

Measurements of mid-stratospheric formaldehyde from the Odin/SMR instrument

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Measurements of mid-stratospheric formaldehyde (H_2CO) have been obtained from the limb-viewing sub-millimeter radiometer (SMR) instrument aboard the Odin satellite. The analysis is based upon the only weak ($8_{08} \rightarrow 7_{07}$) rotational transition line of H_2CO that can be measured by Odin/SMR at 576.7083150 GHz in the band dedicated to the measurement of carbon monoxide (CO). The signal-to-noise ratio is increased by averaging about 1000 spectra within 2-km width vertical layers in the stratosphere over periods from 1 to 7 days and within 3 latitude bands: Southern Hemisphere (90°S – 45°S), tropics (30°S – 30°N), and Northern Hemisphere (45°N – 90°N). The faint H_2CO line can then be retrieved using the standard scientific ground-segment developed for the Odin/SMR measurements. The mid-stratospheric H_2CO shows maxima in the tropics for every period considered (January 2006, February 2005, March 2005, and September 2005). The spring-time extra-tropical mid-stratospheric H_2CO is more intense than the fall-time extra-tropical amounts. The simulations from the three-dimensional chemical-transport model Reprobus satisfactorily show these general features.

Keywords: Radiative transfer; Spectroscopy; Inversion; Formaldehyde; Remote sensing; Satellite; Stratosphere

1. Introduction

Remote sensing of the chemical composition of the Earth's atmosphere using passive microwave techniques has been intensively used since the beginning of the 1990s. Ground-based (e.g. [1]), balloon-borne (e.g. [2]), airborne (e.g. [3]) and satellite-based (e.g. [4]) instruments have indeed monitored a great number of molecules (ozone (O_3), chlorine monoxide (ClO), water vapor (H_2O), nitric acid (HNO_3), nitrous oxide (N_2O), etc.). These data have provided valuable information to understand the evolution of the atmosphere, in particular the O_3 layer, and its impact on climate change, and conversely, how climate change impacts upon the chemical

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composition of the atmosphere. More recently, by the use of very sensitive receivers either cooled or un-cooled, both the millimeter and the sub-millimeter domains have become accessible to heterodyne technology. The possibility of detecting weak microwave lines in the Earth's atmosphere has widened the spectrum of measurable molecules to include isotopologues (e.g. O_3 , H_2O , etc.), weakly abundant species (e.g. methyl cyanide (CH_3CN) [5], etc.) and vibrationally excited weakly populated states (e.g. O_3 , HNO_3 , etc.).

The limb-viewing Odin satellite launched in February 2001 contains a sub-millimeter radiometer (SMR) tuned to the frequency domains 486.1–503.9 and 541.0–580.4 GHz [6]. In its basic modes, it offers the possibility to measure target species like O_3 , ClO , N_2O , HNO_3 , H_2O , and carbon monoxide (CO), and also some isotopologues of O_3 and H_2O . Given the great quantity of spectra recorded so far, a statistical analysis based upon the average of thousands of measured spectra in order to reduce the random radiometric noise and thus increase the signal-to-noise ratio can characterize very weak line species in the sub-millimeter domain. Indeed, heavy isotopologue of water (HD^{18}O), methanol (CH_3OH) and vibrationally excited N_2O have already been detected in the 501-GHz Odin/SMR band by averaging more than 400,000 spectra [7]. We apply the same methodology for detecting the only weak ($8_{08} \rightarrow 7_{07}$) rotational transition line of formaldehyde (H_2CO) that can be measured by Odin/SMR at 576.7083150 GHz, in the band originally dedicated to the measurement of the strong CO rotational transition ($5 \rightarrow 4$) line at 576.2679305 GHz together with the strong O_3 rotational transition line ($10_{28} \rightarrow 9_{19}$) at 576.5148750 GHz. In addition, we use the Odin/SMR scientific ground-segment developed for the standard operational mode in order to estimate the vertical distribution of H_2CO in the middle stratosphere.

Measurements of H_2CO are available mainly in the troposphere. They are in the form of integrated column or vertically resolved profiles. Different techniques and platforms are used: space-borne sensors in the UV–VIS with the Global Ozone Monitoring Experiment (GOME) [8], ship borne [9] and ground-based [10] Fourier transform infrared spectrometers, airborne and balloon-borne sensors using tunable diode laser absorption spectroscopy [11], aqueous collection and enzyme-fluorescence detection [12]. Since there are no measurements of mid-stratospheric H_2CO in the literature to validate our retrievals except a stratospheric column amount [13], we finally compare the Odin/SMR measurements with the output from the three-dimensional chemical-transport model Reprobus [14].

The main sources of tropospheric formaldehyde (H_2CO or CH_2O) are the surface emission of pollutants from anthropogenic activity (industrial exhaust, cars, etc.), and from biomass burning. The main source of stratospheric H_2CO is linked to the oxidation of methane (CH_4) by OH and $\text{O}(^1\text{D})$ that produces different organic compounds (CH_3 , CH_3O_2 , CH_3OOH , CH_3NO_2 , CH_3O , CH_3OH , and $\text{CH}_3(\text{OH})\text{O}_2$) that finally, chemically or by photolysis, produce H_2CO (see Fig. 1). The main sinks of H_2CO are the photolysis and reactions with OH , HO_2 , NO_3 , Cl and Br . Note that H_2CO is an excellent tracer in the troposphere for

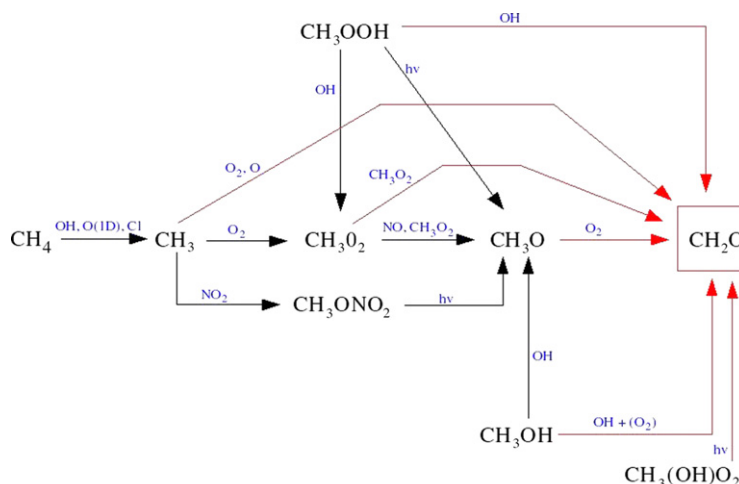


Fig. 1. Schematic representation of the stratospheric sources of formaldehyde.

diagnosing pollution [15], while in the stratosphere, H_2CO indirectly acts on the O_3 budget since its photolysis produces CO, an O_3 precursor when oxidized by OH.

The datasets used in the present manuscript are presented in Section 2, namely the Odin/SMR measurements and the Reprobus model. Due to a failure in the Odin/SMR phase-lock loop (PLL), measured spectra need to be calibrated in frequency prior to the averaging process. The method is also explained in Section 2. The estimation of H_2CO vertical profiles from averaged measured spectra is detailed in Section 3. The measured H_2CO vertical profiles obtained during several months and latitude bands are shown and discussed in Section 4, and finally compared with the outputs from the Reprobus model.

