree well. To avoid influences of measurement noise the daily median of the total column-averaged \( N_2O \) mole fraction is used. The derived degree of subsidence is also applied to HF a priori profiles.

To compare the derived tropospheric \( xCH_4 \) with in situ measurements, measured \( CH_4 \) profiles need to be integrated. At the same time, the averaging kernel effect of the FTS measurements should be taken into account. For our purpose only the tropospheric part is important, and it is expected that the integration only extends up to tropopause for both in situ profiles and the averaging kernel. It can be proved that the integration takes the following format (see Appendix A),

\[
X_{CH_4}^{trop} = \frac{\int_{P_t} P_s a_{CH_4} \frac{dp}{mg}}{\int_{P_t} P_s a_{CH_4} dp}, \tag{3.11}
\]

where \( P_t \) is tropopause pressure. \( f_i \) is the true \( CH_4 \) profile and replaced by the in situ profiles.

The total columns of \( CH_4 \), \( N_2O \) and HF are used in the derivation above, but the total columns directly retrieved from spectra include errors arising from spectroscopic imperfections and instrumental effects. The TCCON products are the dry air column averaged mole fractions, which are obtained through creating a ratio of the retrieved total columns of a species to a dry air column inferred from a retrieve \( O_2 \) column. This is because the ratio with the \( O_2 \) column can decrease instrumental effects. The dry air column averaged mole fractions have been corrected by air-mass independent and air-mass dependent calibration factors to account for spectroscopic inaccuracies. These corrections should be taken into account in calculating the tropospheric \( xCH_4 \) and the Eq. (3.10) is changed to,

\[
X_{CH_4}^{trop} = \frac{1}{\psi_{CH_4}} \left[ X_{CH_4} - \frac{Y_{CH_4}}{V_{C_{air}}} b \mu_y (X_y - \frac{Y}{V_{C_{air}}} - \psi_y X_y^{trop}) \right], \tag{3.12}
\]

where \( X_{CH_4} \) and \( X_y \) are the dry air column averaged mole fractions of \( CH_4 \) and \( y \).

3.1.4. Comparison of between the \( N_2O \) and HF methods and in situ data

To test the method described in Sect. 3.1.3, data from four TCCON sites at Ny-Ålesund, Orléans, Bialystok and Darwin are used. Figures 3.4-3.7 show the results for these sites. We compare FTS-measured tropospheric \( xCH_4 \) to in situ data from NOAA at Ny-Ålesund, and the low aircraft data at Orléans and Bialystok. These low aircraft profiles have been extended into the whole troposphere as described in Sect. 3.1.2, and then integrated to produce a tropospheric \( xCH_4 \). For each site with available in situ data the results using \( N_2O \) are in better agreements with the in situ measurements than when using HF. The difference between the results using \( N_2O \) and HF has both seasonal and site dependence. At Ny-Ålesund the results using \( N_2O \) are about 30 ppb higher than those using HF, about 20 ppb at Bialystok and Orléans, and about 10 ppb lower at Darwin. Such a difference might result from the uncertainty in the HF column. The HF column used here is not calibrated through in situ profile measurements since HF is located completely in the stratosphere and there are no such
measurements currently available. The inaccuracy in the spectroscopy of HF will force the retrieved HF column away from the truth. Such an effect also depends on the HF total column. A stronger signal is more sensitive to a spectroscopy parameter error. This might partly explain the site dependence of the difference between the results using N₂O and HF since the tropopause pressure and HF column generally decrease from Arctic to tropics.

Another difference is that the results using HF present a larger scatter at Darwin than at the other three sites, while the results using N₂O have similar scatters at all four sites. This difference also arises from the HF column error. The TCCON HF column is retrieved from a weak spectral absorption line that is located at the shoulder of a water line. Therefore, the retrieval of HF suffers from water vapor interference. The interference depends on both the water amount and its vertical distribution, and could result in a large scatter. In the tropics the higher amount of water vapor in the atmosphere will significantly influence the retrieved HF column. Another factor is that the HF column amount decreases from high to low latitudes, since HF locates completely in the stratosphere and generally the tropopause height increases from high to low latitudes. The retrieval of HF has better precision and worse accuracy for larger HF columns due, respectively, to a stronger signal and larger effect from spectroscopy error, and vice versa. The performance of the HF method should be more stable but has a larger offset for high-latitude sites like Ny-Ålesund owing to the dry conditions and more significant signals, and be less stable and has a smaller offset for tropical sites like Darwin because of the moisture conditions and relatively weaker signals.

The main uncertainty in the N₂O approach comes from applying a simple model to predict latitudinal and temporal variations of tropospheric N₂O mole fractions and ignoring the vertical and longitudinal variations. This is a reasonable approximation because of its long lifetime in the atmosphere. However, in the presence of strong regional sources, like biomass burning and industrial sources, such an assumption might not be valid. A sensitivity test reveals that a 2 ppb perturbation in the assumed tropospheric N₂O mole fraction results in perturbations in the derived tropospheric xCH₄ of 4.0-4.4 ppb at Darwin, 4.2-5.6 ppb at Orléans and 4.5-5.5 ppb at Ny-Ålesund.

Figure 3.8 presents seasonal cycles of the tropospheric xCH₄ derived through averaging the time series given by Figs. 3.4-3.7. Generally the seasonal features of results from N₂O and HF are similar except an almost constant offset (with a variability of about 8 ppb) at each site. As previously mentioned, these might come from the error in the HF total column.
Figure 3.4. Results at Ny-Ålesund, the red points correspond to the tropospheric column-averaged CH$_4$ mole fraction derived from N$_2$O, the blue to those derived using HF and the open circles are in situ CH$_4$ data measured at Zeppelin mountain. The upper panel shows the difference between the in situ and tropospheric column-averaged CH$_4$ mole fractions, the middle panel is the difference between the results using N$_2$O and HF.

Figure 3.5. Same as Fig. 3.4 except for at the Orléans site and with the black circles lower panel.
representing tropospheric column-averaged CH$_4$ mole fraction from low altitude aircraft profiles.

Figure 3.6. Same with Fig. 3.4 except for at Bialystok.

Figure 3.7. Results at Darwin.
Figure 3.8. The multi-annual mean seasonal cycles of tropospheric column-averaged CH$_4$ mole fraction for four sites. The red points correspond to the results derived from N$_2$O and the blue to HF.

3.1.5. Comparison with aircraft profile measurements

The derived tropospheric xCH$_4$ are compared against in situ measurements from the HIPPO and IMECC aircraft campaigns and the inter-site consistency of the N$_2$O and HF methods is assessed. The comparison between the integrated in situ profiles and the HF- and N$_2$O-derived tropospheric xCH$_4$s is shown in Fig. 3.9. The aircraft data at Białystok and Orléans are from the IMECC campaign, and at Darwin from the HIPPO-4 campaign. According to the definition, the tropospheric xCH$_4$ is the mean abundance between the surface and the chemical tropopause. The aircraft profiles do not extend high enough to identify the chemical tropopause, so the thermal tropopause is used instead. The GFIT a priori profile is used for altitudes above the highest in situ measurement altitude. The a priori profile has been scaled to match the aircraft profile in the troposphere. The mole fraction at the lowest sample point is used to extrapolate to the surface to complete the profile below the lowest measured point during the aircraft flight.

The constructed profiles are then integrated using Eq. 3.11. Results from the FTS during the aircraft measurement period are averaged, and the uncertainty of the FTS data is estimated as the standard deviation of these results. The uncertainty of the tropospheric xCH$_4$ integrated from the extended aircraft measurement is calculated as the mean of the uncertainties at all sample points along the
altitude axis, weighted by the partial air column at each point. Comparing the GFIT a priori and the in situ measurements reveals that the standard deviation of the ratios of the a priori to the measurement is 1.8 %. Therefore, for the altitude range where the scaled GFIT a priori is used, an uncertainty of 1.8 % is assumed. This part represents the largest contribution to the total uncertainty. The uncertainties of the points below the aircraft ceiling are estimated from instrumental performances and the variation of CH$_4$ mole fractions along the aircraft path. In general the results using N$_2$O fall closer to the fitted line. The distances between the points and the fitted line are 3.5, 4.6, 2.1, 0.8, 0.2, 5.7 ppb for the results derived using the N$_2$O method, and 7.6, 9.0, 6.9, 0.4, 7.1, 17.2 ppb for the HF method.

Figure 3.9. Comparison results of FTS tropospheric column-averaged CH$_4$ mole fraction with aircraft data. The aircraft profiles are smoothed using GFIT averaging kernels in troposphere using Eq. 3.11. The FTS data are averaged through aircraft measurements periods, and the error bars of FTS data are standard deviations of these averaged data.

3.1.6. Uncertainty analysis

The Gaussian error propagation equation is used to estimate the uncertainty in calculating the tropospheric xCH$_4$ using Eq. 3.12. The errors in the assumed tropospheric mole fraction of N$_2$O were not taken into account since significant departure only occur in the present of strong local N$_2$O sources. Also, the errors in the coefficients accounting for the averaging kernel effect are overlooked since they are unknown.
Figure 3.10. Relative error estimation of the tropospheric column-averaged CH$_4$ mole fraction using Gaussian error propagation equation for four sites, the blue corresponds to the error for the method using HF and the red to that of method using N$_2$O.

Figure 3.11. Same as Fig. 3.10 except for that the relative error is estimated as the standard deviation of tropospheric column-averaged CH$_4$ mole fractions during one day divided by the daily mean.

The errors of the slope parameters $b$ are estimated as 0.011 (N$_2$O) and 1.9 (HF). The errors of the dry air column averaged mole fractions of CH$_4$, N$_2$O and HF are taken as the values estimated in GFIT. Except for using the Gaussian error propagation equation, we calculate the standard deviation
of the derived tropospheric xCH$_4$ during a day as an alternative estimation of the uncertainty. To ensure the calculated standard deviation is significant only the days with fine weather conditions are considered. In practice, those days during which there are more than 50 spectra available at Ny-Ålesund and 100 spectra at other three sites are considered. Figure 3.10 presents the estimated relative uncertainties for all sites using the Gaussian error propagation equation method and Fig. 3.11 presents the results using the standard deviation method. The two methods produce similar results. The mean relative standard deviation of the tropospheric xCH$_4$ using N$_2$O is 0.15% (Darwin), 0.30% (Ny-Ålesund), 0.28% (Orléans) and 0.14% (Bialystok). And they are 0.93%, 0.45%, 0.50%, and 0.20%, respectively, in the case of HF. It could be concluded that the method using HF produces larger uncertainties, especially at Darwin. In addition, The method using HF suffers from stronger H$_2$O interference, which results in higher uncertainties when H$_2$O columns are larger. The two methods are comparable in the case of low H$_2$O columns. While using the Gaussian error formulation the HF method results in marginally lower uncertainties under the low H$_2$O condition, the relative daily standard deviations are always smaller for the N$_2$O method.

3.2. Profile retrieval method

The algorithm of determining the tropospheric mole fraction of CH$_4$ through profile retrieval is developed in the Karlsruhe Institute of Technology (KIT, Germany) (Sepúlveda et al., 2012, 2014). The method is applied to NDACC high-resolution mid-infrared solar spectra, which include more profile information than TCCON near-infrared spectra. In this section, the algorithm is compared to the posterior correction method using N$_2$O as a proxy.

3.2.1. FTS measurements and surface in situ datasets

NDACC is a global ground-based FTS network monitoring atmospheric composition changes. The FTS records direct solar spectra in the mid-infrared spectral region (740-4250 cm$^{-1}$), with a resolution of 0.0035-0.005 cm$^{-1}$. Measurements at two sites which are involved in both TCCON and NDACC, Ny-Ålesund (78.9°N, 11.9°E, 20 masl), Spitsbergen, and Bremen (53.1°N, 8.85°E, 27 masl), Germany, are used. The mid-infrared spectra are recorded using an Indium-Antimonide (InSb) detector cooled with liquid nitrogen and a CaF$_2$ beam splitter. The high-resolution FTS allows for a detailed observation of absorption line shape of atmospheric species. The line width of an atmospheric absorber includes natural broadening and collision (pressure) broadening. The natural broadening is proportional to frequency and the square root of temperature. So it decreases in the troposphere slowly with altitudes and increases in the stratosphere at a specific frequency. The collision broadening is proportional to pressure and the inverse of the square root of temperature. So the collision broadening decreases exponentially with height. Because of the dramatic variation of natural broadening, the vertical distribution of an atmospheric species can be inferred from its absorption line shape presented on the spectra recorded by a ground-based FTS. The information content for the vertical distribution depends on the resolution and signal-noise ratio of the spectra.

Two surface in situ datasets are used to empirically validate tropospheric CH$_4$ retrieved from FTS.
spectra. At Ny-Ålesund the same dataset from NOAA as described in Sect. 3.1.2 is used. However, there is not in situ data available near the Bremen FTS site. A NOAA site Mace Head, Ireland (53.326°N, 9.899°W, 5 masl) locates at the west coast of Ireland. The Mace Head site is influenced by air masses from the North Atlantic ocean (about 70% according to trajectory analysis), and from North America and Northern Europe (about 30%). The weekly surface flask measurements are used as a reference for retrieval at the Bremen site although its large distance from Bremen.

3.2.2. Profile retrieval setup

The mid-infrared spectra are analysed with the code PFOFFIT (Hase et al., 2004). The atmosphere is discretized into 49 levels which extend from a FTS observation altitude to 120 km and the increments between them increase from 0.4 km at the lowest levels to 14 km at the highest levels. The profiles of atmospheric temperatures and pressure are from NCEP reanalysis data, with intraday variabilities included. Applied spectral microwindows are: 2613.70-2615.40 cm\(^{-1}\), 2650.60-2651.30 cm\(^{-1}\), 2682.00-2684.20 cm\(^{-1}\), 2919.64-2920.40 cm\(^{-1}\), and 2922.73-2924.16 cm\(^{-1}\). In these regions CH\(_4\) has dominant absorption features, but there are discernible absorptions from other species as well. To simulate measured solar radiation in these regions absorptions of H\(_2\)O, HDO, CO\(_2\), O\(_3\), N\(_2\)O, CH\(_4\), NO\(_2\), HCl, OCS, CH\(_3\)OH are considered. The spectroscopic parameters of these gases are from HITRAN 01 for CH\(_4\), HITRAN 08 for the others (Rothman et al., 2009). The spectral line shape is assumed to be the Voigt function. Simulation effect for a spectrum measured at Bremen is shown in Fig. 3.12.

The state vector consists of CH\(_4\) mole fractions at discretized levels, scale factors for a prior profiles of all interfering species except for O\(_3\), OCS and CH\(_3\)OH, and some other parameters. A prior profiles of CO\(_2\), N\(_2\)O, H\(_2\)O and HDO are taken as GFIT a priors (the GFIT a priors of H\(_2\)O and HDO are basically from NCEP reanalysis data). The climatologies of the Whole Atmosphere Community Climate Model (WACCM) are used as a prior profiles of other species. Because the spectra do not contain full information of CH\(_4\) profiles, a first-order Tikhonov-Phillips constraint is applied to constrain variabilities of its profile shape. CH\(_4\) retrieval is performed on a logarithmic scale. The degrees of freedom for signal (DOFS) is about 2.6 for Bremen spectra and 2.3 for Ny-Ålesund's. The a posterior correction (Sepúlveda et al., 2014) is applied to the retrieved CH\(_4\) profiles to separate the stratospheric and tropospheric signals further. The corrected CH\(_4\) profiles and corresponding averaging kernels at Ny-Ålesund are shown in Figure 3.13.

The tropospheric CH\(_4\) mole fraction is derived from the retrieved profiles through averaging mole fractions at the lowest six levels (up to about 2 km). The averaging kernels of the tropospheric CH\(_4\) are shown in red lines in Fig. 3.13. In contrast to the almost uniform weights in the troposphere of TCCON CH\(_4\) retrieval, the tropospheric CH\(_4\) from the profile retrieval has large weight in the lower troposphere with a peak at about 3 km.
Figure 3.12 The five microwindows used for the retrieval of CH$_4$ profiles for an example spectrum at Bremen. Lower panel is the transmission with black points representing measurements and black line representing simulation. Upper panel are the differences between the measurement and simulation.

Figure 3.13 The averaged CH$_4$ profiles and its characteristics at Ny-Ålesund in the period 2007-2012. Left panel is the a prior (dashed line) and average of retrieval (solid line, error bar is the standard deviation). Right panel is the average of averaging kernel, with the red lines representing averaging kernels of CH$_4$ mole fractions at lowest six layers.

The second peak of the averaging kernels of the tropospheric CH$_4$ is at about 20 km, which could
bring variabilities of stratospheric CH$_4$ though the amplitude is much smaller than that of the peak in the troposphere. The tropospheric column-averaged CH$_4$ mole fraction from the profile retrieval is referred to lower tropospheric xCH$_4$ hereafter.

3.2.3. Comparison with a posterior correction method and in situ data

![Figure 3.14](image)

Figure 3.14 The tropospheric column-averaged CH$_4$ mole fraction from the posterior correction method using N$_2$O (red pluses) and lower tropospheric column-averaged CH$_4$ mole fraction (blue crosses) at Ny-Ålesund (mid panel) and Bremen (lower panel). Black circles represent in situ surface CH$_4$ measured at Zeppelin mountain (upper panel) and Mace Head (lower panel). Upper panel is the difference of FTS CH$_4$ to in situ CH$_4$ at Ny-Ålesund, difference is not performed at Bremen because of the large distance between the FTS and in situ sites. Daily medians are shown for all measurements.

In Fig. 3.14 the lower tropospheric xCH$_4$ is validated empirically with in situ surface measurements and compared with the tropospheric xCH$_4$ from the N$_2$O correction method. As expected the lower
tropospheric x\(CH_4\) has a better agreement with the in situ measurements than the tropospheric x\(CH_4\) at Ny-Ålesund in terms of the absolute value and seasonal cycle. The in situ measurements could represent lower tropospheric \(CH_4\) concentrations because of quite clear air conditions there, and have a closer meaning with the lower tropospheric x\(CH_4\). Both the tropospheric and, especially, lower tropospheric x\(CH_4\) present larger scatters than in situ measurements at Bremen. The reason could be the FTS observation at Bremen is conducted in the City of Bremen, while the in situ samples mostly represent marine boundary air. But the large scatter in the lower tropospheric x\(CH_4\), like in 2009 and 2010, could also come from some instability of the instrument, such as alignment variabilities and mechanical perturbations. The \(CH_4\) retrieval by GFIT is performed with three large spectral windows (116, 11 and 138 cm\(^{-1}\) wide, respectively), and the \(O_2\) column retrieved from the same spectra is used to infer the dry air column. Then the tropospheric x\(CH_4\) should be much less sensitive to instrumental perturbations than the lower tropospheric x\(CH_4\). Due to a higher requirement of profile retrieval for the accuracy of molecular spectroscopy, only a set of microwindows is used where spectral residuals between simulations and measurements are small. Line-mixing has been shown to be important but is not included in simulating molecular absorption here (Tran et al., 2006), which adds an asymmetrical component to the Voigt function.

### 3.3. Summary

In this chapter, we propose using N\(_2\)O to correct for the stratospheric contribution to the total column of \(CH_4\) in order to derive a tropospheric x\(CH_4\) mole fraction. This method is applied to data from four TCCON sites. At Ny-Ålesund and Orléans, the tropospheric \(CH_4\) derived using N\(_2\)O and HF are compared with surface flask measurements and low aircraft profiles, respectively. At both sites, the results using N\(_2\)O agree better with in situ measurements than the HF derived results. The mean relative standard deviations are 0.23 % and 0.52 % for the methods using N\(_2\)O and HF, respectively. Especially, at Darwin the HF method produces a much larger uncertainty (0.93 % compared with 0.15 % of N\(_2\)O method) due to interference from H\(_2\)O, which is absent for the N\(_2\)O method. Under drier conditions, the relative uncertainties of the two methods are comparable, however the N\(_2\)O method shows a clear advantage in more humid situations. The methods have also been compared with aircraft profiles at three sites, and the results reveal that the N\(_2\)O method has a better inter-site consistency. However, it needs to be verified across a wider range of sites. The sensitivity of the N\(_2\)O method to the assumed tropospheric N\(_2\)O mole fraction is about 4-6 ppb per 2 ppb.

The directly profile retrieval for tropospheric \(CH_4\) is examined and compared to the proposed a posteriori correction method using spectra measured at Ny-Ålesund and Bremen. The profile retrieval method has a large weight in the lower troposphere in contrast to an almost uniform weight of the proposed method in the whole troposphere, and then could reflect the sources and sinks of \(CH_4\) more directly. There is a larger scatter in the results from the profile retrieval, which could arise from a larger sensitivity of the profile retrieval to measurements error and usage of the retrieved \(O_2\) column as the dry air column in the proposed method.
4. Validation of European CH$_4$ models using ground-based and satellite measurements

It is always important to validate model simulations with independent measurements. Given sources and sinks of GHG (greenhouse gas) and meteorological fields a chemical transport model predicts mole fractions of GHGs in the atmosphere. Inverse modeling goes in the opposite direction, retrieving the sources and sinks of the GHG from measured mole fractions. The theory of the inverse modeling can be described by Eq. 2.3 and 2.4 as well, which search for a solution minimizing the function given by Eq. 2.4. The forward function is replaced by the chemical transport model, and the measurements usually are mole fractions at surface provided by global networks and total columns from space-based remote sensing. A prior knowledge is usually provided by process-based models of sources and sinks. Because direct measurements of the sources and sinks are rare, the evaluation of simulated mole fractions with independent measurement is an important step to assess the quality of the retrieved sources or sinks. In this chapter, CH$_4$ mole fractions predicted by three inverse modeling systems, TM3, TM5-4DVAR and LMDz-PYVAR, are compared with ground and space-based remote sensing and in situ measurements.

4.1. Description of measurements

The tropospheric xCH$_4$ is derived with the posterior correction using N$_2$O as described in Chapter 3. But approximate averaging kernels, which are from interpolations in SZA to a set of reference averaging kernel, are applied. With the tropospheric CH$_4$ known, the stratospheric column-averaged CH$_4$ mole fraction is easily calculated given tropopause pressure, which is from NCEP reanalysis here.

The tropospheric xCH$_4$ derived using the approximate averaging kernel is validated against in situ measurements. The validation method is the same as in Sect. 3.1.5 except for using the approximate averaging kernels. The same aircraft campaigns HIPPO and IMECC, which has been described in Sect. 3.1.2, together with Aircore measurements are used. Figure 4.1 presents the calibration results, the mean distance between scatter points and the fitted line is 3.0 ppb, with a standard deviation of 2.0 ppb.

The TCCON sites referred in this study are list in Table 4.1.

The CH$_4$ profiles retrieved from mid-infrared spectra measured at NDACC sites Bremen and Ny-Ålesund in Sect. 3.2 are compared to model simulations. The derived lower tropospheric xCH$_4$ and partial stratospheric column are compared with model outputs as well.
Table 4.1. Overview of TCCON sites used for evaluation of models.

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<th>TCCON site</th>
<th>Latitude/°N</th>
<th>Longitude/°E</th>
<th>Altitude/masl</th>
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<td>130.891</td>
<td>30</td>
</tr>
<tr>
<td>Reunion Island</td>
<td>-20.901</td>
<td>55.485</td>
<td>87</td>
</tr>
<tr>
<td>Wollongong</td>
<td>-34.406</td>
<td>150.879</td>
<td>30</td>
</tr>
<tr>
<td>Lauder</td>
<td>-45.038</td>
<td>169.684</td>
<td>370</td>
</tr>
</tbody>
</table>

The used surface CH$_4$ measurements are from NOAA/ESRL network and a Tall Tower station (Trainou tower, TRN) (Schmidt et al., 2014). For the tower measurements, the air sample at 180 magl is selected.

The CH$_4$ profiles from HIPPO-1 to 5 missions (Wofsy et al., 2011) are used to validate simulated CH$_4$ concentrations. The measurements use a quantum cascade laser spectrometer (QCLS). Calibrations derived through comparisons with NOAA Programmable Flask Package (Bergamaschi, et al., 2013; Alexe et al., 2015) are applied, which are 3.5, 3.9, 6.0, 4.5 and 5.2 ppb for the five HIPPO missions, respectively.

GOSAT measurements are the total column-averaged dry-air CH$_4$ mole fraction retrieved by the (UoL-OCPRv5.1) algorithm (Parker et al., 2011). For the retrieval, the CO$_2$ proxy method (Frankenberg et al., 2011) is applied which infers air columns from the CO$_2$ column retrieved from the same spectra used for CH$_4$ retrieval. CH$_4$ and CO$_2$ are retrieved from channels at 1.65 μm and 1.61 μm respectively. Only spectra measured with clear sky condition are taken into account.
ACE-FTS (Atmospheric Chemistry Experiment) is the main instrument on board the Canadian Space Agency SCISAT-1 satellite. It is a high spectral resolution (0.02 cm⁻¹) FTS that measures in a solar occultation mode, tracking the sun during sunrise and sunset from a 74°, 650 km near circular orbit. This allows it to measure vertical profiles of CH₄ within the ~6 to 75 km range covering all latitudes between approximately 85°N and 85°S (Bernath et al., 2005). The data used in this study corresponds with version 3.5.

MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) is a Fourier transform infrared (FTIR) spectrometer aboard ENVISAT (Fischer et al., 2008) for the detection of limb emission spectra in the middle and upper atmosphere. It acquires spectra over the range 685-2410 cm⁻¹. The primary geophysical parameters of interest are vertical profiles of atmospheric pressure, temperatures, and volume mixing ratios of about 25 trace constituents. The product used here is operational V6 data processed by ESA.

4.2. Description of models

A chemistry transport model describes the evolution of atmospheric compositions by solving the continuity equation, which is a mathematical representation of the principle of conservation of mass. In the case where the effect of molecular diffusion can be neglected, the continuity equation can be expressed as,

\[ \frac{\partial x_i}{\partial t} = -\vec{v} \nabla x_i + P(\vec{x}) + L(\vec{x}), \]  

(4.1)

where \( x_i \) is the mole fraction of the interested composition, \( \vec{v} \) is wind vector, \( P \) and \( L \) are production and loss rates of the composition, which are functions of all species that react with the interested one in the atmosphere, collected in the vector \( \vec{x} \). The wind field is prescribed from other sources before integrating Eq. 4.1, such as reanalysis meteorological data. In practice the continuity equation must be discretized onto model grids. There are always atmospheric motions occurring at a scale smaller than the model grid scale because the atmosphere is a continuum. The transport of atmospheric composition by sub-scale motions is usually parameterized through relating to variables at the model grid. One is the eddy diffusion parameterization that treats the composition transport induced by turbulent motion of air in a way of treating molecular diffusion. Wet convective motion is another small-scale motion, and usually related to large-scale convergences and vertical instabilities. The production and loss term involves solving chemical kinetic equations, which usually account for more species than the interested species. Except for chemical reactions, the exchange between the earth surface and the atmosphere also produces or removes species. The dry deposition is the uptake of atmospheric species at the surface of the earth, and the surface can emit species as well. The uptake and emission fluxes provide a surface boundary condition for the continuity equation. Precipitation in the atmosphere scavenges soluble gases, which acts as a loss term. The chemical transport model differs in meteorological data used, discretization methods, parameterizations of small-scale motions, descriptions of production and loss processes, and
integration methods.

<table>
<thead>
<tr>
<th>Model</th>
<th>Institute</th>
<th>Resolution (lat×lon)</th>
<th>No. of model levels</th>
<th>output Time step (hour)</th>
<th>Meteorology</th>
</tr>
</thead>
<tbody>
<tr>
<td>TM3</td>
<td>Max Plank Institute for Biogeochemistry</td>
<td>4×5</td>
<td>26</td>
<td>3.0</td>
<td>ERA-Interim</td>
</tr>
<tr>
<td>TM5-4DVAR</td>
<td>European Joint Research Centre</td>
<td>1×1 for Europe, 6×4 for the rest of world</td>
<td>25</td>
<td>1.5</td>
<td>ECMWF-IFS</td>
</tr>
<tr>
<td>LMDz-PYVAR</td>
<td>Laboratoire des Sciences du Climatet de l'Environment</td>
<td>2.5×3.75</td>
<td>19</td>
<td>3.0</td>
<td>Prediction by LMDz</td>
</tr>
</tbody>
</table>

Table 4.2. The models used in the comparison with solar absorption measurements.

The details of the models are listed in Table 4.2. The important chemical reactions involving CH₄ in the atmosphere is oxidations by OH in the troposphere, and by OH, Cl and O(¹D) in the stratosphere. The concentrations of these radicals are prescribed based on other model outputs, for example, tropospheric OH fields based on Carbon Bond Mechanism 4 chemistry and stratospheric radicals based on a photochemical model are applied in TM5-4DAVR inversion (Bergamaschi et al., 2009). The outputs of TM3 are from an inversion spanning from 2005 to 2012, and those of LMDz-PYVAR are from an inversion covering 2007 to 2011. TM5-4DVAR outputs are from a 6 year inversions series 2007-2012, consisting of 6 individual 14-month inversions, each of them includes 1 month spin-up and 1 month spin-down. Only in situ measurements at surface are used in the inversion run of the models, involved sites are presented in Figure 4.2. Detailed information on the inversion methodology was discussed in Bergamaschi et al. (2015).

The details about the global atmospheric tracer model TM3 can be found in Heimann and Köerner (2003) and inversion method is described in Rödenbeck (2005). TM5-4DVAR is a four-dimensional variational data assimilation system for inverse modeling of atmospheric methane emissions (Meirink et al., 2008). The system is based on the TM5 atmospheric transport model (Krol et al., 2005). LMDz-PYVAR is a framework that combines the inversion system PYVAR (Chevallier et al., 2005) with the transport model LMDz (Hourdin et al., 2006).

For evaluations of the model, model simulations are matched to measurement through interpolations in time, latitudes, longitudes and pressure. For the total and tropospheric column-averaged CH₄ the model profile is integrated taking a priori and averaging kernel into account.
according to Rodgers and Connor (2003), and actually Eq. 3.9 and 3.11 are applied.

### 4.3. Comparison between FTS and surface measurements

The difference between the tropospheric xCH$_4$ and surface CH$_4$ mole fractions qualitatively reflects a vertical gradient of CH$_4$ in the troposphere. However, surface measurements are influenced by the turbulence and local emissions in the boundary layer while the tropospheric xCH$_4$ mainly reflects CH$_4$ in the free troposphere. To reduce this difference long-term trends are extracted from their time series. The TCCON and corresponding in situ sites are selected to locate closely so that the two kinds of instrument measure similar airmass. The sites used are listed in Table 4.3.

<table>
<thead>
<tr>
<th>FTS site</th>
<th>In situ site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Lat/°N</td>
</tr>
<tr>
<td>Ny-Ålesund</td>
<td>78.923</td>
</tr>
<tr>
<td>Sodankylä</td>
<td>67.367</td>
</tr>
<tr>
<td>Orléans</td>
<td>47.965</td>
</tr>
<tr>
<td>Park Falls</td>
<td>45.945</td>
</tr>
<tr>
<td>Lamont</td>
<td>36.604</td>
</tr>
<tr>
<td>Izaña</td>
<td>28.300</td>
</tr>
<tr>
<td>Lauder</td>
<td>45.038</td>
</tr>
</tbody>
</table>

Table 4.3. The sites used for comparison of FTS tropospheric column-averaged CH$_4$ mole fraction and in situ surface/tower CH$_4$ mole fraction.

A curve fitting procedure similar to that described in Dlugokencky et al. (1994) is applied to extract a long-term variation in which variabilities with temporal scale shorter than 1.4 years is filtered out. Firstly, a daily median series is constructed from original data. Then a curve that is a quadratic polynomial and a series of four harmonics is fitted to the daily median series. The Kolmogorov-Zurbenko (KZ) filter (Eskeidge et al., 1997) is applied to the residual between data and the fitted curve to extract variations with periods greater than 1.4 years. Then the long-term variation is obtained via adding the quadratic function and extracted variation. The procedure is used iteratively and values outside 2.8 standard deviations are removed at each step until no outliers are recognized.

Figure 4.3 shows a comparison between the long-term variations and increases of measured tropospheric xCH$_4$ and in situ surface CH$_4$. The difference between the tropospheric xCH$_4$ and in situ surface CH$_4$ reflects a mean vertical gradient of tropospheric CH$_4$, which is influenced by
surface emissions, transports and OH fields. Generally there are negative vertical gradients in the northern hemisphere and positive vertical gradients in the southern hemisphere (except for above southern continents with strong emissions). Here we refer to decreasing CH$_4$ mole fractions with altitudes as a negative vertical gradient, while increasing CH$_4$ with altitudes is a positive vertical gradient. This occurs because most CH$_4$ is emitted at northern surfaces and mixed into southern air and transported by the southward branch of the southern hemispheric Hadley cell, which prevails in the mid and upper troposphere. In the troposphere, surface emissions cause decreasing CH$_4$ with altitudes, while OH oxidations cause a positive vertical gradient.