2. ODIN dataset

2.1. Measurements

The Odin mini-satellite is a Swedish-led project funded jointly by Sweden, Canada, France, and Finland [6,16]. It was placed into a 600-km Sun-synchronous, terminator orbit (i.e. crossing equator at 18:00 local time) by a START-1 rocket on 20 February 2001, and is still operational. Observation time is equally shared between astronomy and aeronomy. Odin includes two instruments. A UV-visible and infrared instrument, the optical spectrograph and infrared imager system (OSIRIS), that is capable of detecting O_3 , NO_2 , and aerosol in the scattered sunlight in the wavelength range 280–800 nm and the related oxygen airglow emission at $1.27\text{ }\mu\text{m}$ [17]. The second instrument is the SMR [18] that can measure O_3 , ClO, N_2O , HNO_3 , H_2O and isotopologues, and CO in the frequency domains 486.1–503.9 and 541.0–580.4 GHz. The great majority of these molecules have been validated (see e.g. [19–21] for CO). Data processing for both instruments uses temperature and pressure fields analyzed by the European Centre for Medium-range Weather Forecast (ECMWF).

In the aeronomy mode, several frequency bands have been optimally selected in order to study the above-mentioned target species [16]. The only H_2CO transition that can be detected in the pre-selected frequency bands is the weak ($8_{08} \rightarrow 7_{07}$) rotational transition line at 576.7083150 GHz. This line is measured in the band dedicated to the observation of the strong CO rotational transition ($J = 5 \rightarrow 4$) line at 576.2679305 GHz together with the strong O_3 rotational transition line ($10_{28} \rightarrow 9_{19}$) at 576.5148750 GHz [22]. Different observation modes, namely “odd hydrogen,” “stratospheric” and “water isotopologues,” enable the detection of the CO and O_3 lines, and consequently the H_2CO line, from either strato-mesospheric scans from 7 to 110 km or mesospheric scans from 55 to 110 km. The full auto-correlator bandwidth of 800 MHz is used in this band, with an effective resolution of 2 MHz. The altitude step between consecutive spectra can vary from 1.5 to 3 km in the stratosphere and is set to 5.5 km in the mesosphere. This corresponds to integration times varying from 1 to 3 s in the stratosphere, while it is 4 s in the mesosphere.

2.2. Spectrum correction and average

As already presented in [19], the local oscillator frequency of the 572-GHz radiometer is no longer stable due to a failure in the PLL. This means that the measured frequency of the 800-MHz total band is randomly shifted compared to the expected frequency. Typical values for the years 2005 and 2006 are ranging from -180 to $+30$ MHz. The two 800-MHz auto-correlators are in fact constituted of 8 sub-bands of 100-MHz bandwidth. The two correlators had a failure in one of the sub-bands. The unavailable sub-band has been pushed towards the edge of the 800-MHz total bandwidth, reducing the effective total bandwidth to 700 MHz. As a consequence of these two independent failures (the PLL and the 100-MHz sub-band), for some periods, the CO line or the O_3 line, and consequently the H_2CO weak line, cannot be observed even if the radiometer has been tuned to the CO band.

Nevertheless, in order to analyze the information contained in the CO band, an original method has been developed and slightly improved compared to the one explained in [19]. All the spectra measured during one scan are frequency calibrated by comparing the observed and calculated center frequencies of the CO line for tangent heights above 20–25 km. The variation of the frequency shift within one scan is very weak, less than ± 1 MHz, i.e. within the spectral resolution of the auto-correlator. Below 20–25 km, it is essentially impossible

to calibrate in frequency the measured spectra since the CO line is absorbed in the strong O₃ line wings. We then assume that the variation of the frequency shift along a scan is constant, to within 1 MHz, and we use this value to calibrate all the measured spectra belonging to one particular scan.

As an example, Fig. 2 shows spectra averaged within 2-km width vertical layers over the entire Earth (from 90°S to 90°N) in January 2006. This corresponds to 7 days of measurements and a number of ~ 5000 spectra averaged within each vertical layer. The CO and O₃ lines are clearly detected and stabilized in frequency at 576.268 and 576.515 GHz, respectively. The H₂CO weak line is highlighted by a vertical dotted line but is not visible using this large vertical scale. Note the dip in the measured brightness temperatures at frequencies greater than 576.9 GHz corresponding to the presence of the unavailable 100-MHz sub-band. For the same period, Fig. 3 shows a zoom around the transition frequency of the H₂CO line at 576.708 GHz for vertical layers between 30 and 62 km. The H₂CO line (vertical dotted line) is now clearly visible, well detached above the random noise. Other very faint lines are also detected. Over the total bandwidth of the CO band, Fig. 4 highlights the presence of transition lines from several atmospheric species: ClO, various isotopologues of O₃, vibrationally excited O₃, etc.

Fig. 5a–d shows for different altitude layers, namely 38, 40, 42 and 44 km, respectively the evolution of the H₂CO spectra when averaged within different latitude bands: mid-to-high Southern Hemisphere latitudes (SH: 90°S–45°S), tropics (30°S–30°N), mid-to-high Northern Hemisphere latitudes (NH: 45°N–90°N), and global (90°S–90°N). The spectra correspond to an average over the January 2006

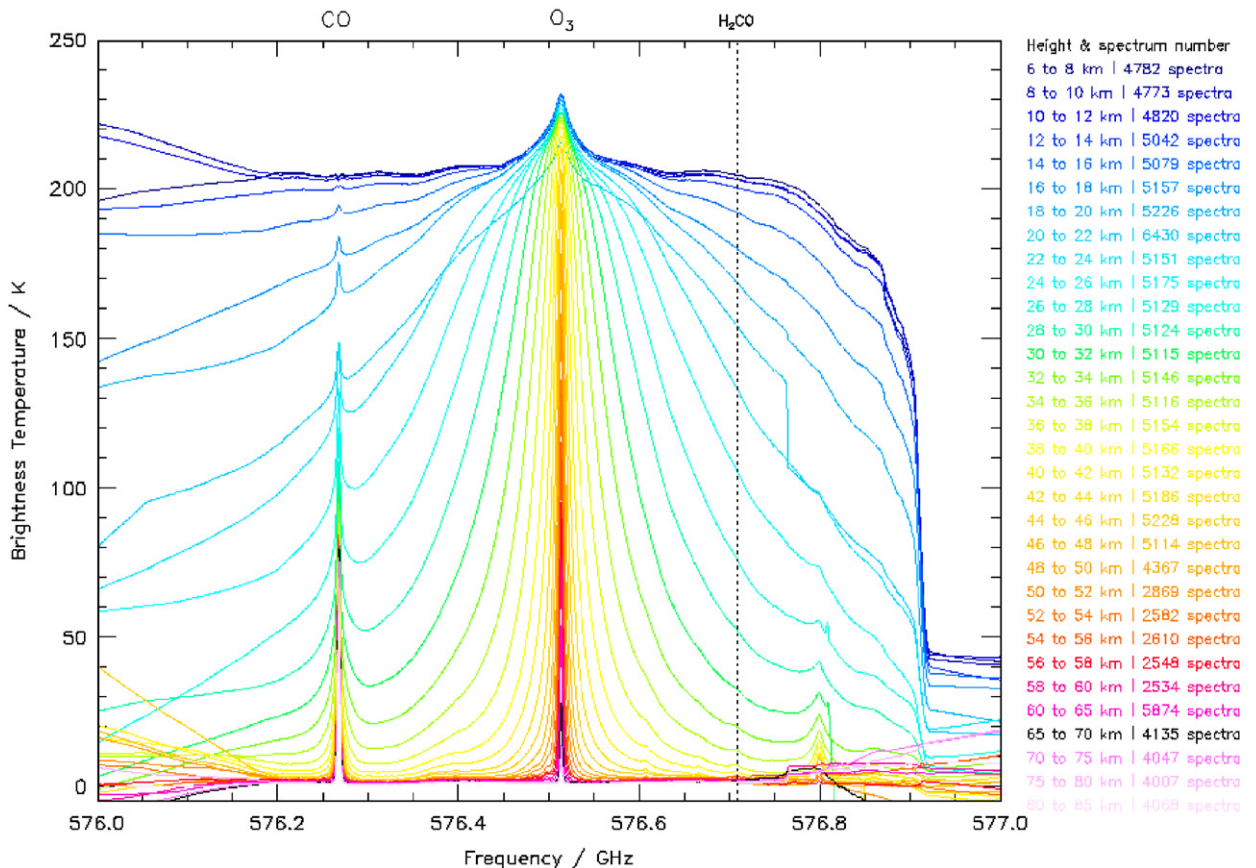


Fig. 2. Spectra representative of the band containing the CO and O₃ transitions at 576.2679305 and 576.5148750 GHz, respectively, globally averaged from 90°S to 90°N over 7 days from 13 to 31 January 2006 within 2-km width vertical layers in the stratosphere and 5-km width vertical layers in the mesosphere. The vertical dotted line shows the weak ($8_{08} \rightarrow 7_{07}$) rotational transition frequency of the H₂CO line at 576.7083150 GHz.

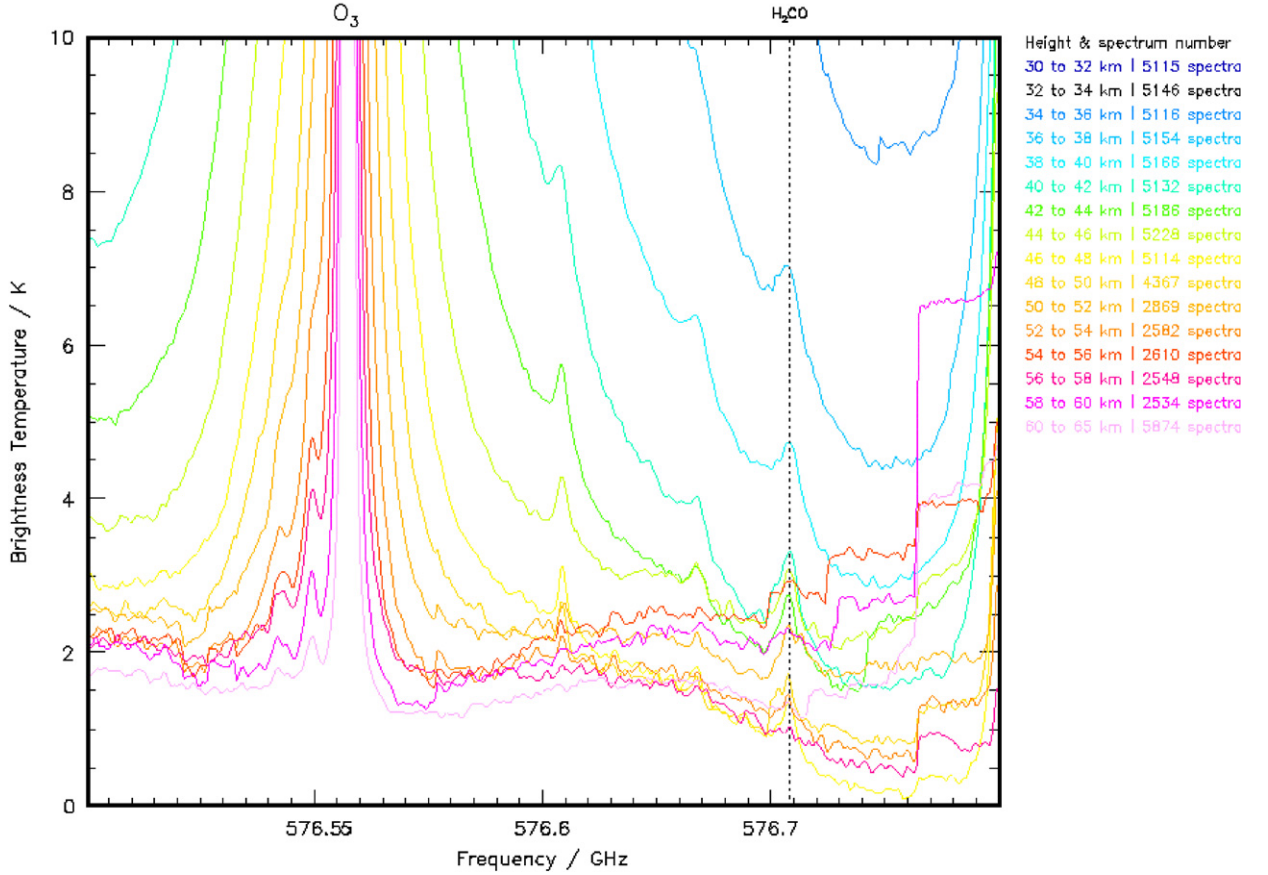


Fig. 3. Same as Fig. 2, but focussing around the H_2CO line at 576.7083150 GHz (vertical dotted line).

period. The maximum line intensity is about 1 K and the tropical line appears to be more intense than the other lines whatever the layer considered in the mid-stratosphere. Considering the retrieval as a linear problem, this already suggests that the amount of mid-stratospheric H_2CO is higher in the tropics than at high latitudes.

In order to perform retrievals of the measured H_2CO spectra, all the measurements obtained so far by the Odin/SMR instrument tuned to the CO band have been (1) frequency calibrated using the above-mentioned method, and (2) averaged within vertical layers of 2-km width from 0 to 60 km, and of 5-km width from 60 to 110 km. The latter point ensures that the set of averaged spectra from 0 to 110 km is consistent with the vertical resolution of a single scan in a “strato-mesospheric” mode. As an example, the number of spectra averaged within a 2-km stratospheric layer during the January 2006 period is ~ 1000 in the NH and SH bands, and ~ 1800 in the tropics. Given that the thermal noise for 1-s integration time is typically of 3 K, this reduces the averaged random noise down to 0.1 K, well below the measured 1-K amplitude of the H_2CO line.

New level 1B files (containing information relative to the radiometers and calibrated and averaged spectra) are created that can be directly analyzed using the scientific data-processing segment maintained and updated at the Laboratoire d’Aérodologie (France), the so-called Chaîne de Traitement Scientifique Odin (CTSO) Version V225. This version of the scientific segment is presented in [21], and enables the retrieval of CO and O_3 vertical profiles in the 576-GHz band. Once frequency calibrated, all the measured spectra are stored into 823 1-MHz channels from 576.038 to 576.862 GHz. The integration time associated to each averaged spectrum is simply the sum of the integration times of all the spectra taken into account.