In the absence of horizontal transports and OH oxidations, the growth rate of the tropospheric xCH$_4$ would be smaller than, and follows the variations of the surface CH$_4$. As shown in Fig. 4.3, there are significant positive anomalies in the surface CH$_4$ growth rate during 2007 for all sites. This is consistent with other studies (Dlugokencky et al., 2009) and was attributed to wetland emissions. As a result, the CH$_4$ vertical gradient becomes more negative at all sites. However, as can be seen from Fig. 4.3, there are many cases where tropospheric xCH$_4$ presents a larger growth rate, or its growth rate rises faster than that of the surface CH$_4$ and sometimes even rises when the growth rate of the surface CH$_4$ drops. The CH$_4$ vertical gradient at Ny-Ålesund has significantly changed toward positive since 2008 (increases about 15 pbb) compared to other sites except for Park Falls. These results could reveal that there is CH$_4$ from lower latitudes transported into the mid to upper troposphere over this site during that time.

At Park Falls, the CH$_4$ vertical gradient also significantly changes toward positive since 2008 but with more fluctuations than Ny-Ålesund. However, both the tropospheric xCH$_4$ and surface CH$_4$ mole fractions increase in this period, which means there are strengthening surface emissions and would have change the gradient toward negative. The positive change of the gradient could be caused by OH, because strengthening of a loss via reactions with OH will depress increase trends in tropospheric CH$_4$ due to increases in surface emissions, but to a larger extent for surface CH$_4$. Such an explanation could apply to cases when surface CH$_4$ has smaller growth rates than the tropospheric xCH$_4$ at sites over which without horizontal transports induced additions of CH$_4$. At sites in the southern hemisphere, the annual variability in North-South transports will play an important role, which changes CH$_4$ in the mid and upper troposphere more directly. The surface CH$_4$ is influenced by southern emissions as well, e.g. natural wetlands and agriculture in South America and southern part of Africa. The change in the vertical gradient of tropospheric CH$_4$ could be a result of combined effects of transport, surface emissions and OH.
Figure 4.1. Validation results of FTS derived tropospheric column-averaged CH₄ mole fractions with in situ measurements. The in situ profiles are smoothed using GFIT CH₄ averaging kernels in troposphere as described in Sect. 3.1.5. The FTS data are averaged through the aircraft measurements periods.

Figure 4.2. Global distribution of surface sampling/in situ sites at which measurements are assimilated into TM3 (square), TM5-4DVAR (diamond) and LMDz-PYVAR (horizontal line) in their inversion run.
Figure 4.3. Comparison between FTS derived tropospheric column-averaged CH₄ and in situ surface/tower CH₄. In the left panel, the black and blue crosses represent the daily median of in situ CH₄ and tropospheric column-averaged CH₄, respectively. The curves are fitted long-term variations with time scale longer than 1.4 years. The lines in the right panel represent the difference between the long-term variations of tropospheric and in situ CH₄ (black), and the long term increase rate of tropospheric (green) and in situ (blue) CH₄.

4.4. Comparison between measurements and models

4.4.1. FTS, GOSAT and HIPPO

Temporal variabilities of the difference between models and FTS of the tropospheric and total xCH₄ is given at selected sites in Fig. 4.4. The measured tropospheric xCH₄ rises faster than the modeled since 2009 at Ny-Ålesund and Sodankylä. The differences (model – FTS) change from about 20 ppb to 10 ppb for TM3 and TM5-4DVAR, 10 ppb to 0 ppb for LMDz-PYVAR during 2009-2011.

The measured vertical gradient of tropospheric CH₄ changes toward positive since 2009 at Ny-Ålesund as shown in Fig. 4.3. But the models did not capture such a variation in the vertical
Differences between the long-term variations of tropospheric xCH₄ and surface CH₄ change about 5 ppb during the period 2007-2012 for all three models (see Fig. 4.5), much smaller than the measured 15 ppb during 2009-2013. It is shown in this section that all models underestimate the absolute value of the vertical gradient of tropospheric CH₄ at almost all TCCON sites. As said before, the measured change of 15 ppb could be caused by a CH₄ addition in mid and upper troposphere caused by transports from lower latitudes. Since the difference in CH₄ concentrations between in mid or upper troposphere and at surface is smaller in the models than in reality, the strengthening effect of input CH₄ is then depressed. This could explain the smaller increase of tropospheric xCH₄ in the models.

Figure 4.4. Differences of total (right) and tropospheric (left) column-averaged CH₄ concentration between FTS measurements and model simulations at European sites. The differences are shift for clarity and black dash line indicate zero position for each site. The increment of Y-axis is 30 ppb. The green, blue and yellow points represent difference between FTS measurement and TM3, TM5-4DVAR and LMDz-PYVAR simulations. Each point is the average over 7 days.
Figure 4.5. Anomalies of measured (black) and simulated (yellow: TM3; blue: TM5-4DVAR; green: LMDz-PYVAR) vertical gradient of CH$_4$ in the troposphere with respect to their averages. The anomalies have been shifted for clarity and dashed line indicate zero level for each site.

The CH$_4$ column meridional distribution is sensitive to the latitudinal distribution of CH$_4$ sources and sinks, tropopause altitudes, inter-hemisphere transport in the troposphere, and the residual circulation in the stratosphere. Assessing latitudinal variabilities of biases of a model could reveal how well these processes are represented in the model. Another important concern is to show whether model biases in the troposphere or the stratosphere contribute more to the total bias. The model to FTS comparison is for the period 2007-2011 when FTS measurements are available and the comparison to GOSAT is for the period 2009-2011.

The latitudinal behavior of the model biases in total, tropospheric and stratospheric xCH$_4$ are revealed by comparisons to FTS and GOSAT measurements as presented in Figure 4.6 and 4.7. CH$_4$ is emitted mainly in the northern hemisphere, destroyed mainly in the tropics by OH and has a slow inter-hemisphere transport on a temporal scale of 1 year. These factors altogether result in the final latitude distribution of CH$_4$ shown in Fig. 4.6, 4.7. The model biases present a latitudinal dependence in both the troposphere and stratosphere, and the latitudinal behavior is consistent.
between FTS and GOSAT. Similar results were shown by other studies (Alexe et al., 2015; Ostler et al., 2016), which compared models against TCCON total xCH₄. In the troposphere, the model bias in the troposphere present a North-South gradient with positives at northern high-altitudes northward of 50°S. Figure 4.8 shows latitudinal variations of the measured and simulated vertical gradients of tropospheric CH₄. There are mostly positive biases in mid and high northern latitudes, negative ones in other latitudes. So the overestimated tropospheric CH₄ in mid to high northern latitudes could not originate from too strong emissions, which should result in a more negative vertical gradient there. The models underestimate absolute values of the vertical gradient of tropospheric CH₄. A too strong convection mixing can lead to a vertically uniform distribution of CH₄ in the troposphere. However, it could not be a reason to the incorrect vertical gradients here. The underestimation at high latitudes has similar amplitudes with that at lower latitudes, but convection mixing should be much weaker in high latitudes.

With FTS derived tropospheric and stratospheric xCH₄ (Wang et al., 2014) it is possible to examine how the tropospheric and stratospheric columns contribute to the model bias in total xCH₄. Figure 4.9 shows yearly and seasonal median model biases scaled by air column fractions of the troposphere and stratosphere. It is clear that model biases in the troposphere exhibit a North-South gradient with positive values in northern high-latitude during all seasons for all models. In the stratosphere model biases do not present any clear latitudinal pattern that exists through the whole year, and show significant seasonal variabilities for TM3 and TM5-4DV AR. That is consistent with the fact that stratospheric CH₄ distributions cycle between summer and winter hemispheric states. The stratospheric bias of LMDz-PYVAR shows a ‘U’ shape with the minimum located in the tropics. Comparing to Fig. 4.6 one can see that the latitudinal pattern of model biases in total xCH₄ results from both the stratosphere and troposphere for LMDz-PYVAR, but arises from the troposphere for the other two models. Because model biases change signs yearly and seasonally it is more appropriate to use the amplitudes (absolute model to FTS differences) to evaluate contributions of the troposphere and stratosphere, as shown in Fig. 4.10. The medians of model bias amplitudes over all FTS sites and years are 7.4±5.1 ppb in the troposphere and 4.3±9.9 ppb in the stratosphere for TM3, 6.72±4.8 ppb and 4.7±9.9 ppb for TM5-4DV AR, and 7.1±5.6 ppb and 10.3±15.9 ppb for LMDz-PYVAR. So the stratosphere dominates in model biases of LMDz-PYVAR but contributes less or comparably with the troposphere for the two other models.

Evaluations of the models at the surface with in-situ measurements, which are assimilated into the models, show smaller biases than the tropospheric xCH₄. The amplitudes are mostly below 10 ppb in the northern hemisphere except for a few outliers and below 5 ppb in the southern hemisphere (not show). The model biases at the surface do not show any significant latitudinal dependence. It is not clear how the model biases at the surface look like in the regions where no measurements are assimilated. However, it could be true that the overestimation of the tropospheric CH₄ meridional gradient is due to model biases in the mid and upper troposphere. That means, vertical distributions of CH₄ in the troposphere are not represented correctly in the models.
Figure 4.6. Annual mean total, tropospheric and stratospheric column-averaged CH$_4$ mole fractions plotted as a function of latitude. The upper panel is the results of FTS measurements while the lower panels is the difference between the measurements and the TM3 (yellow), TM5-4DVAR (blue) and LMDz-PYVAR (green) simulations. The annual mean is calculated as yearly mean of the fitted long-term variation. Medians over all time, and also split into different seasons, are shown for the differences.
Figure 4.7. Total column-averaged CH₄ mole fraction measured by GOSAT (upper panel) and difference with simulations by the models (lower panel). The results are averaged over the period 2009-2011 and along longitude, with a latitude bin of 4°. Both averages for whole year (marked solid line) and different seasons (DJF: solid; MAM: dashed; JJA: dotted; SON: dash dot) are shown. The yellow, blue and green points represent results for TM3, TM5-4DVAR and LMDz-PYVAR respectively.

Figure 4.8. Measured (black) and simulated (yellow: TM3, blue: TM5-4DVAR, green: LMDz-
vertical gradients of CH$_4$ in the troposphere (top panel) and differences between the measurement and simulations (lower panel) against latitude.

Figure 4.9. Yearly and seasonal medians of the stratospheric and tropospheric contributions in modeled total column biases at TCCON sites. The white bar denotes the tropospheric bias, the grey bar the stratospheric bias. The scale factor for the model bias is the air column fraction $P/1000$ (stratosphere) and $(1-P/1000)$ (troposphere), where $P_t$ is the tropopause pressure. The standard deviations of the bias amplitudes are shown separately for the troposphere (black error bar) and the stratosphere (blue error bar). The results are averaged for 2007-2011 where FTS measurements are available.
Figure 4.10. Same as Fig. 4.9 except for medians of model bias amplitudes (absolute model to FTS differences). The standard deviations of the bias amplitudes are shown separately for the troposphere (black error bar) and the stratosphere (blue error bar).
Figure 4.11. HIPPO measured CH$_4$ distribution in the stratosphere (short panel) and the troposphere (high panel) and differences with model simulations. The results are averages for five HIPPO missions, for latitudinal bins of 4° and vertical increments of 10 hPa.

Figure 4.11 shows a comparison between model simulations and HIPPO measurements. The results are averaged for all five HIPPO missions and longitudinally, and within grids of 4° latitude and pressure increments of 10 hPa. A significant feature is an overestimation of CH$_4$ in the lowermost stratosphere over latitudes higher than 30°S/N, much larger than the biases in the troposphere. It is not clear whether the overestimation arises from the residual transport in the stratosphere, which appears to be too strong, a too high tropopause or an incorrect vertical CH$_4$ gradient across the tropopause. Underestimations dominate in the southern troposphere, especially in upper southern troposphere, consistent with the observation that modeled gradients of tropospheric CH$_4$ are biased negative as revealed by FTS and surface measurements. There are no significant patterns for the vertical gradient bias in the northern troposphere. The model biases in the tropospheric xCH$_4$ revealed by HIPPO do not present a significant latitudinal trend as that by FTS (not shown). If the tropopause is shifted 200 hPa upward to include the lower stratosphere with high overestimated CH$_4$, the model biases comparing with HIPPO become closer to that by FTS. In deriving FTS tropospheric CH$_4$ the stratospheric CH$_4$ is removed by its linear correlation with N$_2$O. The tropopause in the FTS data therefore has a chemical definition. The difference between the
thermal/dynamical tropopause used in integrating HIPPO measurements and the chemical one could lead to the different behaviors of tropospheric model biases as revealed by FTS and HIPPO. If this is true, such an explanation could be applied to the North-South gradient in the tropospheric model biases shown in Fig. 4.6.

### 4.4.2. Stratospheric satellite

To further assess the ability of the models to capture the stratosphere and upper troposphere we look at comparisons with ACE-FTS. Figure 4.12 shows CH$_4$ concentrations along the latitude and altitude, while Fig. 4.13 shows the median (Model – ACE-FTS) bias per season. As one can see, there is a significant difference to what extent the models capture the entire profile. The typical vertical profile of CH$_4$ consists of quasi-constant concentrations in the upper troposphere to lower stratosphere after we see a sharp decrease to low upper stratosphere concentrations.

Compared to ACE-FTS TM3’s tropospheric concentration levels reach higher altitudes after which they see a sharper drop to reach upper stratospheric concentration levels that are slightly lower than those obtained by ACE-FTS. This is featured across all latitude bands, however the concentration difference is stronger at higher latitude bands. TM5-4DVAR shows the best agreement with ACE-FTS concerning its profile shape. Its upper stratosphere concentrations are slightly overestimated but the position of the gradient is generally well executed. LMDz-PYVAR’s vertical profile sees a clear mismatch with respect to ACE-FTS as a function of latitude. At higher latitudes lower stratosphere concentrations are clearly overestimated, while at the tropics the sharp decrease to upper stratosphere values occur at a much lower altitude as compared to ACE-FTS, thus significantly underestimating the CH$_4$ concentrations here. Also, (uniform for all latitude bands) all upper stratosphere concentrations are clearly overestimated.

Differences in the stratospheric CH$_4$ between the models and MIPAS are generally similar to the difference with ACE-FTS during 2009-2011 (not shown). However, MIPAS agrees with the models better than ACE-FTS in the lower stratosphere where the later mostly reveals an overestimation by the models. A comparison of the stratospheric xCH$_4$ between MIPAS and the models is given in Figure 4.14. Except for TM3 in the northern hemisphere, significant differences occur during polar vortex period (about 120 ppb higher than yearly median differences). The large differences are also reflected in the difference of total xCH$_4$ revealed by GOSAT, whose value peaks during Sep-Oct-Nov period southward of 60°S (no measurements during northern the polar vortex period northward of 60°N). The latitudes 20°S~60°S with negative differences correspond to the region with both horizontal and vertical uniform CH$_4$ as described in Sect. 4.4.3. For TM3 and TM5-4DVAR, the yearly median difference between models and MIPAS is about 10~20 ppb in 20°N-80°N. It is larger than the bias revealed by FTS (-10~10 ppb) in these latitudes, but is misleading due to different averaging periods (2009-2011 in the case of MIPAS). The difference between the simulated and FTS measured stratospheric CH$_4$ presents interannual variabilities, increases from -35~6 ppb of 2007 to -6~27 ppb of 2011 at sites in the northern hemisphere for TM3 and TM5-4DVAR. The difference in the stratospheric CH$_4$ between models and MIPAS also gives significant increase from
-5~10 ppb of 2009 to about 20~40 ppb of 2011 in 20°N-80°N.

Figure 4.12. Median CH₄ concentrations as a function of latitude and altitude spanning the 2009-2011 period for ACE-FTS, TM3, TM5-4DVAR and LMDz-PYVAR.
Figure 4.13. Median Model - ACE-FTS biases as a function of altitude and latitude for different seasons (DJF = December-February, MAM = March-May, etc) and models (left TM3, mid TM5-4DVAR and right LMDz-PYVAR) spanning 2009-2011 period.