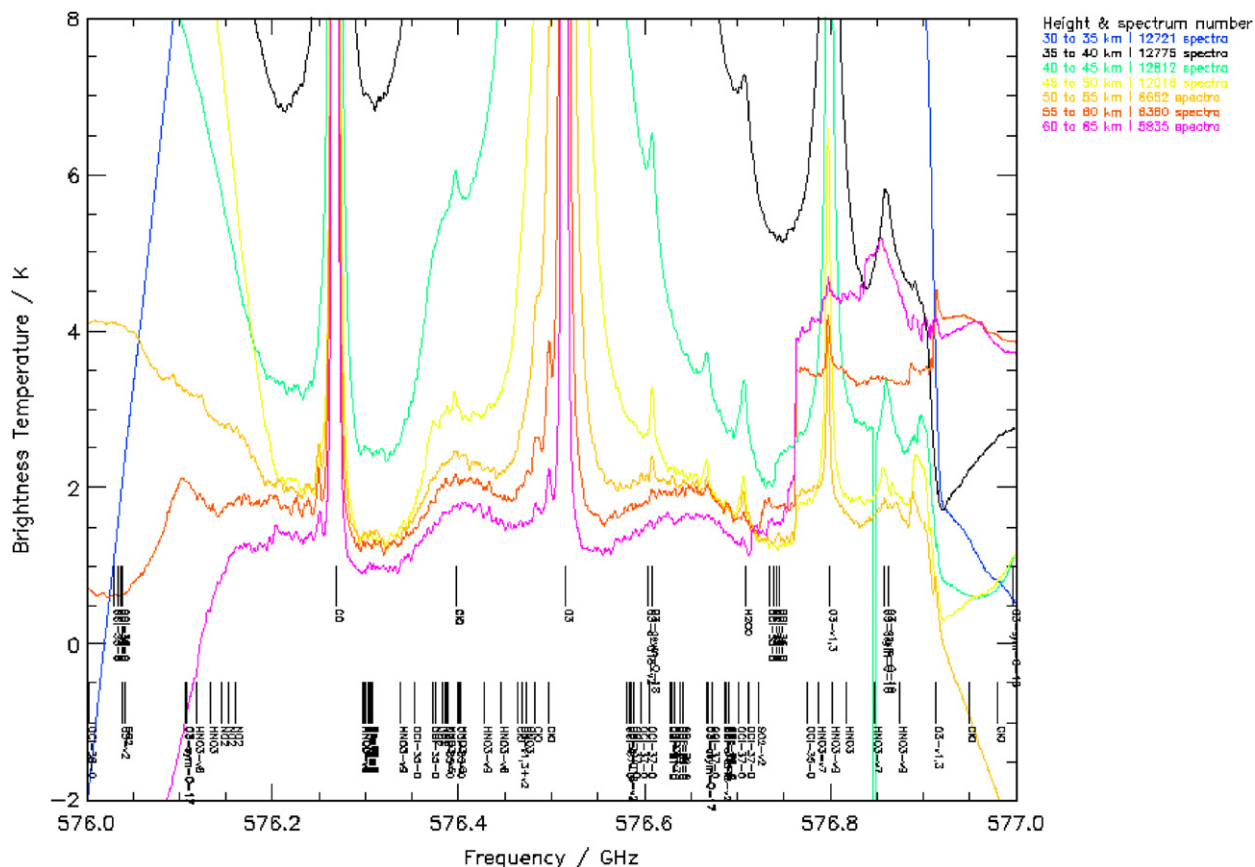


Fig. 4. Same as Fig. 2, but highlighting all the non-negligible transitions and molecules present in the 576-GHz band.

3. REPROBUS model

Three-dimensional simulations of the December 2002–November 2003 period have been performed with the Reprobus Chemical transport model [14,23]. The outputs from this model have been used in different studies for interpreting Odin results, mainly at high latitudes [24,25]. The updated version of the model is presented in [24].

Reprobus was integrated from 1st October 2002 to 31st December 2003. The N_2O , CH_4 , H_2O , HNO_3 and ClONO_2 fields were initialized from the zonally averaged measurements made by the Michelson interferometer for passive atmospheric sounding (MIPAS) instrument aboard the ENVISAT satellite on 1st October 2002. The O_3 field was initialized on 1 October 2002 from the three-dimensional ECMWF O_3 analysis. Other species were initialized from an October zonal mean computed from a long-term simulation of Reprobus. Temperature, winds, and ground pressure were specified from the 3-hourly ECMWF operational analysis. The model extends from the surface up to 0.1 hPa on 42 levels, resulting in a vertical resolution of about 1.3 km in the lower stratosphere. The horizontal resolution is 2° latitude by 2° longitude.

The monthly-averaged H_2CO fields as simulated by the Reprobus model from December 2002 to November 2003 are presented in Fig. 6. The distribution of H_2CO shows two strong maxima in the tropical lower troposphere induced by the tropospheric climatology and in the tropical mid-stratosphere due to methane oxidation. Furthermore, there are very well marked seasonal variations in the mid-stratospheric fields with strong maxima at summer high latitudes and, conversely, minima at high winter latitudes within polar vortices. These seasonal variations are consistent with stronger illumination at summer high latitudes