Figure 4.14. Stratospheric column-averaged CH$_4$ mole fraction measured by MIPAS and simulated by models (upper panel), and difference between the simulations and measurements (lower panel). The results are medians over the period 2009-2011 and along longitude, within a latitude bin of 4°. Both medians for whole year (points) and different seasons (DJF: solid; MAM: dashed; JJA: dotted; SON: dash dot) are shown. The yellow, blue and green points represent results for TM3, TM5-4DVAR and LMDz-PYVAR respectively.

4.4.3. Diagnose by Equivalent length

The equivalent length ($L_e$) is a useful tool to quantify isentropic mixing properties in the atmosphere, which is a measure of the complexity of tracer distribution (Nakamura, 1996; Nakamura and Ma, 1997; Haynes and Shuckburgh, 2000). In the 2D case this quantity is just the length of constant tracer concentration lines if the gradient of the tracer does not change along the isolines. Mixing processes stir and scramble tracer contours and increase its complexity and then enlarge $L_e$.

If looking at stratospheric CH$_4$ distributions in Fig. 4.12 into more details, an uplift region with relative high CH$_4$ concentrations presents in 25°S~25°N and 20~33 km. This is the tropical
reservoir, which has weak mixing with extratropical air (Trepte and Hitchman, 1992). Among the models, TM5-4DV AR and TM3 represent high CH\(_4\) concentration in the reservoir more or less, but the reservoir is nearly absent in LMDz-PYVAR. This is why LMDz-PYVAR modeled CH\(_4\) decreases too quickly with altitudes in the tropics. The contrast in CH\(_4\) concentrations between interior and exterior of the reservoir depends partly on the strength of the subtropical barrier and mixing process in extratropics. The formation of tracer concentration gradients is a result of differential mixing strength, which means small mixing in the barrier region and strong mixing in one or both sides of the barrier (Nakamura, 1996, 1997). This mechanism is applied to both the subtropical barrier and polar barrier (a region having strong tracer gradients and separating air inside polar vortex with that in mid-latitudes). In this part we calculate \(L_e\) from MIPAS measured and modeled CH\(_4\) fields in the stratosphere. The calculation is done on isentropic surfaces in a range 450\textendash2000 K (~18 to 49 km) in a period 2009-2011. An annual cycle of CH\(_4\), \(L_e\) and the zonally mean zonal wind in the stratosphere is show in Figure 4.15. In this cycle the polar vortex beak and rebuilt in the southern hemisphere, and built and break in the northern hemisphere.

In Oct. 2009 the southern polar vortex is still strong, large meridional CH\(_4\) gradients around 60\(^\circ\)S, although it start to break at levels around 1250 K (~38 km), isolines of CH\(_4\) bend toward the pole there. In latitudes approximately 60\(^\circ\)S\textendash30\(^\circ\)S it is the surf zone, which is formed by wealthy wave breaking of planetary waves propagating upward from the troposphere. The planetary wave breaking results into isentropic mixing of tracers, and then a meridional uniform distribution. The measured large \(L_e\) and uniform CH\(_4\) along latitudes in the surf zone is consistent with our knowledge. However, in levels 450\textendash850 K (about 18\textendash30 km) the CH\(_4\) in the surf zone is also almost uniform in the vertical direction. There should be vertical mixing there since CH\(_4\) generally decreases with altitudes in the stratosphere. Some gravity-type waves are necessary to produce vertical disturbances instead of the planetary wave. At about 45\(^\circ\)N the northern surf zone started to develop as indicated by a vertically long zone, mostly visible in levels 650\textendash1850 K, with a little larger than its surroundings \(L_e\).

Large \(L_e\) occurs in the latitudes 30\(^\circ\)S\textendash30\(^\circ\)N as well, but is inconsistent with the results shown in Haynes and Shuckburgh (2000). In their modeled tracer fields the tropics is usually a calm region. However large \(L_e\) does not always mean strong isentropic mixing, and can be produced from diabatic movements as well. Motions cross isentropic surfaces produce anomalies on CH\(_4\) contours on an isentropic surface due to decreasing CH\(_4\) with altitudes. In the upper stratosphere there are diabatically vertical motions associated with the semiannual oscillation (SAO) (Kennaugh et al., 1997). Indeed, there are some correlations between the large \(L_e\) in the tropical stratosphere and the double peak structure in latitude-altitude cross sections of CH\(_4\) in the three years results. Except for the diabatic motions, isentropic mixing is possible in the tropical stratosphere. The vertical motions in SAO are resulted from zonal forces which are due to wave breaking events. Another example is the 2-day wave (Rojas and Norton, 2007), which peaks in the mesosphere and can propagate downward to 40 km (~1350 K) and has the maximum meridional perturbation at the equator. Another difference with the results in Haynes and Shuckburgh (2000) is the highest \(L_e\) occur
poleward of 70°S/N. In their simulation mixing in both regions are really weak in this month. Strong stirring could exist inside the polar vortex but the strongest stirring locates in the surf zone (Chen et al., 1994).

Considering model performances, the polar vortex and surf zone are present in the southern hemisphere more or less. The models give a weaker mixing in the surf zone and higher CH$_4$ in the polar vortex, especially by TM5-4DVAR. The region with both horizontally and vertically well-mixed CH$_4$ is completely absent in the models. This absence is visible as a negative region of model to ACE-FTS differences during the Sep-Oct-Nov period in Fig. 4.13. This is confirmed as well by maximum underestimations or minimum overestimations by the model of FTS measured stratospheric column-average CH$_4$ in this season southward of 30°S (Figure 4.6). The tropical region with large $L_e$ is represented best by TM5-4DVAR, which captures the double peak structure of CH$_4$ to the largest extent (not shown).

In Dec. 2009 the southern polar vortex break already, and the zonal wind changed to easterlies. The strong mixing occurred in the whole extratropics, the polar barrier with small $L_e$ disappeared. This is consistent with the strengthening of planetary wave breaking during polar vortex breaking because of occurrence of weak zonal winds (Holton, 2004, p. 424~429). However, southern CH$_4$ was not well mixed at this time below 900 K (~31 km). In the northern hemisphere the polar vortex, polar barrier and surf zone was well defined now. The surf zone seemed to split into two regions above 850 K (~30 km) with smaller $L_e$ in the region between them, or was extending toward the tropics. Similar to the southern hemisphere, a region (about 20°N~60°N and 450~850 K) with small gradients in both vertical and horizontal directions occurred. In the models southern CH$_4$ is horizontally uniform southward of 30°S unrealistically, and northern surf zone is represented well. CH$_4$ inside the northern polar vortex is overestimated, and most significantly in the case of TM5-4DVAR again.

The northern polar vortex broke above 1050 K (~35 km) in Feb. 2010 and strong stirring occurred as it was in the southern hemisphere. However, it was reestablished in the April but in smaller extent (the polar barrier located northward of 75°N) and without the polar westerly jet. During this period only weak easterlies with a maximum of 10 m/s in February and below it in April occurred northward of 60°N. The surf zone became wider (30°N~70°N) shows stronger isentropic mixing in the April than its counterpart in the February (about 35°N~45°N). The stronger mixing is consistent with weakened westerlies that are suitable for quasi-stationary planetary wave propagation and breaking. In addition, the subtropical barrier is visible, which located along subtropical jet axis and showed low $L_e$. In the April there is large $L_e$ almost symmetrically distributing in the two hemispheres in the tropics above 850 K. It is this month when the double peak structure in CH$_4$ distributions was the most significant and occurred at altitudes above 10 hpa (~30 km) in this year as expected (Randel et al., 1998). In the southern hemisphere the situation in February is similar to that in December. But the large $L_e$ could result from remnants from the southern polar vortex breaking (Hess, 1991) instead of strong stirring since stationary planetary wave can not propagate in easterlies. The equivalent length quantifies complexity of instantaneous contours but does not reveal the reason to it.
The model simulations show CH$_4$ and $L_e$ patterns similar to measurements in February and April. The $L_e$ southward of 60°S is underestimated in the models in February. That could reflect a too fast dissipation of polar vortex remnants. The reappearing of the northern polar vortex is represented by TM3 but a too weak contrast in CH$_4$ between outside and inside it. The wide and strongly stirring surf zone is replaced by a narrow and weakly mixing region in this model. In TM5-4DVAR CH$_4$ is completely uniform in the horizontal direction northward of ~60°N.

In Jun. 2010 the polar vortex disappeared in the northern hemisphere with a strongly stirred region left northward of 50°N and easterlies established. In the southern hemisphere the polar vortex and surf zone started to build themselves. The developing isentropic stirring in the mid-latitudes mixed with the deceasing tropical large $L_e$ region at that time. Propagation of the planetary wave started around 40°S at 450 K level and tilt along isolines of zonal wind, consistent with the theory that the quai-stationary planetary wave propagates in westerlies weaker than an upper limit (Holton, 2004, p. 424). That is reflected in the models as well, but with underestimated amplitudes again. The largely stirring region above 850 K and southward of ~40°S in the southern hemisphere is completely absent in the models. As a result, modeled CH$_4$ presents too large meridional gradients there.

In Aug. 2010 the polar vortex and surf zone matured at last in the southern hemisphere. The meridional distribution of southern CH$_4$ is roughly captured by the models. The deficiencies of the models are too weak isentropic mixing in the surf zone. Large departures occur at the level around 1050 K and below 700 K (~26 km) in the mid-latitudes.
Figure 4.15. Cross sections in Oct. 2009~Aug. 2010 of equivalent length (color: the red indicates large values and the blue for small values and color is plotted on a logarithmic scale, the white means no data or larger values), contour of CH$_4$ (thick black line with an increment of 100 ppb) and zonal mean zonal wind (thin black lines with solid for westerlies and zero values and dashed lines for easterlies, the increment is 10 m/s) along equivalent latitudes (but latitudes for wind) and potential temperatures. The equivalent latitude $\varphi_e$ is defined by $A = 2\pi a^2 (1 - \sin \varphi_e)$, $A$ is the area bounded by a constant CH$_4$ line on an isentropic surface and $a$ is the earth radius. The equivalent length has been scaled by $2\pi r \cos \varphi_e$ and is unitless. Results for MIPAS, TM3, TM5-4DVAR and LMDz-PYVAR are shown, respectively, starting from the uppermost panel.

4.4.4. Validation of simulated CH$_4$ vertical profiles

The algorithm retrieving CH$_4$ profiles described in Sect. 3.2 has not been calibrated with in situ measurements. There is only an empirical validation using in situ surface CH$_4$. It can be seen that the retrieved low tropospheric xCH$_4$ follows variations of the in situ surface CH$_4$ well at Ny-Ålesund. There are significant differences between them at Bremen, but the retrieval is capable to follow the seasonal behavior of the surface CH$_4$. With a DOFS (the degrees of freedom for signal) of around 2.5 in the retrieval stratospheric CH$_4$ variabilities are distinguished from those in the troposphere. Validation of simulated CH$_4$ profiles could provide further insight on performances of the models.
Comparisons of CH$_4$ profiles, partial columns above 11 km and the lower tropospheric xCH$_4$ between FTS and models are given in Figure 4.16 and 4.17. CH$_4$ is well mixed in the troposphere because of its lifetime of about 10 years and strong convection mixing there. The CH$_4$ concentration deceases rapidly with altitude in the stratosphere due to oxidations by OH, Cl and O(1D). The tropopause height varies seasonally with a maximum in summer, and meridional with an increase toward the tropics. The retrieved profiles change following the tropopause as showed by Figure 4.16. In wintertimes of some years measured profiles shift downward as a whole, along with decreasing tropopause, e.g. the year 2007, 2010, 2011 and 2012 at Ny-Ålesund, 2010 and 2012 at Bremen. The shift could be caused by air subsidence associated with the polar vortex, which is stronger in winter and has larger influences at high latitudes. Total and stratospheric columns of CH$_4$ are small in this period.

Figure 4.16. Comparison between FTS retrieved CH$_4$ profiles and those simulated by models at Ny-Ålesund (left) and Bremen (right). The model profiles have been smoothed with averaging kernels of the retrieval taking a prior into account. The first row is the retrieved profiles, and following rows are differences between retrieval and simulation for TM3, TM5-4DV AR and LMDz-PYVAR respectively. The colors indicate CH$_4$ mole fractions.

Differences of stratospheric CH$_4$ between FTS and the models are largest for LMDz-PYVAR. Overestimation of CH$_4$ in the stratosphere by this model is consistent with the results in Sect. 4.4.2.
TM3 overestimates CH\textsubscript{4} in the lower stratosphere and underestimates in the upper stratosphere. TM5-4DVAR overestimates in the whole stratosphere, but has the best agreement with FTS concerning the shape of stratospheric CH\textsubscript{4} profiles. However, overestimation of partial columns by TM3 and TM5-4DVAR are not consistent with their underestimation for the stratospheric xCH\textsubscript{4} showed in Sect. 4.4.2. FTS measured CH\textsubscript{4} profiles should be calibrated with in situ measurements before a clear conclusion is drawn. In the period influenced by the polar vortex, all the models overestimate CH\textsubscript{4} mole fractions in the stratosphere significantly. It is indicated by positive difference zones spreading in the whole stratosphere in Figure 4.16, and large partial column differences in Figure 4.17, with a strength increasing for TM3, TM5-4DVAR and LMDz-PYVAR.

![Figure 4.17. Comparisons of partial column of CH\textsubscript{4} (first two rows) and lower tropospheric column-averaged CH\textsubscript{4} mole fraction (last two rows) between FTS measurements and model simulations at Ny-Ålesund (left) and Bremen (right). The partial column is an integration of CH\textsubscript{4} profile from 11 km to TOA (top of the atmosphere). The lower tropospheric column-averaged CH\textsubscript{4} mole fraction is a mean mole fraction of profile below about 2.4 km. The shown results are daily medians.](image)

The bias in the LMDz-PYVAR partial column deceases with time at both sites, and does not change for the other models. Because such a trend does not occur in differences of the lower tropospheric xCH\textsubscript{4}, and of the tropospheric xCH\textsubscript{4} as shown in Sect. 4.4.2, it could not be source-related. Since the method retrieving the lower tropospheric xCH\textsubscript{4} is not calibrated against in situ measurement, no
conclusion will be drawn on relative performances of the models.

4.5. Summary

In this chapter, the simulated CH$_4$ mole fractions by three European inverse modeling are validated using the measurements from ground-based FTS and satellites, and in situ measurements at surface. The aim is to determine whether most of model biases are located in the stratosphere or troposphere. With FTS stratospheric and tropospheric xCH$_4$, retrieved from total column FTS measurements, it is shown that model bias amplitudes are $7.4\pm5.1$ ppb, $6.72\pm4.8$ ppb and $7.1\pm5.6$ ppb in the troposphere for TM3, TM5-4DVAR and LMDz-PYVAR. For the stratosphere we get $4.3\pm9.9$ ppb, $4.7\pm9.9$ ppb and $10.3\pm15.9$ ppb, respectively. The tropospheric model bias exhibits a North-South gradient with an overestimation in northern high-latitude for all models. There is not a latitudinal pattern existing through the year in the stratospheric model bias except for LMDz-PYVAR, which overestimates stratospheric CH$_4$ at high-latitudes and underestimates in the tropics.

The evaluation of the models at surface shows a smaller bias compared to the tropospheric xCH$_4$. We assume that the tropospheric model biases are mainly located in the middle and upper troposphere although comparisons at the surface are only limited to sites where the measurements have been assimilated into the models. Comparisons with HIPPO show that there are significant underestimations in the southern upper troposphere while biases in the lower troposphere are smaller. HIPPO and FTS reveal different behaviors in tropospheric model biases. A sensitive test shows that differences between thermal/dynamical and chemical tropopause could be the reason, as well as for the FTS revealed North-South gradient in the tropospheric model biases.