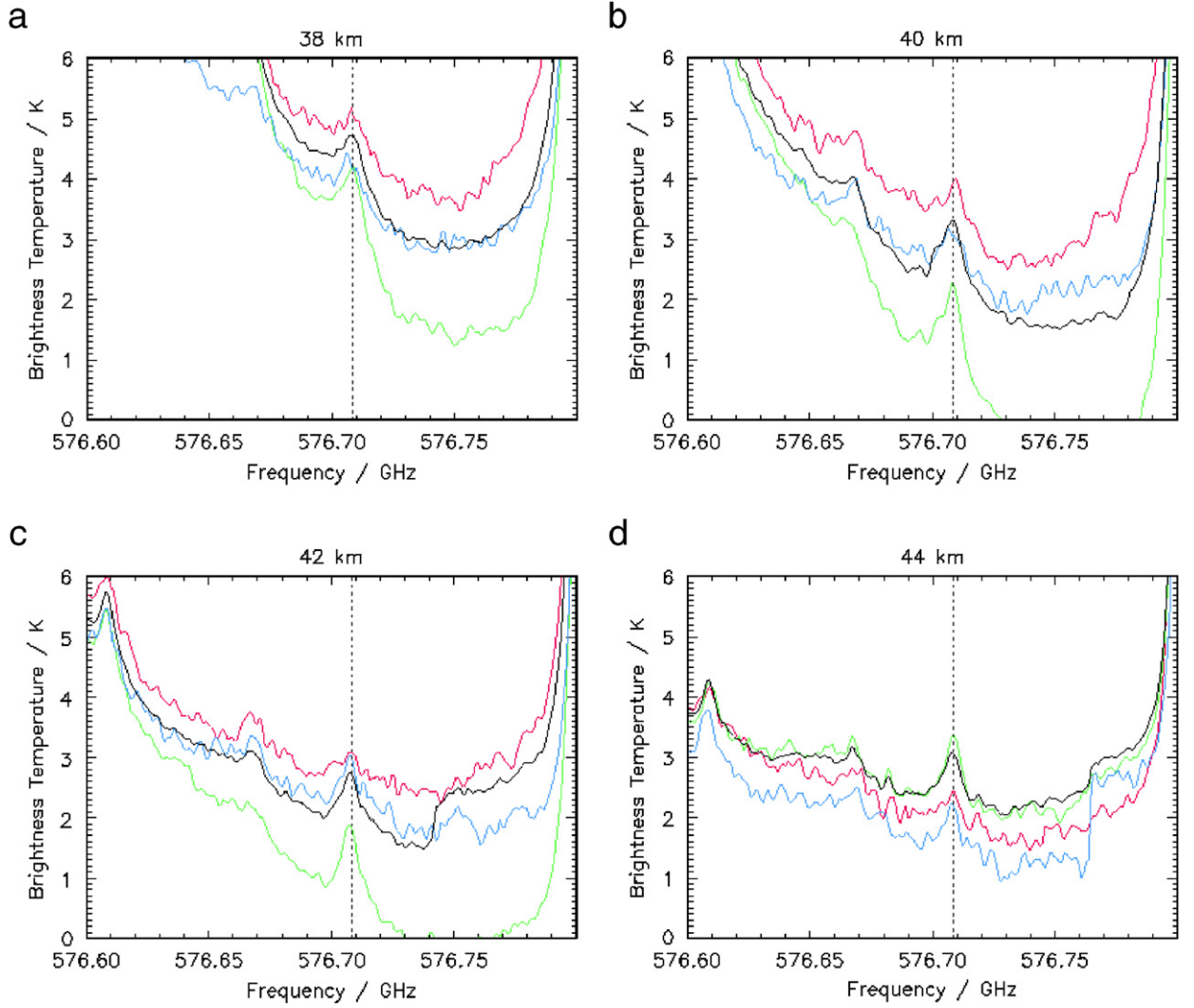


Fig. 5. Evolution of the H_2CO lines when averaged over the January 2006 period within 4 vertical layers: (a) 38 km, (b) 40 km, (c) 42 km, and (d) 44 km, and within different latitude bands: mid-to-high Southern Hemisphere latitudes (SH: 90°S – 45°S) (red line), tropics (30°S – 30°N) (green line), mid-to-high Northern Hemisphere latitudes (NH: 45°N – 90°N) (blue line), and global (90°S – 90°N) (black line).

compared to winter latitudes producing $\text{O}(^1\text{D})$ and OH that oxidize CH_4 and, finally, produces H_2CO . Since the strongest illumination is located in the tropics, we naturally expect H_2CO to show a tropical maximum in the stratosphere.

4. Data analysis

4.1. MOLIERE

The CTSO version V225 uses the generic Microwave Odin Line Estimation and Retrieval (MOLIERE) code [26,27] initially developed for Odin and now used in different programs from ground-based microwave instruments (e.g. O_3 at 110 GHz [28]; ClO at 278 GHz [29]; H_2O at 22 GHz [Motte et al., manuscript in preparation]), to airborne instruments (e.g. ClO at 649 GHz from the airborne sub-mm SIS radiometer (ASUR) [26]) and space-borne projects (e.g. O_3 and CO around 320 GHz with the stratosphere–troposphere exchange and climate monitor (STEAM) [30]).

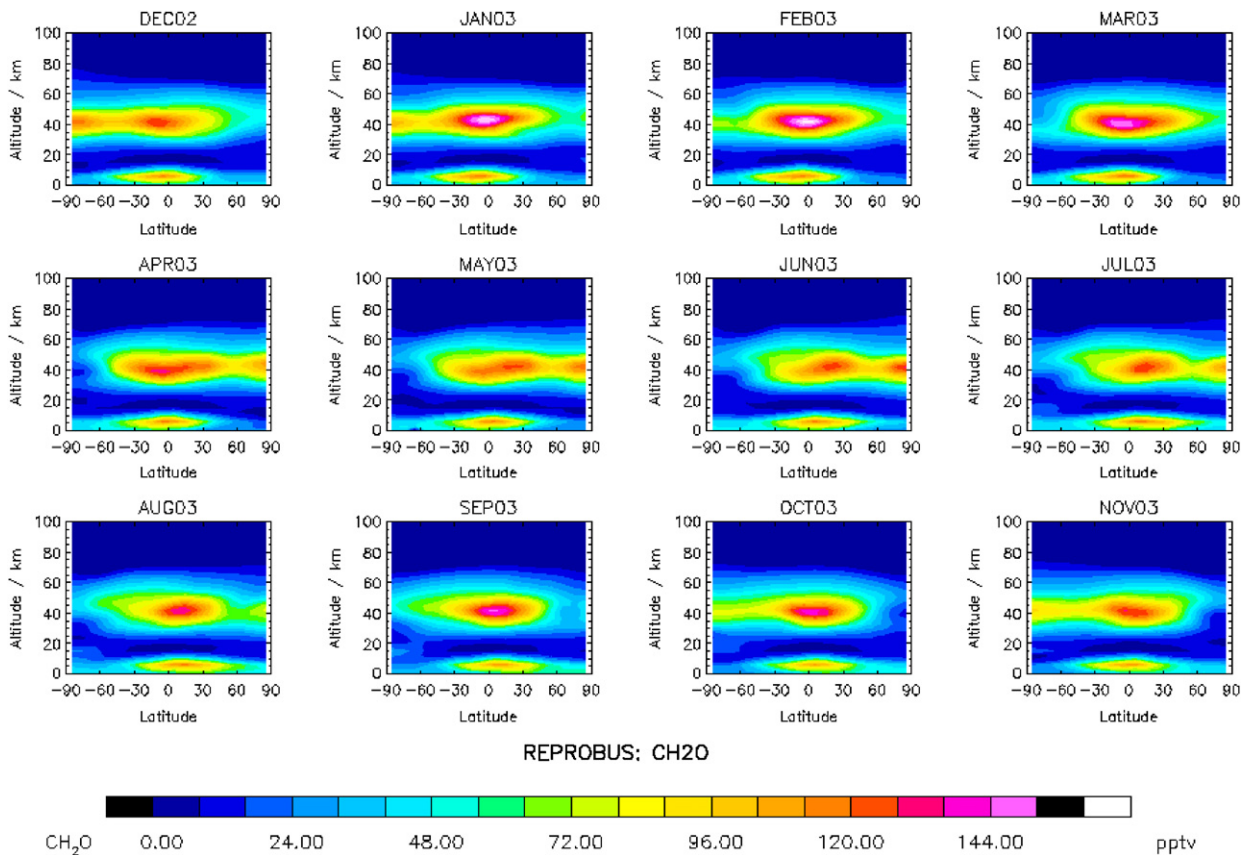


Fig. 6. Monthly averaged zonal mean H_2CO fields as calculated by the three-dimensional chemical-transport model Reprobus from December 2002 to November 2003 (pptv).

The MOLIERE code is separated into a forward model and a retrieval code. The forward model includes modules for spectroscopy, radiative transfer and sensor characteristics (antenna, sideband and spectrometer). It also includes different shape of baseline undulations from linear and quadratic to sine functions. The retrieval code is based upon the optimal estimation method [31] and, coupled with the forward model, allows nonlinear retrievals according to a Newton Levenberg-Marquardt iteration scheme. A *scan bias* parameter can also be estimated between the measured and retrieved tangent heights, together with a *spectrometer shift* parameter that rescales in frequency the measured spectra for each tangent height within 1 MHz. An *additional noise* parameter can also be added to the random radiometric noise in order to cope with any spurious noise that cannot be fitted by an algebraic mathematical function.

Spectroscopic line parameters for the line-by-line calculations have been taken from the Verdandi database (<http://www.rss.chalmers.se/gem/Research/verdandi.html>), which merges frequencies, lines intensities, and lower state energies from the JPL catalog [22] with pressure broadening parameters from the HITRAN compilation [32]. Table 1 lists the spectroscopic information related to the H_2CO line used in our analysis, namely the frequency of the transition, the intensity of the line at 300 K, the lower state energy, the broadening coefficient relative to the air, the self-broadening coefficient, and their temperature dependences. The spectroscopic information relative to the other molecules is similar to the ones presented in the CO studies by [19] and [21].

The *a priori* information for O_3 and all molecules except CO and H_2CO is provided by the Odin climatology set up for all the studies performed so far. The *a priori* information for CO and H_2CO is based upon the monthly average outputs from the REPROBUS model from the surface to 110 km and from December 2002 to November 2003 into latitude bins of 10° . Temperature, pressure, and altitude fields are provided by the

Table 1

Spectroscopic parameters related to the H_2CO line used in our analysis, namely the frequency of the transition (MHz), \log_{10} of the intensity of the line at 300 K (nm^2MHz), the lower state energy (cm^{-1}), the broadening coefficient relative to the air (MHz Torr^{-1}), the self-broadening coefficient (MHz Torr^{-1}), and their temperature dependences

Species	Frequency (MHz)	$\log_{10}(\text{intensity})$ at 300 K (nm^2MHz)	E_{low} (cm^{-1})	γ_{air}^0 at 296 K (MHz Torr^{-1})	γ_{self}^0 at 296 K (MHz Torr^{-1})	n_{air}	n_{self}
H_2CO	576708.3150	-1.6379	67.7252	4.22	4.22	0.5	0.5

ECMWF. We have selected ECMWF profiles at 0° longitude, and latitudes of 70°S , 0° and 70°N , for the SH, tropics, and NH bands, respectively. In general, the ECMWF analyses are taken as close as possible to the middle of the time average interval. The assumed *a priori* error for the retrieved mixing ratios corresponds to 75% of the climatological *a priori* mixing ratios. The *additional noise* parameter is set to 5 K.

4.2. Methodology

The methodology we have used to estimate the H_2CO vertical profiles is divided in two parts. Firstly, once the averaged spectra are produced and an averaged scan is created, we retrieve the vertical profiles of O_3 and CO using the standard setup for the CO band without retrieving temperature information as described in [21]. The retrieved O_3 and CO vertical profiles are then used as *a priori* vertical profiles for actually estimating the distribution of H_2CO from a set of spectra restricted within a micro-window of ± 20 channels around the H_2CO transition line.

The retrieval set up in this second stage is as follows. The *a priori* H_2CO vertical profile is kept the same whatever the latitude and period considered. Indeed, we use the same philosophy as prescribed in the retrieval of the nadir-viewing measurements of pollution in the troposphere (MOPITT) instrument [33] onboard the Terra platform for which the retrievals are non-negligibly contaminated by the *a priori* information [34]. Consequently, any latitudinal and/or time variability in the estimated vertical profile is not caused by the variability of the *a priori* information. The assumed *a priori* error for the retrieved mixing ratios corresponds to 75% of the *a priori* mixing ratios. The *a priori* value of the *spectrometer shift* parameter is tuned to +3 MHz for each tangent height (with an error of 0.5 MHz) in order to converge more rapidly, namely after 2–3 iterations instead of 10 iterations if this parameter is set to 0. A first-degree polynomial function is set up and estimated to reproduce the spectral baseline. The *additional noise* parameter is decreased down to 0.5 K.

Fig. 7a, b, and c show the measured, modeled and fitted spectra at 40-km tangent height in the SH, tropics, and NH bands, respectively for the January 2006 period. The modeled spectra refer to the spectra obtained from the forward model using *a priori* information. The fitted spectra are calculated from the forward model based on the information estimated after 2–3 iterations. Although the modeled spectra is 0.5–1.0 K apart from the measured spectra, after 2–3 iterations the estimated spectra perfectly fit the measured spectra. The associated residuals (difference between measured and fitted spectra) are shown in Fig. 7d, e, and f, respectively. They are all within 0.2–0.3 K, i.e. well within the *additional noise* parameter imposed to be 0.5 K. In order to check the robustness of the retrievals, we have used a sine function with a period of 7 MHz, as can be suggested from the residuals, in addition to the first-degree polynomial spectral baseline. No significant changes were detected in the retrieved H_2CO mixing ratios.

The vertical profiles of H_2CO estimated over the three SH, tropics, and NH bands are presented in Fig. 8a, b, and c, respectively. Superimposed are presented the *a priori* profile which is the same for any of the latitude band, together with the *a priori* error. The right hand-side also shows the H_2CO averaging kernels. The width at half maximum of the averaging kernels can be considered as representative of the vertical resolution of the measurements. The sum of the elements of each averaging kernel (the measurement response) is an indication of the *a priori* contamination upon the retrieved information. We usually flag retrievals as good when the

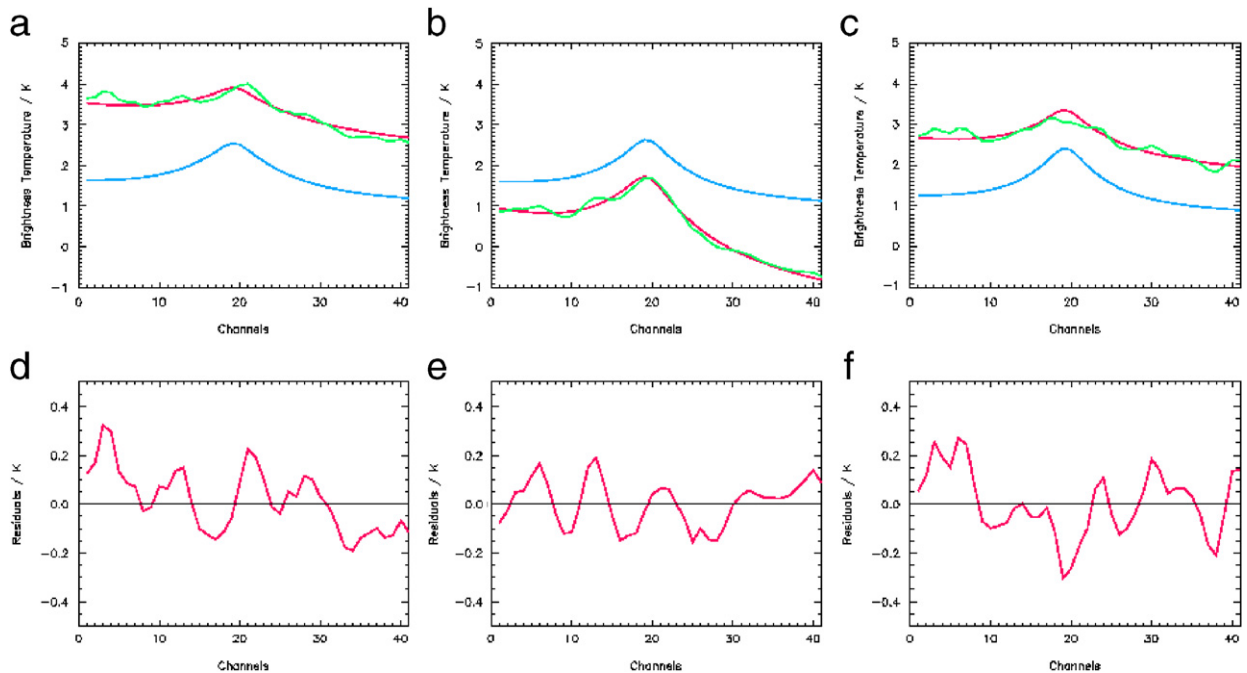


Fig. 7. Formaldehyde spectra averaged over the January 2006 period within a 2-km width layer centered at 41 km measured (green line), modeled (blue line) and fitted after 2 iterations (red line) (a) in the SH, (b) tropics, and (c) NH bands. Residuals (difference between measured and fitted (red line) spectra) corresponding to the (d) SH, (e) tropics, and (f) NH bands.

measurement response is greater than 0.75, meaning that the *a priori* information contaminates the retrieval by less than 25%. In our study, the vertical domain where H_2CO can be retrieved is ranging from ~ 35 km up to ~ 53 km. The vertical resolution is ranging from ~ 4 km in the middle stratosphere up to ~ 7 km in the upper stratosphere. The relative error on the H_2CO profile is about 30%. The correlation between retrieved H_2CO and the estimation of other parameters, namely *scan bias*, *spectrometer shift* and *linear baseline*, is very weak, less than 10%.