The equivalent length is calculated to investigate the causes of model biases in the stratosphere. The modeled surf zone in the southern hemisphere is not developed to the same extent as in the measurement because a too weak planetary wave breaking there. Especially in Jun-Jul-Aug period stratospheric CH$_4$ in southern mid-latitudes presents much larger isentropic gradients in the models than measurements. During the development of the southern surf zone, a region with both vertically and horizontally well mixed CH$_4$ occur between 450 and 850 K (≈18 and 30 km) in surf zone latitudes. Such a region is absent in the models, and underestimations of CH$_4$ within it are visible in comparisons with ACE-FTS and MIPAS measured CH$_4$ profiles, and FTS measured stratospheric CH$_4$ columns. More work are needed to uncover which kinds of atmospheric movement provided this vertical mixing. The modeled polar vortex breaks too fast compared to the measurements. Modeled CH$_4$ concentrations in the polar vortex rise at all levels at same time instead of at high levels initially as in the measurements.
5. Retrieval of the isotopic composition of atmospheric CO$_2$ from ground-based FTS solar absorption measurements

The isotopic composition of carbon is different between its global reservoirs, for example, the ratio $^{13}$C/$^{12}$C increases for fossil fuel, terrestrial biosphere, the ocean and the atmosphere successively. Exchanges of carbon between two carbon reservoirs usually occur along with a distinct selection of one isotope over the other. The photosynthesis of the plants prefers $^{12}$C over $^{13}$C, and respiration releases more $^{12}$C isotope. The relative abundance of carbon isotopes is expressed in parts per thousand, for example, for $^{13}$C/$^{12}$C,

$$\delta^{13}C = \left( \frac{^{13}C/^{12}C_{\text{sample}}}{^{13}C/^{12}C_{\text{standard}}} - 1 \right) \times 1000. \quad (5.1)$$

The standard value of $^{13}$C/$^{12}$C is PDB (Pee Dee Belemnite) that is 0.0112372. The $\delta^{13}C$ is about -6.7 to -7.4 for atmospheric CO$_2$ (Keeling, 1960) that is a major molecule containing carbon in the atmosphere, -10 for the ocean, -12 to -28 with a mean of -26 for the plants (Craig, 1953) and -21 to -28 with a mean of -24 for fossil fuel (Craig, 1953). Measurements of both concentration and $\delta^{13}C$ of atmospheric CO$_2$ can help to infer contributions of various sources and sinks. Atmospheric CO$_2$ is produced mainly by respiration and the burning of fossil fuels, removed mainly by uptake of plants, and exchanged with the CO$_2$ in the oceans. While the exchange with ocean does not significantly influence the isotopic composition of CO$_2$, respiration and fossil fuels burning release more $^{12}$CO$_2$ into the atmosphere, and photosynthesis uptake more $^{12}$CO$_2$ into the plants. An increase in atmospheric CO$_2$ concentration caused by fuel combustion will be accompanied by a decrease in $\delta^{13}C$, such as the well-known increasing atmospheric CO$_2$ concentration and the accompanied decreasing $\delta^{13}C$ since the industrial revolution. In a region where the plants have influence on the atmospheric CO$_2$ concentration, CO$_2$ mole fraction will be anti-correlated to the $\delta^{13}C$ (Keeling et al., 1958, 1979; Mook et al., 1983). The atmospheric CO$_2$ concentration presents minimum in summer when the photosynthesis is strong and the $\delta^{13}C$ has the least negative value. When there is only a small to zero fraction of CO$_2$ originated from the plants, the anti-correlation between atmospheric CO$_2$ and $\delta^{13}C$ will be weak. From a limited measurements (Keeling et al., 1984) the $\delta^{13}C$ of atmospheric CO$_2$ increased steadily southward from -7.55 near 16°N to -7.47 near 17°S, as expected from a dominant CO$_2$ source from fossil fuel combustion in northern hemisphere.

While all the existed data of $^{13}$C/$^{12}$C are from in situ measurements, remote sensing could provide additional data source. In this chapter, the possibility of retrieving $^{13}$CO$_2$/$^{12}$CO$_2$ from ground-based FTS solar spectra will be explored.

5.1. Problems of retrieving atmospheric CO$_2$ isotopes from ground-based FTS spectra

Because the variation of $^{13}$CO$_2$/$^{12}$CO$_2$ is on an order of one per thousand, a measurement needs have
a precession and accuracy above one per thousand. The total column measured by TCCON can achieve a precession of about 0.1% under clear condition. However, the TCCON measurements present an airmass-dependent artifact that causes the retrievals to be approximately 1% larger at 20° SZA (solar zenith angle) than at 80° SZA. The reasons resulting in this phenomenon could be spectroscopic inadequacies and instrumental problems. Currently an empirical correction is applied to remove this artifact, which represents the error as a function of SZA (Wunch et al., 2011). If considering spectroscopic inaccuracies only, it can be proved (Appendix B) that the retrieved quantity can be expressed as,

\[ \hat{x} = \left[ I + C \left( \frac{Y_1 P_s}{\cos(SZA)}, \bar{y}_1; \ldots; \frac{Y_J P_s}{\cos(SZA)}, \bar{y}_J \right) \right] \left[ x + (A - I)(x - x_a) \right] \]  

(5.2)

where, \( \hat{x} \), \( x \), \( x_a \) are the retrieved, true and a prior state. \( A \) is the averaging kernel and \( I \) is a unit matrix, \( C \) is a diagonal matrix function representing influence of spectroscopic inaccuracies. \( \bar{y}_j \) is the mole fraction profile of the \( j \)th gas normalized by its column-averaged mole fraction \( Y_j \). \( P_s \) is surface pressure. The physical meaning is clear that influences of the spectroscopic error depend on abundances and vertical distributions of atmospheric gases, surface pressure in addition to SZA. For a profile scaling retrieval, such as being done in GFIT, the state is the scale factors for a prior profiles. The diagonal elements of the matrix \( C \) is a constant for each retrieved gas. When interference between different gases is ignored and variabilities of vertical profile shape is ignored, which is small for atmospheric CO2, Eq. 5.2 can be written as,

\[ \hat{Y} = \left( \int_0^{P_s} \left[ y + (A - I)(y - y_a) \right] dp \right) \left[ 1 + C \left( \frac{Y P_s}{\cos(SZA)} \right) \right] \]  

(5.3)

In this case the function \( C \) can be derived from retrievals in some days with clear sky when variabilities of the column-averaged mole fraction are small and that of SZA is as large as possible. Then the variabilities of the retrieval are totally from the function \( C \) except for an absolute scale. Although an empirical correction is possible to approximately remove airmass-dependent artifact, it is always preference to reduce retrieval error through improving spectroscopic parameters and instrument performance.

Interference error is another important error source (Sussmann and Borsdorff, 2007), especially that from H₂O for ground-based remote sensing. Interference error originates from spectral residuals due to interfering gases whose spectral features overlap with the signatures of the target gases. Its amplitude depends on vertical profiles and spectroscopic errors of the interfering gases and airmass. H₂O interferes retrievals of most gases because of its widely spread absorption lines in infrared region. The profile and concentration of H₂O in the atmosphere is highly variable, the same is true for its interference.

5.2. Spectroscopy aspect

When solar radiation passes through the atmosphere, interactions between the radiation and the
molecules in the atmosphere take place. The molecules can absorb and emit radiation at frequencies that are specialized for each kind of molecule. The internal states of the molecules are discrete and the same are the energies associated with them. The absorption and emission are achieved through transitions from initial states to final states. The lifetimes of molecular states are limited value, then the energies of the states spread over a range whose width is anti-proportional to the length of the lifetime according to the Heisenberg uncertainty principle. Consequently, the absorption and emission associating with each pair of initial and final states spread over a range of frequency as well, which is described by the spectral line function. For a molecule free from the collision with other molecules and without thermal motion, the lifetime of its states is mainly determined by spontaneous photon emission, the spectral line has negligible width, and can not be resolved by current experimental techniques.

The molecule in the atmosphere undergoes thermal motion all the time. The motion leads to the Doppler shift for the absorbed and emitted radiation frequency. The speed of the motion is described by the Maxwell-Boltzmann distribution, assuming the atmosphere satisfies the local thermal equilibrium condition. The resulted spectral line is broadened, and expressed as,

$$I_D(\omega) = \frac{1}{\sqrt{\pi} \Delta \omega_D} e^{-\left(\frac{(\omega - \omega_0)/\Delta \omega_D}{e}\right)^2}, \quad (5.4)$$

where, $\omega$ is angular frequency, $\omega_0$ is the frequency at the maximum under zero pressure condition. $\Delta \omega_D = \omega_0 \sqrt{2 k_B T/m c}$ is the Doppler half width at the $1/e$ maximum, $T$ is temperature, $m$ the mass of the molecule, $c$ the light speed and $k_B$ the Boltzmann constant.

Collisions between molecules can change the thermal equilibrium distribution of molecular speed. Because the molecular speed prefers changes toward smaller value, the speed distribution is narrowed. As a result, the Doppler line shape is narrowed, namely the Dicke narrowing effect. But it is important for the light molecule only, such as H$_2$ and HF, and is much less important than another collisional effect in the atmosphere. During the collisions there is energy transfer between the energy associated with molecular states and translational energy of the molecules. Because kinetic energy of the molecular thermal motion is much larger than the energy associated with molecular rotation, this energy transfer is efficient to change rotational states of the molecules. The lifetime of molecular states is deceased due to the collisions, and spectral line resulted from the state transition is broadened. The collision-broadened line shape, namely Lorentz profile, can be expressed as,

$$I_L(\omega) = \frac{1}{\pi} \frac{\gamma P}{(\omega - \omega_0 - \delta P)^2 + (\gamma P)^2}, \quad (5.5)$$

where, $P$ is pressure and $\delta$ is collision-induced shift coefficient and $\gamma$ is collision-induced broadening coefficient. The Lorentz profile is derived under the impact approximation, which states that the time spent to the collision is much smaller that the time for the molecule to move freely, and the binary collision assumption that states only two molecules participate during each collision.

When ignoring the Dick narrowing effect, considering both the Doppler and collision broadening,
the resulted spectral line shape is called Voigt profile. The Voigt profile can be expressed as (Hartmann et al., 2008, p. 79),

\[
I_v(x, y) = \int I_D(\tilde{x}') I_L(x - \tilde{x}', y) d\tilde{x}' = \frac{1}{\sqrt{\pi}} \text{Re}\left( \frac{i}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t}}{x - t + iy} dt \right),
\] (5.6)

where,

\[
\tilde{x} = \frac{\omega - \omega_0}{\Delta \omega_D}, \quad x = \frac{\omega - \omega_0 - \delta P}{\Delta \omega_D}, \quad y = \frac{\gamma P}{\Delta \omega_D},
\]

\[
I_D(\tilde{x}) = \frac{1}{\sqrt{\pi}} \exp(-\tilde{x}^2), \quad I_L(x, y) = \frac{1}{\pi} \frac{y}{x^2 + y^2}.
\]

The collision-induced broadening and shift present a dependence on the speed of absorber. An empirical model, the quadratic model (Rohart et al., 1994), is used to describe this behavior,

\[
y(v) = y + y_2 \left( \frac{v^2}{v_2^2} - \frac{3}{2} \right), \quad \delta(v) = \delta + \delta_2 \left( \frac{v^2}{v_2^2} - \frac{3}{2} \right),
\]

where \(v\) is the speed and \(v\) is the most probable speed. \(y\) and \(\delta\) are broadening and shift coefficients averaged over the Maxwell-Boltzmann distribution of the speed. \(y_2\) and \(\delta_2\) are corresponding speed-dependence parameters. After taking the speed dependence, the spectral line shape can be written as (Hartmann et al., 2008, p. 98),

\[
I_{sdv}(\omega) = \frac{1}{\pi} \text{Re}\{ \int f_M(\tilde{v})[y(v)P - i(\omega - \omega_0 - \delta(v)P - \tilde{k} \tilde{v})]^{-1} d\tilde{v} \} = \text{Re}\{ J_{sdv}(\omega) \},
\] (5.7)

where, \(f_M(\tilde{v})\) is the Maxwell-Boltzmann distribution of the velocity of the absorber. \(\tilde{k}\) is radiation propagation vector and \(\tilde{k} \tilde{v}\) is the Doppler shift. In this thesis only \(y_2\) is considered, and speed-dependence of collisional shift is ignored.

Except for narrowing and broadening, there is a further effect resulted from the collisions, namely line mixing. The molecules in the atmosphere spread over all possible internal states according to Maxwell-Boltzmann distribution under the condition of local thermodynamic equilibrium. The equilibrium distribution is achieved through frequent collisions between molecules, which cause exchange of the population of the molecules at each state with the other states. A photon with a frequency \(\omega_{fi}\) is absorbed by a molecule through the transition from initial state \(i\) to final state \(f, f \Leftarrow i\). Because of the collisions there exist transfers between populations of different states, for example \(i \leftrightarrow i'\) and \(f \leftrightarrow f'\), which are not related to absorption or emission. The initial state can change to \(i'\) and transit to \(f\) through absorbing a photon with a frequency \(\omega_{f'i'}\), and then the state \(f\) changes to \(f\) after the collisions. The second path \(f \Leftarrow f' \leftarrow i' \Leftarrow i\) actually contributes absorption with a frequency associating with a different transition \(f' \Leftarrow i'\). Of course, the transition \(f' \Leftarrow i'\) can contribute absorption at the frequency possessed by the transition \(f \Leftarrow i\) as well. The strength of the line mixing
effect depends on the efficiency of collision-induced transfer between different states. The transfer is possible for rotational states of the same kind of molecule and isotope, so the line mixing occurs between lines within the same vibrational band. The transfer efficiency increases with collision frequency and then pressure. To keep an equilibrium distribution the transfer from the state with high population to that with low population needs be less efficient than the inverse direction. Consequently, the line mixing decreases absorption of weak lines and increases that of strong lines.

In a frame of the Rosenkranz first-order approximation, ignoring the speed-dependence of collisional effects, the spectral line density accounting for the line mixing effect can be expressed as (Hartmann et al., 2008, p. 160),

\[ I(x, y) = \frac{S}{\sqrt{\pi}} \Re \left[ \left( 1 - iPY \right) \int_{-\infty}^{\infty} \frac{e^{-t^2}}{x-t+iy} dt \right], \quad (5.8) \]

where, \( Y \) is the first-order line mixing coefficient. \( S \) is integrated intensity of the line, and has a form,

\[ S = \frac{8\pi^3}{3hc} \frac{\omega_0}{\Delta \omega_D} \left[ 1 - \exp\left( -\frac{h \omega}{2\pi k_B T} \right) \right] \rho d^2, \]

where, \( \rho \) is the equilibrium relative population of the initial state of the line, \( d \) is the reduced matrix element of the dipole moment that couples radiation and the molecules. When both the line mixing and speed-dependence of collisional broadening are taken into account, the spectral line density will become (Hartmann et al., 2008, p. 338),

\[ I(\omega) = \Re \left[ \left( 1 + iPY \right) J_{sdv}(\omega) \right] \quad (5.9) \]

There are several other mechanisms influencing spectral line shape, but not considered in the thesis. As a summary, the parameter describing the absorption coefficient of a line are, intensity, pressure broadening and shift coefficient, first-order line mixing coefficient, speed-dependence parameter of collisional broadening and those specifying their temperature-dependence.

### 5.2.1. Inversion of spectroscopy parameter from ground-based FTS spectra

With function format of spectral line shape at hand, the next step is to determine the parameters in the function. The parameters can be predicted theoretically (Hartmann et al., 2013; Lamouroux et al., 2010; Gabard and Boudon, 2010) or determined from laboratory measured spectra (Toth, 2005; Jenouvrier et al., 2007; Devi et al., 2007). An alternative approach is retrieving the line shape parameters from the solar spectra measured by ground-based FTS (Schneider and Hase, 2009). While for the measurements in the laboratory the pressure, temperature and constituents of the gas can be controlled, it is not the case for atmospheric spectra. A further problem is that the vertical distribution of the gas in the atmosphere is variable and not easy to measure. During measurements, the atmospheric state usually changes, which make it not feasible to measure over a long time in order to reduce noise, as being done in laboratory. However, the amount of the gas in the atmosphere can be much larger than that can be provided in the laboratory, for example H₂O and
CO2. The solar line is an exception, which is resulted from absorption by the sun itself, must be investigated using, either ground- or space- based solar spectra (Hase et al., 2010).