5. Results and discussion

The vertical distribution of H_2CO in the mid-stratosphere during the January 2006 period shows very interesting results that were expected from the intensities of the line (see Section 2.2). Indeed, the vertical distribution of H_2CO in the tropics (Fig. 8b) shows a broad maximum reaching a value of ~ 120 pptv (part per trillion volume = 10^{-12}) centered at the altitude of about 40 km. In the SH and NH bands (Fig. 8a and c, respectively), the vertical distribution of H_2CO does not exhibit such a broad maximum. In the SH band, H_2CO decreases with height from ~ 100 pptv at 37 km down to ~ 30 pptv at 53 km, while in the NH, the vertical distribution of H_2CO does not show lots of variability with values within 50–70 pptv.

We have then decided to use the maximum of data of good quality obtained so far with Odin/SMR in order to study the temporal and latitudinal distribution of H_2CO . Because of the sporadic frequency of CO measurements over the entire Odin mission, and of the two main failures of the system (the PLL and one of the 100-MHz sub-band of the auto-correlator), only four periods have been actually selected. We name these four periods: January (13–31 January 2006, 7 days of measurement), February (15–16 February 2005, 1 day of measurement), March (23–24 March 2005, 1 day of measurement), and September (19–20 September 2005, 1 day of measurement). For these four periods, the methodology presented above has been applied.

To our knowledge, there are no measurements of mid-stratospheric H_2CO published so far in order to validate our retrievals. We thus have used the output from Reprobus in order to check the consistency of our results. The vertical profiles of H_2CO as measured by Odin/SMR and the monthly averaged Reprobus outputs

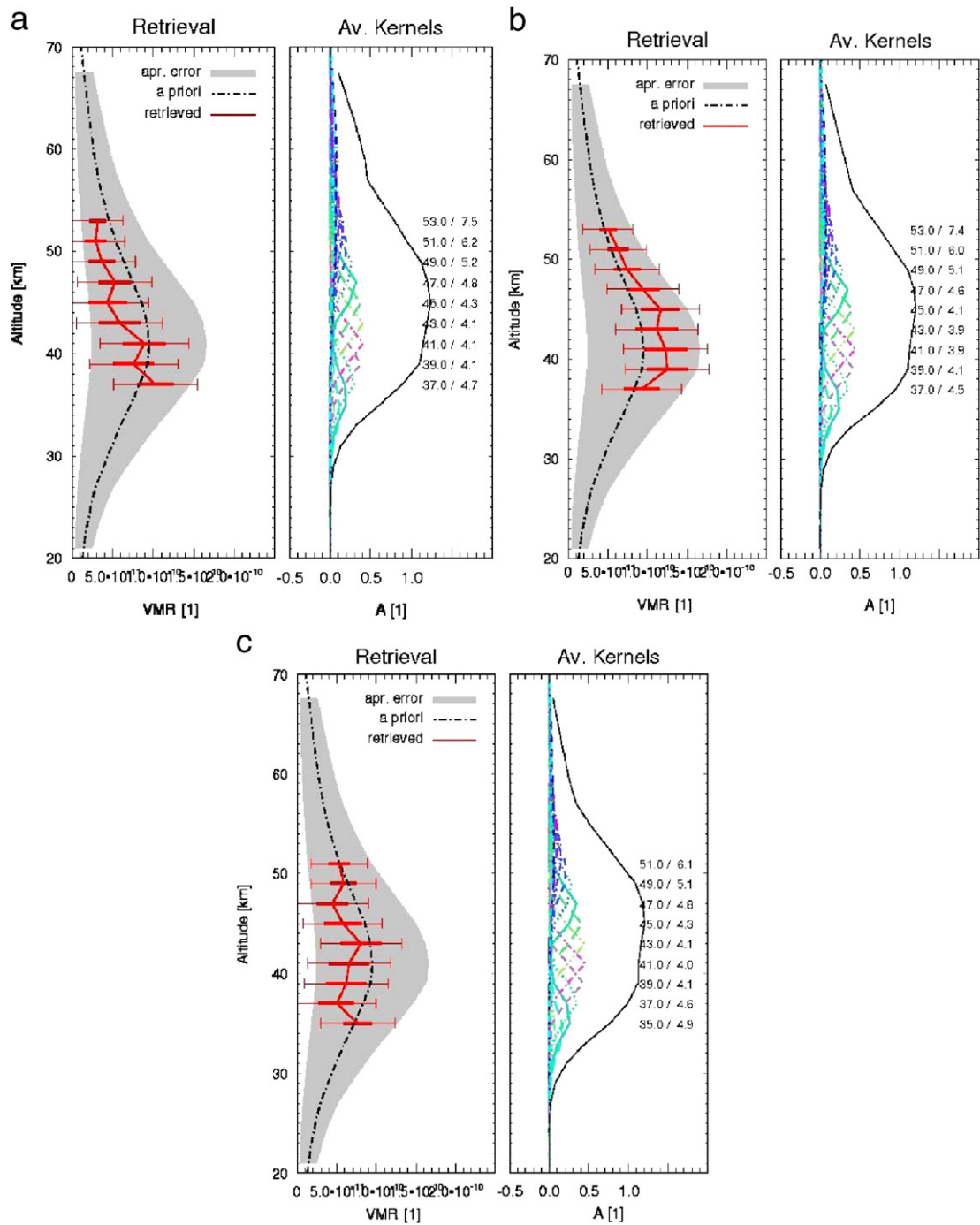


Fig. 8. (Left-hand side) Vertical profiles of H_2CO estimated from the spectra averaged over the January 2006 period in (a) SH, (b) tropics, and (c) NH bands. Superimposed are presented the *a priori* profile (dotted line) which is the same for any of the latitude band, together with the *a priori* error (shaded area). The horizontal lines represent the total error (thin red line) and the measurement error (thick red line). (Right-hand side) H_2CO averaging kernels. The sum of the elements of each averaging kernel (the measurement response) is an indication of the *a priori* contamination upon the retrieved information. The width at half maximum of the averaging kernels (representative of the vertical resolution of the measurements) together with the height where the averaging kernel is peaking are indicated on the right of each figure for altitudes where the measurement response is greater than 0.75, i.e. the *a priori* contamination is less than 25%.

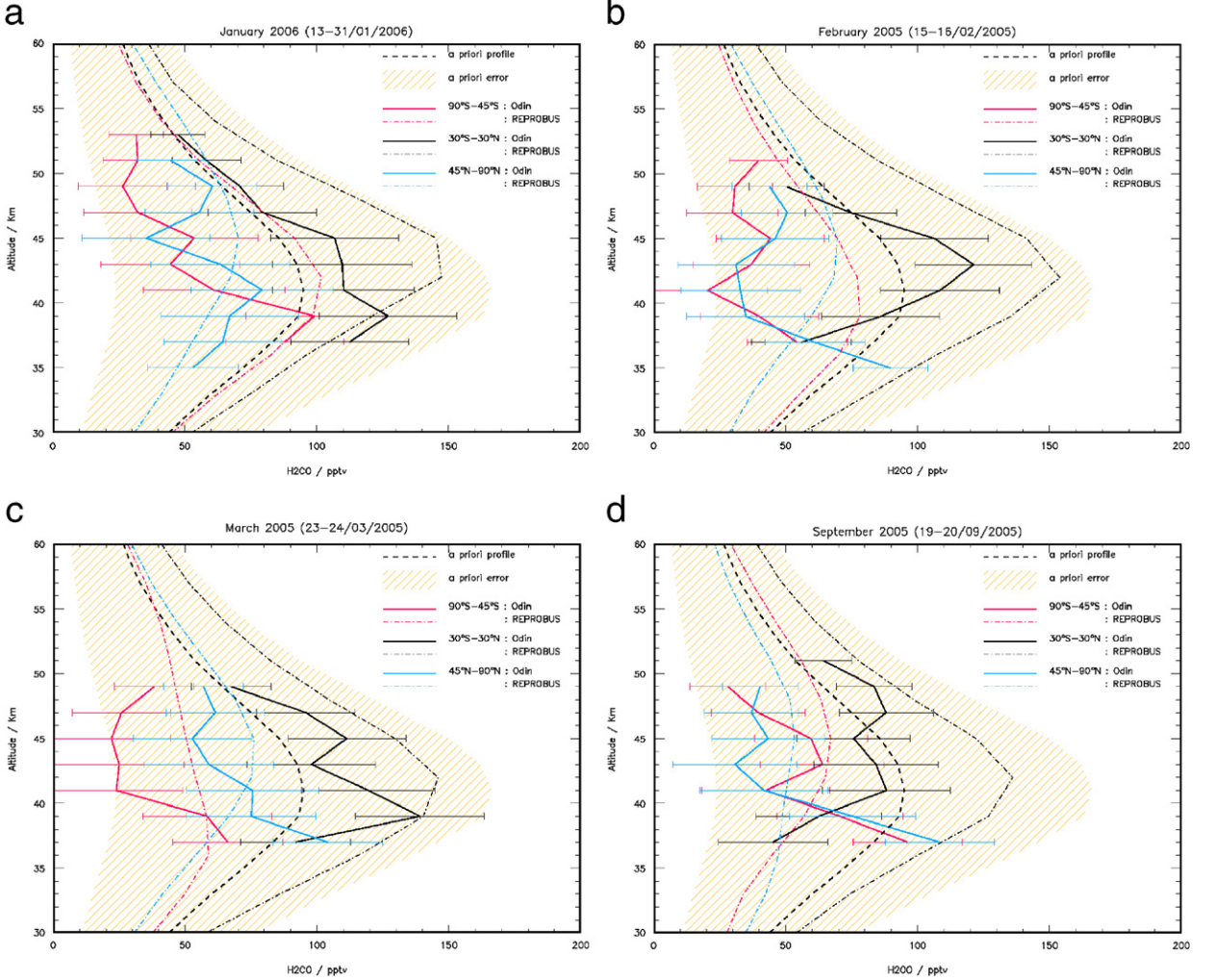


Fig. 9. Vertical profiles of H_2CO as measured by Odin/SMR (coloured solid line) and the monthly averaged Reprubus outputs (coloured dashed line) corresponding to the month under consideration, together with the *a priori* H_2CO profile (black dashed line) for the three latitude bands: SH (red lines), tropics (green lines), and NH (blue lines) for the 4 periods: (a) January 2006, (b) February 2005, (c) March 2005, and (d) September 2005, together with the *a priori* error (orange shaded area), and the measurement error (horizontal bars).

(see Section 3) corresponding to the month under consideration, together with the *a priori* H_2CO profile, are presented in Fig. 9a, b, c and d for the 4 periods (January, February, March and September, respectively), and for the three bands (SH, tropics, and NH). We first note that for all the periods the tropical mid-stratospheric H_2CO is higher than the SH and NH H_2CO . The tropical maximum is peaking around 40–43 km and reaches about 100–130 pptv for the periods January, February and March while it is less intense in September reaching values of 80–90 pptv. Reprubus also shows tropical H_2CO maxima (120–150 pptv) more intense than SH and NH H_2CO (≤ 100 pptv). The tropical seasonality is also calculated by Reprubus with January, February and March maxima (~ 150 pptv) greater than September maxima (120–140 pptv). The modeled H_2CO in the tropics is consistently more abundant than measured by Odin/SMR.

In January, the SH profile gradient is more accentuated than the gradient in the NH profile. Indeed, SH H_2CO decreases from 100 pptv at 37 km to 30 pptv at 53 km while it only decreases from about 70 pptv at 40 km to about 50 pptv at around 51 km in the NH. This is to a lesser extent present in the modeled profiles, with maxima of H_2CO more pronounced in the SH (100 pptv) than in the NH (70 pptv). In February, the SH and NH measured profiles are practically identical, decreasing with height from 60 pptv at 37 km to 40 pptv at

49 km. There are very little differences (<10 pptv) between the modeled SH and NH profiles, being slightly greater than the measured profiles by about 20 pptv. In March, the measured NH profile is much greater than the measured SH profile by about 20–30 pptv. This is also observed in the modeled SH and NH profiles. In September, the SH and NH measured and simulated profiles are within 10 pptv. Finally, we must note that Reprobus H_2CO mid-stratospheric amounts are generally slightly greater than Odin/SMR retrievals.

6. Conclusions

The sub-millimeter radiometer (SMR) instrument onboard the Odin satellite has been sounding the Earth's atmosphere since February 2001 and is still operational. In addition to the rotational transitions of target species defined prior to the launch of the mission, namely O_3 , ClO , etc., measured in the frequency domains 486.1–503.9 and 541.0–580.4 GHz, some particular micro-windows enable the detection of weak line species. The present study focuses on the only weak ($8_{08} \rightarrow 7_{07}$) rotational transition line of H_2CO that can be measured by Odin/SMR at 576.7083150 GHz in the band dedicated to the measurement of CO . A methodology is explained based upon the average of spectra within 2-km depth vertical layers in order to increase the signal-to-noise ratio so that the 1-K amplitude of the H_2CO line is well above the 0.1-K averaged random noise. Due to the failure of the Phase-Lock Loop and of the 100-MHz sub-band of the auto-correlator, all the measured spectra have been frequency calibrated prior to the averaging processing. A two-step retrieval process (1) enables the estimation of O_3 and CO from the two strong lines in this particular band, and (2) used as an *a priori* information, helps characterizing mid-stratospheric H_2CO using the scientific ground-segment developed for analyzing the Odin/SMR measurements. Vertical profiles of H_2CO have been estimated for the first time from 37 to 53 km with a relative error of about 30% and a vertical resolution ranging from 4 to 7 km within three different latitude bands: mid-to-high Southern Hemisphere latitudes (SH: 90°S – 45°S), tropics (30°S – 30°N), and mid-to-high Northern Hemisphere latitudes (NH: 45°N – 90°N). These original profiles have been studied over four different periods: January 2006, February 2005, March 2005, and September 2005. During all of these periods, the tropical mid-stratospheric H_2CO is more intense than the SH and NH values. Interestingly, the spring-time extra-tropical H_2CO is more intense than the fall-time amounts. While no other measurements of mid-stratospheric H_2CO exist, comparisons with the three-dimensional Reprobus chemical-transport model are very encouraging showing a strong tropical maximum whatever the month considered, and seasonal variability of the extra-tropical H_2CO . Our future program is to analyze all the measurements obtained so far containing spectroscopic information on the H_2CO line in order to build climatology of mid-stratospheric H_2CO and to characterize its impact upon the distribution of stratospheric ozone.

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