In this section, the spectroscopy parameters of H2O, solar line and CO2 are retrieved using ground-based FTS solar spectra. The influences of these derived parameters on the retrieval of these gases are checked. The algorithm is based on the optimal estimation theory (OE), as described in Chapter 2. The code basically contains two parts: 1) execute GFIT/PROFFIT to adjust amount of atmospheric gases and fit solar spectra; 2) adjust spectroscopy parameters of target gas based the OE theory to fit the spectra further. The step 1 and 2 are iteratively executed until a convergence of the retrieved parameter is achieved. Spectroscopic parameters usually present a smooth variation along with quantum number $m$, which is $-J''$, $J''$ and $J''+1$, respectively, for $P$, $Q$ and $R$ branch transitions and $J''$ is rotational quantum number of initial state. The algorithm allows a usage of a smooth constraint for variations along $m$. Instead of using the Gauss-Newton method to search spectroscopy parameters minimizing fitted residuals, the Levenberg-Marquardt method (Kelley, 1999, p. 56) is used,

$$x_{i+1} = x_i + (S_a^{-1} + k_i^T S_e^{-1} k_i + \lambda B_1^T B_1 + \nu D)^{-1} [k_i^T S_e^{-1} (y - f(x_i)) - (S_a^{-1} + \lambda B_1^T B_1)(x_i - x_a)],$$

where $D$ is a diagonal matrix with the same diagonal elements with the matrix $S_a^{-1} + k_i^T S_e^{-1} k_i + \lambda B_1^T B_1$, the other symbols have the same meaning as in Chapter 2. The factor $\lambda$ determines the strength of the smooth constraint. $B_1$ is the second matrix in Eq. 2.12, but its rows and columns are rearranged because spectroscopic parameters are not arranged along $m$ (along wavenumber of spectral lines here) in $x$. Only the rows of $B_1$ corresponding the parameters with smooth constraint applied have non-zero elements. The scale factor $\nu$ is used to adjust step size and direction, and is determined based on the trust region method (Kelley, 1999, p. 57). the a priori covariance $S_a$ is constructed using uncertainties given in HITRAN database, the measurement error covariance is diagonal and its elements are estimated from measured spectra. The state vector $x$ contains the parameters of all lines, $y$ and $f(x)$ are vectors containing all measured and calculated spectra. The Jacobean $k$ contains derivatives of the line parameters with respect to all the calculated spectra.

The evaluation of the Jacobean of spectroscopy parameters uses numerical perturbation method and is time-consuming. An approximate method is applied when a lot of spectra and absorption lines are involved. When calculating perturbation effects of parameters of a line, only the absorption of this line is considered. Then the Jacobean is obtained through multiplying the perturbation effects by spectra containing absorption of all lines. The calculation would be accurate if ignoring instrumental effect, which convolves spectra with the instrumental line shape function.

The information about spectroscopy parameters contained in the ground-based spectra is much less than that can be obtained from laboratory spectra since temperature, pressure and gas concentration in the atmosphere vary in much smaller ranges than those achieved in the laboratory. Including spectra measured at FTS stations at different altitudes can enlarge pressure variability, and measured
at different latitudes and seasons enlarge temperature variability. The spectra measured at larger
SZA contain more contribution from lower atmosphere, and then increase equivalently pressure. At
the same time, the amount of absorbers increases approximately with \(1/\cos(SZA)\), then changing
SZA is an efficient method to control it.

5.2.2. H\(_2\)O

Although there is a large amount of work on the H\(_2\)O spectroscopy already, the accuracies of them
are still not enough for atmospheric remote sensing using ground-based observation, such as
TCCON and NDACC spectra. In the region around 4901 cm\(^{-1}\) where a strong \(^{13}\)CO\(_2\) band presents
there is strong H\(_2\)O absorption as well. There is some residual features corresponding to H\(_2\)O lines
always exist when using either GFIT spectroscopy parameter, which is basically from Toth (2005)
with some weak lines added, or HITRAN 12 for H\(_2\)O. These residuals could inference the retrieval
of \(^{13}\)CO\(_2\), especially when air is humid and SZA is large.

Near-infrared spectra at TCCON site: Darwin (12.456°N, 130.892°E, 30 masl), Orléans (47.970°N,
2.113°E, 130 masl), Bialystok (53.231°N, 23.026°E, 183 masl) and Lamont (36.604°N, 97.486°W,
320 masl), totally 13 records, are used. Because large variabilities of H\(_2\)O vertical distribution, in
situ measurements are used to prescribe the vertical profile shape. At Darwin and Lamont, Vaisala
RS92 radiosonde (Miloshevich et al., 2009) measurements are used, together with a correction for
RS92 H\(_2\)O measurements. The aircraft measurements from the IMECC campaign (see Sect. 3.1.2)
are used for the spectra measured at Orléans and Bialystok. The in situ measurements are matched
with the FTS measurements within 5 minutes. The measured H\(_2\)O, temperature and pressure profiles
will act as a prior, in the case of H\(_2\)O, or forward model parameter, in the case of Tp profiles, in the
retrieval code GFIT/PROFFIT. The temperature and H\(_2\)O profiles are shown in Figure 5.1. For a
H\(_2\)O line with an intensity of 8.5×10\(^{-25}\) cm\(^{-1}\) the DOFS is about 4.8 when the six parameters (vacuum
wavenumber, intensity, air- and self- broadened half width, air pressure-induced shift, temperature-
dependence exponent for the air-broadened half width) are fitted.

The algorithm is applied to invert H\(_2\)O spectroscopy in the region 4724.40 to 4773.60 cm\(^{-1}\), where
absorption is dominated by H\(_2\)O and with small contribution from CO\(_2\) and N\(_2\)O. The a prior H\(_2\)O
spectroscopy is the GFIT one (Toth, 2005). Only the lines with intensities larger than 2.0×10\(^{-26}\) cm\(^{-1}\)
are considered. For lines stronger than 1.5×10\(^{-25}\) cm\(^{-1}\), four parameters (vacuum wavenumber,
intensity, air- and self- broadened half width) are adjusted, and only the first three for others. In this
test, GFIT is executed to fit measured spectra. The a prior profiles are scaled for species, H\(_2\)O,
\(^{12}\)CO\(_2\), \(^{13}\)CO\(_2\), C\(^{18}\)OO and N\(_2\)O and just kept as climatologies for all other species.
Figure 5.1. Temperature (left) and H$_2$O (right) profiles measured by radiosonde (Darwin and Lamont) and aircraft (Bialystok and Orléans) near the time of FTS measurements used for inverting H$_2$O spectroscopy parameter.

Figure 5.2. Example fit effect using H$_2$O spectroscopy from Toth (2005) (the first panel), inversion (the second panel), HITRAN 12 (the third panel). The lowest panel gives transmission measured (dot) and calculated (solid line). The spectrum is measured at TCCON site Bremen.
Figure 5.3. Retrieved $\text{H}_2\text{O}$ profiles (Blue dashed line) from the spectra measured at Bremen using three different spectroscopy, Toth (2005) (left), Inverted (middle) and HITRAN 12 (right). The black line is NCEP daily mean $\text{H}_2\text{O}$ profile and yellow is a prior.

Figure 5.4. Standard deviation (upper panel) of residual and DOFS (lower panel) for the retrieval in Figure 5.3.

The spectra measured at TCCON site Bremen on the days 15 and 01 Oct. 2011 are analyzed with PROFFIT to retrieve $\text{H}_2\text{O}$ profiles. The same spectral region as that used for inverting $\text{H}_2\text{O}$
spectroscopy is used. The considered species are H$_2$O, N$_2$O and $^{12}$CO$_2$, $^{13}$CO$_2$ and all other isotopes of CO$_2$. A first-order Tikhonov-Phillips constraint is applied for H$_2$O profile retrieval, which is performed on a logarithmic scale. The profile scaling approach is applied to retrievals of other species, and a prior profiles are GFIT a prior. Three sets of spectroscopy from Toth (2005) (used in GFIT), inversion and HITRAN 12, are compared for H$_2$O, and only GFIT spectroscopy is used for CO$_2$ and N$_2$O. Figure 5.2 shows the residual reduction when using the inverted spectroscopy compared to Toth (2005) and HITRAN 12. Atmospheric temperature and pressure profiles are from NCEP reanalysis data, and intra-day variabilities are allowed. Figure 5.3 and 5.4 show retrieved profiles, the standard deviation of residual and the DOFS. The H$_2$O profile from Toth (2005) and inverted spectroscopy have better agreement with NCEP profile than HITRAN 12, and the inverted spectroscopy gives a better agreement than Toth (2005) on the humid day. Together with the reduction of residual, the DOFS using the inverted spectroscopy increases. The overestimation of H$_2$O mole fraction in mid troposphere and underestimation in the boundary layer when using HITRAN 12 could indicate too large air-broaden half width.

Figure 5.5. Same as for Fig. 5.2 except for a region 4886.70 to 4916.30 cm$^{-1}$ and that line mixing effect is modeled for CO$_2$, and there is not N$_2$O absorption in this region.

The test reveals that the algorithm of inverting H$_2$O spectroscopy is feasible. It is then applied to the region 4884.50 to 4917.50 cm$^{-1}$ to reduce residuals from H$_2$O lines there. Because there is strong CO$_2$ absorption, the region is split into several smaller windows and the algorithm is applied in each of them separately. Then another algorithm is applied to the whole region to make sure the inversion
for the small windows are consistent with each other. It adjusts intensity scales and vacuum wavenumber shifts only that are shared by all lines within each small window. The other details on the inversion is the same as for the region $4724.40$ to $4773.60 \text{ cm}^{-1}$. Figure 5.5 gives a comparison between different sets of H$_2$O spectroscopy, the inverted one reduces residual compared to Toth (2005) and HITRAN 12.

5.2.3. Solar line

The solar spectrum is not a smooth blackbody spectrum, in contrast, there are a lot of absorption features on it resulted from the solar photosphere. They should be taken into account in analysis of ground-based spectra. The absorption species include molecules CO, OH and CN etc., and atoms Fe, Si, Mg and C etc. A solar line contains absorptions occurring in a depth of the solar photosphere where both pressure and temperature vary considerably. Summation of these absorptions can result in various line shapes. The solar rotation leads to Doppler-broadening in observed solar line if the field view covers a part only of solar disk. The width and strength of solar lines change with respect to the projected distance from the solar disk center. Accounting for all these effects, Hase et al. (2006) give an empirical line shape model and corresponding database in the infrared region. Line shape model is expressed as,

$$ I(\Delta \sigma) = A \exp \left( \frac{-\left(\Delta \sigma\right)^2}{b^4 + w \left( -0.54 b^4 + 0.33 b^3 |\Delta \sigma| + 0.12 b^2 (\Delta \sigma)^2 + 0.342 b |\Delta \sigma|^3 \right)} \right), $$

where $A$ is the amplitude, $b/\ln 2$ is the half width at half maximum, $\Delta \sigma$ is the distance from line center measured in wavenumber (cm$^{-1}$). $w$ is a parameter adjusting line shape, which is Gaussian ($w=0$), Lorentzian ($w=1$) and cusp-shaped ($1 < w \leq 1.85$). In addition, the line parameters $A$ and $b$ are allowed to vary as a function of projected solar disk radius $\rho$ for describing the center-limb variation of line width and strength, $A(\rho) = A(0)(1+V_A \rho^2), b(\rho) = b(0)(1+V_b \rho^2), 0 \leq \rho \leq 1$.

The line-by-line model of solar line is used in the forward model of PROFFIT. However, the line parameters are not accurate enough in the region $6180.00$ to $6260.00 \text{ cm}^{-1}$ where a strong CO$_2$ band exists that is used to retrieve $^{12}\text{CO}_2$ in this Chapter. To reduce residuals from solar line, a set of ground-based spectra is used to improve the line parameters based on OE theory. The spectra are measured at TCCON site Bialystok, under lower SZA and dry air condition. All lines with strength larger than $1.0 \times 10^{-2}$ are inverted, in which six parameters, center wavenumber, $A, b, w, V_A$ and $V_b$, are adjusted for lines stronger than $5.0 \times 10^{-4}$, only the first four for lines stronger than $5.0 \times 10^{-2}$ and only the first three for other lines. A prior is just taken as the database used by PROFFIT (Hase et al., 2006), uncertainties are estimated as $0.01 \text{ cm}^{-1}$ for center wavenumber, 25% for $A$, 40% for $b$ and $w$, 40% and 50% for $V_A$ and $V_b$ respectively. And the allowed minimum uncertainties for the last five parameters are $1.0 \times 10^{-4}$, $1.0 \times 10^{-2} \text{ cm}^{-1}$, $1.0 \times 10^{-2}$, $5.0 \times 10^{-3}$ and $5.0 \times 10^{-3}$. The PROFFIT is executed to fit the spectra, and considered species are CO$_2$, H$_2$O, and CH$_4$. 

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Figure 5.6. Example fit effect using solar line database of PROFFIT (the first panel) and from inversion (the second panel). The lowest panel gives transmission measured (dot) and calculated (solid line). The spectrum is measured at TCCON site Bialystok.

Figure 5.7. CO$_2$ column-averaged mole fraction retrieved from spectra measured at Bremen using solar line database of PROFFIT (black) and that inverted (blue). The first panel is difference, the second CO$_2$ mole fraction, the third SZA. Air column is derived from surface pressure.
CO₂ spectroscopy is from Toth (2008a) (used in GFIT) with an addition of line mixing parameter of PROFFIT, which is calculated using the software (Lamouroux et al., 2010), H₂O from Toth (2005) and CH₄ from HITRAN 12. Profiles are adjusted with the first-order Tikhonov-Phillips constraint for CO₂ and GFIT a prior is scaled for others. In the case where adjusting line parameters can not reduce residual to a required level, the solar line will be split into several lines. Figure 5.6 shows a reduction of residual by using the inverted solar line parameter. The spectra measured at Bremen are used to test influences of solar line parameter on retrieval of CO₂ in this region. The retrieval is done with PROFFIT, considered species are ¹²CO₂, other isotopes of CO₂, CH₄ and H₂O. The used spectroscopy is the same as that used in inverting solar line parameters, except for only Toth (2008) is used for CO₂ without line mixing taken into account. GFIT a priors are scaled for retrievals of all species. Tp is from NCEP reanalysis and intra-day variabilities are included. As can be seen from Figure 5.7, inverted solar line parameters reduce CO₂ column by about 2 ppm and the airmass-dependence by 2 ppm. This reduction could be similar for all measurements, except for the high-altitude site. Because the influence of solar lines does not depend on atmospheric state except for CO₂ concentration, which is quite uniform globally.

This algorithm is also applied to the region 4887.00 to 4916.00 cm⁻¹, however, solar line is weak there, reduction of residual is small and will not shown here.

5.2.4. CO₂

The majority of CO₂ spectroscopy is given assuming a Voigt line shape (Toth et al., 2008a), and a few studies consider line mixing and speed-dependence effect in limited regions (Devi et al., 2007; Predoi-Cross et al., 2007; Miller et al., 2005). A theoretical method is developed to predict line mixing of CO₂ in Lamouroux et al. (2010), which is applied to all CO₂ lines. There are a lot of work contributing to measurement of all relevant line parameters for the main isotope ¹²CO₂ lines, such as the region 6180.00 to 6260.00. However, the measurements for minor isotopes, such as ¹³CO₂ band used in this Chapter in the region 4887.00 to 4916.00, are limited to vacuum wavenumber and intensity only (Miller et al., 2004; Toth et al., 2008b). The other parameters of ¹³CO₂ lines are predicted with theory.

The CO₂ line parameters in the regions around 6220 and 4901 cm⁻¹ are inverted from ground-based solar spectra measured at TCCON site Bialystok, totally 14 records the SZA of which range from 30° to 82°. The code PROFFIT is executed to fit the spectra. For the ¹²CO₂ region 6180.00 to 6260.00 cm⁻¹, considered species are ¹²CO₂, other isotopes of CO₂, H₂O, HDO and CH₄. The used spectroscopy database are Toth et al. (2008a) with addition of line mixing parameter of PROFFIT for CO₂ that acts as a prior spectroscopy in inverting line parameter step, Toth (2005) for H₂O and HDO and HITRAN 12 for CH₄. Profile retrieval under the first-order Tikhonov-Phillips constraint is applied to ¹²CO₂, and scaling GFIT a prior is used for other species. For ¹³CO₂ region 4886.70 to 4916.30 cm⁻¹, considered species are H₂O, ¹²CO₂, ¹³CO₂, CO₁⁸O and other isotopes of CO₂. The used spectroscopy database is the inverted one for H₂O, and the same as in ¹²CO₂ region for CO₂. The inverted solar line parameters are used for both regions. Profile retrievals with the first-order
Tikhonov-Phillips constraint are performed for $\text{H}_2\text{O}$ on a logarithmic scale, and for $\text{CO}_2$ on a linear scale. For the profile retrieval in both regions, a prior is from WACCM climatology for $\text{H}_2\text{O}$, and a mean profile of CarbonTracker for $\text{CO}_2$ at Bialystok. The channeling is considered in both regions, and $T_p$ profiles are from NCEP reanalysis with intra-day variability allowed.

Spectroscopy parameter inversions with and without speed-dependence of air-broadening effect taken into account are performed, and both of which with line mixing taken into account. Spectroscopy of lines with intensity larger than $1.0 \times 10^{-24} \text{ cm}^{-1}$ only are inverted and involved parameters are intensity $S$ and air-broaden half width $\gamma_{\text{air}}$ at 296 K, first-order line mixing coefficient at 260 K $Y_{260}$. In the case that the speed-dependence parameter of air broadening $\gamma_2$ at 296 K is inverted, it is adjusted for lines stronger than $3.0 \times 10^{-24}$ only. A prior of the speed-dependent parameter is taken as zero. The uncertainty of the line mixing coefficient is set to be 0.0035 atm$^{-1}$, and that of the speed-dependent parameter 0.01 cm$^{-1}$atm$^{-1}$. A smooth constraint for variations along $m$ is applied for the speed-dependent parameter. $J''$ is rotational quantum number of lower states.

Figure 5.8 and 5.9 give an example for fitting effect using different sets of spectroscopy for $\text{CO}_2$ in both regions. It can be seen that inverted line parameters reduce the residual. Taking speed-dependence of air-broadening into account does not improve the fit any further.

Figure 5.8. residual variations when using different spectroscopy, Toth (2008a) (the first panel), Toth (2008a) with line mixing (the second panel), optimized Toth (2008a) with line mixing (the third panel) and optimized Toth (2008a) with line mixing and speed-dependence of air-broadening effect (the fourth panel), for $\text{CO}_2$ in region 6180-6260 cm$^{-1}$. The lowest panel give transmission, the spectrum is measured at Bialystok under a SZA of 81.7°.
Figure 5.9. Same as Fig. 5.8 except for region 4887-4916 cm$^{-1}$.

Figure 5.10. Comparison of intensities at 296 K of CO$_2$ lines in regions 6180-6260 cm$^{-1}$ (left) and 4887-4916 cm$^{-1}$ between Toth (2008a) (black), optimized with line mixing (blue) and both line mixing and speed-dependence of air-broadening (red) taken into account. The first panel gives percent differences and the second absolute value.
Figure 5.11. Same as Fig. 5.10 except for air-broaden half width at 296 K, $\gamma_{\text{air}}$.

Figure 5.12. Same as Figure 5.10 except for the first-order line mixing coefficient at 260 K, $Y_{260}$. 

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The comparisons between the inverted and a priori line parameters of CO\textsubscript{2} in both regions are given in Figure 5.10-5.13. The differences of $S$, $\gamma_{air}$ and $Y_{260}$ between inversions and a prior are smaller in region 6180-6260 cm\textsuperscript{-1} than 4887-4916 cm\textsuperscript{-1}. It reflects that there is a lot of laboratory measurements in the first region and then the uncertainties of $S$ and $\gamma_{air}$ given in HITRAN are smaller than that in the second region. The larger difference and scatter of $Y_{260}$ in the region 4887-4916 cm\textsuperscript{-1} could come from a strong interference between different isotopes of CO\textsubscript{2} or weaker line mixing effect due to smaller line strength. The absorption of CO\textsubscript{2} in region 6180-6260 cm\textsuperscript{-1} is almost completely from a $^{12}\text{CO}_{2}$ band $30013\leftarrow00001$ and each line locates distinct from the others. In both regions, the inverted $\gamma_{air}$ is smaller than a prior around $|m|=20$, which exists for both inversions with and without speed-dependence parameter taken into account. It is not clear whether the laboratory or atmospheric measurement is closer to the true value. The inverted speed-dependence parameter only differs from a prior (zero) for strong lines, and presents large scatter. It indicates information about this parameter is rare in the current set of spectra. If additional spectra measured at high-altitude sites are included, the information on speed-dependence of air-broadening effect could be improved.

The measurements at Bremen are used to test influences of different spectroscopies on the retrieval of CO\textsubscript{2}. The retrieval is done with PROFFIT and its setup is same as for inverting CO\textsubscript{2} spectroscopy except for that scaling GFIT a prior and a profile retrieval based on the optimal estimation theory, which will be detailed in Sect. 5.3.2, are applied to CO\textsubscript{2}. In region 4887-4916 cm\textsuperscript{-1}, only scaling GFIT a prior is used for CO\textsubscript{2} isotopes other than $^{13}\text{CO}_{2}$. The channeling is not taken into account.

There are four sets of line parameters compared for CO\textsubscript{2}, which are Toth (2008a), Toth (2008a) with line mixing parameters of PROFFIT, the optimized Toth (2008a) and line mixing parameters, and the optimized Toth (2008a) with line mixing and speed-dependent parameters together. Figure 5.14
shows variations of CO$_2$ columns resulted from using different spectroscopies for CO$_2$. The inverted line parameter reduces airmass-dependence of $^{13}$CO$_2$ columns by about 5 ppm, and about 1-2 ppm for $^{12}$CO$_2$ on these two days. Including speed-dependence parameter only create positive shift than without it, which is 0.5-1 ppm at SZA above 80°. Addition of line mixing parameters has negligible influence without an optimization applied. Figure 5.15 presents variations of $\delta^{13}C$, reduction of its airmass-dependence by using the optimized spectroscopy of CO$_2$ is about 7 with a slight better performance from including both line mixing and speed-dependence of air-broadening effect.

Figure 5.14. Comparison of column-averaged $^{12}$CO$_2$ (red) and $^{13}$CO$_2$ (black) mole fractions retrieved from two days measurements at Bremen using different spectroscopy, Toth (2008a) (plus), Toth (2008a) with line mixing parameter (cross), optimized with line mixing (horizontal line) and both line mixing and speed-dependence of air-broadening (vertical line) taken into account. The first panel is difference, the second CO$_2$ mole fraction and the third SZA. Surface pressure is used to calculate air column.
Figure 5.15. Same as Fig. 5.14 except for δ\(^{13}\)C.

Figure 5.16. Comparison of \(^{12}\)CO\(_2\) profiles retrieved from two days measurements at Bremen using different spectroscopy, Toth (2008a) (the first panel from the left), Toth (2008a) with line mixing parameter (the second panel from the left), optimized with line mixing (the third panel from the left) and both line mixing and speed-dependence of air-broadening (the fourth panel from the left) taken into account. The blue line is the retrieval and black is GFIT a prior.
Figure 5.16 and 5.17 show variations of retrieved $^{12}$CO$_2$ and $^{13}$CO$_2$ profiles using different spectroscopies. The inverted spectroscopy largely improves $^{13}$CO$_2$ profiles, by increasing mole fractions in the stratosphere and lower troposphere and decreasing them in the mid and upper troposphere, which indicates an overestimation of $\gamma_{air}$ in Toth (2008a). However, it is hard to say if $^{12}$CO$_2$ profiles are improved or degraded. Including speed-dependence effect increases mole fractions in the boundary layer, because the air-broaden half width averaged over the thermal distribution of molecular speed is smaller than that at the mean speed (Hartmann et al., 2008, p.92).

5.3. Retrieval aspect

The column of CO$_2$ could differ among different retrieval setups, e.g. profile scaling or a profile retrieval is applied to CO$_2$ itself; treatment of interference species, like H$_2$O; Tp profiles, e.g. use NCEP reanalysis or retrieve them simultaneously.

5.3.1. Influence of Interference species

The only important inference species is H$_2$O in region 4887-4916 cm$^{-1}$ for $^{13}$CO$_2$ retrieval. The influence of H$_2$O depends on its concentration and vertical distribution, which can be retrieved through scaling a profile, e.g. that from NCEP reanalysis, or adjusting its profile. In addition, the accuracy of H$_2$O spectroscopy could matter as well.
Figure 5.18. Variations of $^{13}$CO$_2$ column using different setups for fitting H$_2$O, using optimized Toth (2005) line parameter and adjusting profile (plus), using Toth (2005) line parameter and adjusting profile (cross), using HITRAN 12 line parameter and adjusting profile (horizontal line), using optimized Toth (2005) line parameter and scaling (vertical line) GFIT a prior. In all cases, $^{13}$CO2 is retrieved thorough scaling GFIT a prior and using the optimized Toth (2008a) with both line mixing and speed-dependence of air-broadening taken into account.

Figure 5.19. The $^{13}$CO$_2$ profiles, which are retrieved using optimal estimation approach, under various H$_2$O fitting setups as in Fig. 5.18. Note a different x axis scale is used for the first panel from the left.
Figure 5.18 and 5.19 show influences of H2O retrieval setups on the retrieval of 13CO2 columns and profiles for the two days measurements at Bremen. Four setups are compared, which are using optimized Toth (2005) line parameters and adjusting H2O profiles under the first-order Tikhonov-Phillips constraint, as the former except for using Toth (2005) line parameters, as the first except for using HITRAN 12 and using optimized Toth (2005) line parameters but scaling GFIT a prior to fit H2O absorption. The 13CO2 column and profile are retrieved by scaling GFIT a prior for retrieving columns, and using optimal estimation approach for retrieving profiles, respectively. The CO2 spectroscopy is the optimized Toth (2008) including line mixing and speed-dependence effect of air-broadening. Other details are the same as in Sect. 5.2.4.

Comparing with the first setup of H2O retrieval, using HITRAN 12 leads to the largest difference as expected because the large residuals resulted from it. The second largest difference is from using the profile scaling, up to 2‰. An interesting thing is that the difference from applying the profile scaling is larger for a day with less humidity. It could indicate an importance of adjusting H2O profile for in a retrieval of δ13C. Using H2O spectroscopy that is not optimized creates the smallest difference, about 1‰. However, the conclusion might not be general since only two days measurements are used. The influence of H2O on retrieved 13CO2 profiles is much more significant, the variation is up to 20 ppm in the stratosphere. Because stratospheric CO2 is known quite well, as shown by the GFIT a prior, the results using the first setup for H2O should be the closest to true profiles.

5.3.2. Influence of retrieval method

The column averaging kernels of 13CO2 and 12CO2 should be similar as much as possible for a correct retrieval of their ratio. The stronger a CO2 line is, the larger the weight of a retrieval in lower atmosphere is. The retrieval with more DOFS has vertically uniformer column sensitivity, e.g. a profile retrieval compared to a profile scaling approach. In this section, two retrieval strategies are compared for CO2, scaling GFIT a prior and profile retrieval using the optimal estimation theory.

A prior covariance of CO2 is constructed empirically, with diagonal elements derived from CarbonTracker simulations implemented by WACCM in upper atmosphere. Off-diagonal elements are calculated as $S_{a,ij} = \sigma_i \sigma_j \exp\left[-(z_i - z_j)^2/l^2\right]$, where $\sigma$ is the square root of the diagonal elements and $z_i$ is the altitude of the $i$th grid on which CO2 profiles are sampled, $l=3 km$. A prior profile is the average of the merged model profiles, which is scaled to follow interannual increase of atmospheric CO2. The DOFS is about 1-2 for both 12CO2 and 13CO2. The used spectroscopy is, optimized Toth (2008a) added with line mixing and speed-dependence of air-broadening for CO2, the optimized Toth (2005) for H2O. Profile retrieval and scaling are used for H2O in regions 4887-4916 cm$^{-1}$ and 6180-6260 cm$^{-1}$, respectively. Other aspects of setups in both the regions are the same as in the former sections.

Figure 5.20 shows the correlation matrix $r_{ij} = \exp\left[-(z_i - z_j)^2/l^2\right]$ and a prior profile of CO2. The CO2
mole fraction at the lowest layer is assumed to be uncorrelated with that at other layers, since there are a lot of small-scale variations in the boundary layer. Figure 5.12 presents column averaging kernels of CO$_2$ in both regions. It is clear that the column averaging kernel for profile retrieval has less a difference between the two regions, and variabilities with SZA.

Figure 5.20. Correlation matrix of a prior covariance $r_{ij} = S_{a,ij} / (\sigma_i \sigma_j)$ (left) and a prior profile with square root of diagonal elements of a prior covariance represented by the error bar (right).

Figure 5.21. Column averaging kernels of CO$_2$ retrieval for region 6180-6260 cm$^{-1}$ (black) and 4887-4916 cm$^{-1}$ (blue) using profile retrieval (solid line) and scaling (dashed line). The kernels are
Near-infrared spectra measured at Bialystok during 2009-2011 are used to test the two methods of retrieving CO₂, and the results are showed in Figure 5.22. The difference of δ¹³C between the two methods presents a seasonal behavior in a range of -2 to 1, because the influence of the averaging kernel depends on CO₂ profiles that vary seasonally. The seasonal cycles of δ¹³C from FTS are similar to that of in situ measurements. Mole fractions of CO₂ peak and δ¹³C reaches minima in winter because of a release of CO₂ by the respiration of the plants which is enriched in ¹²C relative to atmospheric CO₂. The opposite occurs in summer because the plants fix CO₂, with a preference to ¹²CO₂. However, disagreements occur in the period August of 2009 to March of 2010. The FTS was not evacuated in that period, one of its effects is scaling the measured frequency by a factor that
depends the refractive index of air at that frequency and the laser frequency of a FTS. However, applying a calibration to the measured frequency did not produce any significant difference.

5.3.3. Influence of atmospheric T, P profiles

In all the former setups of CO₂ retrievals, Tp profiles are from NCEP reanalysis data. However, it is also possible to retrieve atmospheric temperature from the spectra, and pressure can be calculated based on the barometric formula given surface pressure. The strength of a molecular absorption line is related to the equilibrium relative population of the initial state, as showed in Eq. 5.7, which can be expressed as \( \rho \propto \exp(-E/k_B T) \), where \( E \) is the initial state energy. The lines with different initial states will differ in the temperature-dependence of their strength. Atmospheric temperature can be retrieved based on such dependence.

In this section, retrievals with and without fitting temperature are compared. The profile retrieval based on optimal estimation is applied to both \(^{13}\)CO₂ and \(^{12}\)CO₂, used spectroscopy databases and other details are the same as in Sect. 5.3.2. While the same region 4887-4916 cm\(^{-1}\) is used for \(^{13}\)CO₂ and temperature retrieval, there are additional microwindows, where H₂O lines with various initial state energies present, used except for the region 6180-6260 cm\(^{-1}\) to improve information on temperature in the case of \(^{12}\)CO₂. These windows are 4724.00-4728.30, 4732.30-4736.50, 4738.70-4740.70, 4750.00-4751.50 and 4755.70-4766.40 cm\(^{-1}\). The optimized Toth (2005) is used for H₂O, and a profile retrieval is applied to it. Temperature profiles are retrieved based on an optimal estimation approach in both regions.

![Figure 5.23. Comparison of δ\(^{13}\)C between with (cross) ans without (plus) fitting temperature. The](image)

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spectra are measured at Bremen on two days.

Figure 5.24. Comparison of $^{13}$CO$_2$ (the first and second columns) and $^{12}$CO$_2$ (the third and fourth columns) profiles retrieved from spectra measured at Bremen on two days. Blue lines are retrieval and black are GFIT a prior. The fifth column presents differences between with and without fitting temperature for $^{13}$CO$_2$ (black) and $^{12}$CO$_2$ (red).

Figure 5.23 and 5.24 show comparisons for columns and profiles of CO$_2$ retrieved from spectra measured at Bremen on two days. Fitting temperature does not improve retrievals of $\delta^{13}$C and CO$_2$ profiles on these two days.

5.4. Instrumental aspect

In this section, the influences of errors arising from instrumental imperfection are investigated. Retrieval setups for $^{12}$CO$_2$ and $^{13}$CO$_2$ are kept unchanged in this section. It is a profile retrieval based optimal estimation for $^{12}$CO$_2$ and $^{13}$CO$_2$, a profile retrieval with the first-order Tikhonov-Phillips constraint for H$_2$O in the region 4887-4916 cm$^{-1}$, scaling GFIT a prior for other species and H$_2$O in the 6180-6260 cm$^{-1}$ region. The optimized Toth (2008a) with line mixing and speed-dependence is used for CO$_2$, optimized Toth (2005) for H$_2$O. Tp profiles from NCEP reanalysis are used. Other details are the same as in the former sections.

5.4.1. Laser sampling error

The interferogram recorded with a FTS is sampled on discrete values of optical path difference (OPD). Errors in assumed OPD values could result in artifact spectral lines. The interferogram is sampled at the zero crossings of reference laser interferogram, the laser is fed into the spectrometer
and goes in the same ways as signal being measured, e.g. solar radiation. An incorrect mean intensity level of laser interferogram can lead to a periodic sampling error, and distortions of the true spectrum after Fourier transformation (Dohe et al., 2013). The spectra measured at Bialystok during the period 2009-2011 are used to investigate influences of the laser sampling error on CO₂ retrievals. The laser sampling error (LSE) represented in a fraction of sampling increment ranges -0.004 to 0.004 in this period. Figure 5.25 and 5.26 present influences of LSE on retrievals of δ¹³C and CO₂ profiles. It can be seen that the influences on the both are small, -0.4 to 0.4 for δ¹³C and -5 to 5 ppm for CO₂ profiles.

Figure 5.25. Daily mean of retrieved δ¹³C from spectra measured at Bialystok in the period 2009-2011 with and without LSE correction, and the difference between them (the fourth panel). The together showed are GFIT $X_{CO_2}$ (the first panel), NOAA surface δ¹³C (the second panel) measured at Ochsenkopf (50.030°N, 11.808°E, 1009 masl), Germany.
5.4.2. Instrumental line shape

In all the former retrieval, the instrumental line shape (ILS) is assumed to be a nominal one. In this section the true ILS retrieved from laboratory HCL cell measurements with code LINEFIT 14 (Hase et al., 1999) are used and its influences are investigated. The spectra measured at Bialystok in the period 2009-2011 are used, to which LSE corrections has been applied.

Figure 5.27 and 5.28 give retrieved ILS and parameters characterizing them. The FTS at Bialystok is not evacuated between August of 2009 and August of 2010, correspondingly retrieved H₂O columns from the laboratory spectra significantly depart from zero. Maximum phase error shows larger scatter in this period. As mentioned before, the retrieved δ⁰¹³C presents incorrect seasonal behavior. Firstly it was expected the distorted ILS contributes to the abnormal δ¹³C. However, retrievals accounting for these distortions in ILS do not differ from that using nominal ILS too much, as can be seen in Figure 5.29. The difference of δ¹³C between using the two kinds of ILS is only about -0.5 to 0.1. It need to be noted here that the nominal ILS is used for spectra in 2011 because tests in 2009-2010 do not show any improvement and then the retrieval applying the retrieved ILS was not continued.
Figure 5.27. The ILS of FTS at Bialystok retrieved from laboratory measurements. The first panel shows modulation efficiency and the second phase error variabilities along with OPD. The third panel is ILS functions. The colors indicate time.

Figure 5.28. The modulation efficiency at maximum OPD (the first panel) and maximum phase error over the whole OPD (the second panel), and $\text{H}_2\text{O}$ in the FTS (the third panel). The period with significant $\text{H}_2\text{O}$ indicate that the FTS was not evacuated there.
Figure 5.29. Daily mean of retrieved $\delta^{13}C$ (the third panel) from spectra measured at Bialystok in the period 2009-2011 with nominal (black) and retrieved ILS (blue) and the difference (the fourth panel). The together showed are GFIT $X_{CO_2}$ (the first panel), NOAA surface $\delta^{13}C$ (the second panel) measured at Ochsenkopf (50.030°N, 11.808°E, 1009 masl), Germany.
Figure 5.30. Comparison of $^{13}$CO$_2$ (the first and second columns) and $^{12}$CO$_2$ (the third and fourth columns) profiles retrieved from spectra measured at Bialystok in the period 2009-2011 with nominal (the second and fourth columns) and retrieved (the first and third columns) ILS. The fifth column presents differences between with nominal and retrieved ILS for $^{13}$CO$_2$ (black) and $^{12}$CO$_2$ (red).

Influences of ILS on the retrieval of CO$_2$ profiles concentrate in the stratosphere, instead of the troposphere such as those of LSE, with a larger amplitude in the case of $^{13}$CO$_2$. This is because non-ideal ILS distorts the center of a spectral line more significantly, which mostly comes from contribution of molecular absorption in the stratosphere where the absorption line is narrow. The absorption lines of $^{13}$CO$_2$ are weaker and less saturated than $^{12}$CO$_2$ lines and then more sensitive to the distortion at line center.

5.5. Summary

In this chapter, the possibility of retrieving $\delta^{13}$C from ground-based solar FTS spectra is explored. To correct inaccuracies of spectroscopic parameters of H$_2$O, solar line and CO$_2$, an algorithm retrieving molecular spectroscopy from ground-based FTS spectra is developed. It is applied to H$_2$O, solar line and CO$_2$. While the Voigt line shape is assumed in the case of H$_2$O, both line mixing and speed-dependence of air-broadening are taken into account for CO$_2$.

Comparisons with other existing spectroscopic datasets demonstrate applicability of the algorithm. While the inverted spectroscopic parameter reduces H$_2$O interference and the airmass-dependence artifact in CO$_2$ retrieval that mainly arises from errors in CO$_2$ spectroscopy, the retrieved $\delta^{13}$C is still not reasonable enough. Tests on retrieval method setup are taken as well, a profile retrieval is applied to CO$_2$ instead of a commonly used profile scaling approach. Results reveal that column averaging kernels of $^{12}$CO$_2$ and $^{13}$CO$_2$ become closer to each other when the profile retrieval is used compared to the scaling approach. Differences in $\delta^{13}$C between the two retrieval methods are significant, varying from -2 to 1. However, there still exists some incorrect seasonal behavior for spectra measured at Bialystok. Tests on H$_2$O retrieval setups indicate a necessity of using correct H$_2$O spectroscopic data and adjusting its profile in retrieving both $\delta^{13}$C and CO$_2$ profiles correctly. The last test is about imperfect instrumental performances, namely the laser sampling error and non-ideal instrumental line shape. Using spectra with LSE corrections applied results in minor differences in $\delta^{13}$C, -0.2 to 0.6 only. When ILS retrieved from laboratory HCL cell spectra is used, the retrieved $\delta^{13}$C differs from that using nominal ILS by -0.5 to 0.1 only. The incorrect seasonal behavior of $\delta^{13}$C in some period of measurements at Bialystok still presents.

There are more error sources, probably in the instrument, left to be identified before obtaining correct isotopic compositions of CO$_2$ from ground-based FTS spectra.
6. Conclusions

A posterior correction method is developed to derive the tropospheric column-averaged mole fraction of CH$_4$ from total columns of CH$_4$ and N$_2$O. The N$_2$O column is used to infer contribution of stratospheric CH$_4$. Validation with in situ measurements reveals an accuracy of about 5 ppb for the method. Comparisons with other methods, e.g. the HF method and direct profile retrieval, reveal a more stable behavior of the developed method with respect to H$_2$O interference and variations of instrumental performance. A remaining problem of the method is the assumption about tropospheric N$_2$O mole fractions, which are not suitable to regions influenced by significant N$_2$O sources.

The method is applied to column measurements at TCCON sites, and derived tropospheric together total column-averaged CH$_4$ mole fractions are compared with three inverse modeling simulations. A combination of total and tropospheric column-averaged CH$_4$ separates biases in the simulations between the troposphere and stratosphere. While stratospheric bias has mostly dynamical reasons, the bias in the troposphere contains both sources (sinks) -related and transport reasons. The isentropic mixing processes in the stratosphere are diagnosed using the equivalent length. The modeled southern surf zone is not developed enough because of a too weak planetary wave breaking there. Consequently, in Jun-Jul-Aug period stratospheric CH$_4$ in southern mid-latitudes presents much larger isentropic gradients in the models than measurements. During the development of the southern surf zone, a region with both vertically and horizontally well mixed CH$_4$ occur between 450 and 850 K (~18 and 30 km) in surf zone latitudes. Such a region is absent in the models. The modeled polar vortex breaks too fast compared to the measurements. Modeled CH$_4$ concentrations in the polar vortex rise at all levels at same time instead of at high levels initially as in the measurements.

Retrieval of isotopic compositions of atmospheric CO$_2$ from ground-based FTS spectra is investigated. There are three aspects explored, spectroscopy, retrieval method and instrumental performance. An algorithm is developed to invert spectroscopic parameters using ground-based solar FTS spectra. The spectral line parameters of the molecules H$_2$O, CO$_2$, and solar line are inverted in several regions. The line mixing and speed-dependence of air-broadening effect are taken into account in inverting CO$_2$ spectroscopy. The inverted parameters reduce residuals of spectra fit which arise from the lines of these species, improve profile retrievals in the case of H$_2$O and $^{13}$CO$_2$, and weaken airmass-dependence of retrieved $^{12}$CO$_2$ and $^{13}$CO$_2$ columns. Tests on retrieval methods reveal that importance of H$_2$O interference on $^{13}$CO$_2$ retrieval, and applying profile retrieval for both $^{12}$CO$_2$ and $^{13}$CO$_2$ in a retrieval of the isotopic ratio of CO$_2$. On deficiencies of FTS instrument, only laser sampling errors and distortions of instrumental line shape are examined and results show their minor influence. More works are needed to explore other aspects of instrumental performance.
Appendix

A. Derivation of formula for integrating in situ profile

The formula Eq. 3.11 for integrating in situ profile to validate a derived tropospheric column-averaged mole fraction of CH₄ is derived here. Inserting the expression for retrieved total column Eq. 3.9 into Eq. 3.10 and considering the expression of \( \phi_y \), we have,

\[
X_{CH_4}^{trop} = \frac{\int_0^P a_{CH_4} f_t^{CH_4} \frac{dp}{mg} - b \mu_y \left( \int_0^P a_y (f_t^y - X_y^{trop}) \frac{dp}{mg} \right)}{\phi_{CH_4} V C_{air}}. \tag{A.1}
\]

The integration in the second term in the numerator contains the averaging kernel of species \( y \), and the multiplier \( \mu_y \) in front of it is used to convert it into an integration contain the averaging kernel of CH₄. The calculation of this multiplier needs the true profile of \( y \) as shown in Eq. 3.10. But in practice the true profile is not available, and approximated by a subsided reference profile as being described in section 3.1.3. Assuming such approximation creates only small error, then

\[
X_{CH_4}^{trop} = \frac{\int_0^P a_{CH_4} f_t^{CH_4} \frac{dp}{mg} - b \left( \int_0^P a_{CH_4} \left( f_t^y - X_y^{trop} \right) \frac{dp}{mg} \right)}{\phi_{CH_4} V C_{air}}. \tag{A.2}
\]

Because \( f_t^y - X_y^{trop} \) is zero in the troposphere, and splitting integration for the true profile of CH₄ into the troposphere and stratosphere,

\[
X_{CH_4}^{trop} = \frac{\int_0^{P_t} a_{CH_4} f_t^{CH_4} \frac{dp}{mg} + \int_{P_t}^P a_{CH_4} \left( f_t^{CH_4} - b \left( f_t^y - X_y^{trop} \right) \right) \frac{dp}{mg}}{\phi_{CH_4} V C_{air}}, \tag{A.3}
\]

where \( P_t \) is tropopause pressure. According to Eq. 3.1 the mole fractions of \( y \) and CH₄ are linearly correlated in the stratosphere, then the term \( f_t^{CH_4} - b \left( f_t^y - X_y^{trop} \right) \) is a constant representing tropospheric CH₄ concentration. The first term in the numerator of Eq. A.3 is the tropospheric column of CH₄, and can be rewritten as,

\[
\left[ \left( \int_0^{P_t} a_{CH_4} f_t^{CH_4} \frac{dp}{mg} \right) / \left( \int_0^{P_t} a_{CH_4} \frac{dp}{mg} \right) \right] \int_0^{P_t} a_{CH_4} \frac{dp}{mg} \tag{A.4}
\]

Assuming the tropospheric CH₄ concentration represented by the constant \( f_t^{CH_4} - b \left( f_t^y - X_y^{trop} \right) \) is a same quantity as the term in the square bracket in Eq. A.4, and considering the expression of \( \phi_{CH_4} \), we have,
\[ X_{CH_4}^{\text{top}} = \left( \int_{P_i}^{P_r} a_{CH_4} f_i^{CH_4} \frac{dp}{mg} \right) / \left( \int_{P_i}^{P_r} a_{CH_4} \frac{dp}{mg} \right) \]  

(A.5)

B. Derivation of formula for correcting airmass-dependent artifact

From Eq. 2.10 the retrieved quantity include contribution from true and a prior quantity, error in forward model parameters, error in forward model and measurement noise. Replacing \( \Delta f \) in Eq. 2.10 with the difference between forward function and forward model using Eq. 2.9, ignoring measurement noise and rearranging, we have following equation,

\[ \hat{x} = x + (A - I)(x - x_a) + G(f(x, b, b') - F(x, \hat{b})), \]  

(B.1)

where, \( G \) is a \( n \times m \) matrix representing sensitivity of the retrieval to the measurements, \( n \) is the dimension of state vector \( x \) and \( m \) is the dimension of measurement vector describing accurately by the forward function \( f \) or approximated by the forward model \( F \). \( b \) and \( b' \) are known and unknown forward function parameters, \( \hat{b} \) is an estimation of the known parameters in the forward function. Here, the hat symbol always means an estimation of a corresponding quantity. Averaging kernel \( A \), which has a dimension of \( n \times n \), and sensitivity matrix \( G \) are both evaluated at the retrieved state \( \hat{x} \) but hat notations are drop for convenience. \( I \) is a unit matrix with the same dimension with the averaging kernel. \( \hat{x}, x, x_a \) are retrieved, true and a prior state vectors with a dimension of \( n \), respectively. For ground-based FTS spectra, ignoring instrumental effects the forward function can be written as,

\[ f(x, b, b') = CL(\sigma) \exp\left(-\sum_i \sum_j g_{ij}(\sigma) S_{ij} \tilde{y}_{ij} d_i l_i \frac{Y_j P_s}{\cos(SZA_i)}\right), \]  

(B.2)

where, \( CL \) is solar radiation at top of the atmosphere, \( \sigma \) is wavenumber that is a vector with a dimension of \( m \). \( g_{ij}, S_{ij}, \tilde{y}_{ij} \) are line shape function, line intensity and mole fraction normalized by total column-averaged mole fraction \( Y_j \), the subscript \( j \) means the \( j \)th gas and \( i \) the \( i \)th altitude level. \( d_i, l_i, SZA_i \) are number density of air molecule normalized by surface pressure \( P_s \) and vertical length of the \( i \)th level and solar zenith angle at that altitude. Correspondingly, the forward model can be expressed as,

\[ F(x, \hat{b}) = \hat{CL}(\sigma) \exp\left(-\sum_i \sum_j \hat{g}_{ij}(\sigma) \hat{S}_{ij} \tilde{y}_{ij} d_i l_i \frac{Y_j P_s}{\cos(SZA_i)}\right). \]  

(B.3)

Ignoring the difference between \( CL \) and its estimation, and because spectroscopic errors are constant, the difference between the forward function and forward model can be expressed as,
\[ f(x, b, b') - F(x, \hat{b}) = \begin{pmatrix} \ddots & \vdots & \vdots \\ 0 & \prod_{j} h\left(\frac{Y_j P_s}{\cos(SZA)}, \tilde{y}_j\right) - 1 & \vdots \\ \vdots & \vdots & \ddots \end{pmatrix} \times F(x, \hat{b}), \] (B.4)

where,

\[ h\left(\frac{Y_j P_s}{\cos(SZA)}, \tilde{y}_j\right) = \exp\left(-\sum_{i} \left( g_{ij} S_{ij} - \hat{g}_{ij} \tilde{S}_{ij}\right) \tilde{y}_{ij} d_{ij} \frac{Y_j P_s}{\cos(SZA)}\right). \] (B.5)

In deriving Eq. B.4, the variation of SZA along path of solar radiation is ignored. Because the sensitivity matrix \( G \) means doing a retrieval, from Eq. B.1 we have,

\[ GF(x, \hat{b}) = x + (A - I)(x - x_a). \] (B.6)

The error terms in Eq. B.1 have been disregarded since the measurement is just the forward model \( F \) vector. Since matrix \( E \) is a function of \( Y_j P_s/\cos(SZA) \) and \( \tilde{y}_j \), then we might have following relation,

\[ GEF(x, \hat{b}) = C\left(\frac{Y_1 P_s}{\cos(SZA)}, \tilde{y}_1; \ldots; \frac{Y_J P_s}{\cos(SZA)}, \tilde{y}_J\right)[x + (A - I)(x - x_a)]. \] (B.7)

where, \( C \) is a diagonal matrix function and \( J \) is the total number of the gases considered. Inserting Eq. B.7 into Eq. B.1, we have,

\[ \hat{x} = [I + C\left(\frac{Y_1 P_s}{\cos(SZA)}, \tilde{y}_1; \ldots; \frac{Y_J P_s}{\cos(SZA)}, \tilde{y}_J\right)][x + (A - I)(x - x_a)]. \] (B.8)

If correction function \( C \) is known, the error in the retrieval, including airmass-dependent artifact, resulted from spectroscopic inaccuracies could be removed.
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