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Atmospheric Chemistry and Physics Discussions

Retrieval of global upper tropospheric and stratospheric formaldehyde (H_2CO) distributions from high-resolution MIPAS-Envisat spectra

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Abstract

The Fourier transform spectrometer MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) on Envisat measures infrared emission of the Earth's atmosphere in a limb viewing mode. High spectral resolution measurements of MIPAS are sensitive to formaldehyde from the upper troposphere to the stratopause. Formaldehyde single profile retrieval is formally possible, however with a large noise error (more than 60%), which is the dominant error source. The number of degrees of freedom for single profile retrieval ranges from 2 to 4.5 depending on latitude and number of cloud-free tangent altitudes. Calculation of zonal mean values for 30 days of data during 8 September 2003 and 1 December 2003 reduces the noise induced error by a factor of 20 or more. In the upper tropical troposphere zonal mean values of about 70 parts per trillion by volume (pptv) were found, which have been attributed to biomass burning emissions. In the stratosphere, formaldehyde values are determined by photochemical reactions. In the upper tropical stratosphere, formaldehyde zonal mean maximum values can reach 130 pptv. Diurnal variations in this region can be up to 50 pptv. Comparisons with other satellite instruments show generally good agreement in the region of upper troposphere and lower stratosphere as well as in the upper stratosphere.

1 Introduction

1.1 Formaldehyde sources, sinks and measurements

Formaldehyde (H_2CO) is a principal intermediate in the oxidation of hydrocarbons in the troposphere (Chance et al., 2000). The main sources of H_2CO in the troposphere are biomass burning, anthropogenic, and biogenic emissions as well as methane oxidation. It is destroyed via photolysis and reaction with OH. In continental boundary layers, non-methane hydrocarbons (NMHCs) emitted by biogenic and anthropogenic sources usually dominate over methane as a source of H_2CO (Munger et al., 1995).

In the stratosphere, the H_2CO profile results from an equilibrium between production by methane oxidation and destruction as described above (Brasseur and Solomon, 1986), which means that a diurnal variation in formaldehyde abundances is expected in the stratosphere where production and destruction processes are dominated by photochemistry.

First stratospheric measurements of formaldehyde have been made with a ground-based Fourier Transform infrared (FTIR) instrument (Barbe et al., 1979). Global distributions of H_2CO columns have been derived with the GOME (Global Ozone Monitoring Experiment) instrument (Burrows et al., 1999; Chance et al., 2000) which are dominated by the tropospheric signal. Vertically resolved satellite measurements of H_2CO have been made recently with the sub-millimeter radiometer (SMR) aboard the Odin satellite (Ricaud et al., 2007), with an altitude region of about 35 to 50 km, and with the Atmospheric Chemistry Experiment - Fourier Transform Spectrometer (ACE-FTS) (Coheur et al., 2007) with focus on the upper tropospheric and lower stratospheric (UTLS) region. In the following we show that MIPAS has the potential to provide day and night profile information of formaldehyde from the upper troposphere to the stratopause on a global scale.

1.2 MIPAS-Envisat description

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a Fourier transform infrared (FTIR) spectrometer measuring the emission of the Earth's atmosphere in limb-viewing mode (Fischer and Oelhaf, 1996; Fischer et al., 2007). MIPAS was launched on the environmental satellite Envisat on 1 March 2002 into a sun-synchronous polar orbit with equatorial crossing times of 10:00 (descending node) and 22:00 local mean time (ascending node). MIPAS operated in its nominal mode from July 2002 to March 2004 in high spectral resolution of nominal 0.025 cm^{-1}. Flight altitude of Envisat is 800 km and one orbit takes about 100 min allowing to measure 72 limb sequences per orbit with a sampling of about 550 km along track. With these characteristics, MIPAS is able to provide vertical profiles of temperature and a large number of

trace gases globally during day and night. The nominal observation mode comprises 17 tangent altitudes per limb sequence from 6 to 68 km (3 km step-width between 6 and 42 km, and at 47, 52, 60, and 68 km). The 3 km step-width was chosen due to the vertical instantaneous field-of-view (FOV) of MIPAS, which is about 3 km, while the across track FOV is about 30 km. The generation of calibrated radiance spectra, the so-called level 1B data, is performed by the European Space Agency (ESA) (Nett et al., 2002). ESA additionally provides vertical profiles of temperature and 6 key species (H_2O, O_3, HNO_3, CH_4, N_2O, and NO_2), the so-called Level 2 product. Furthermore, there are several institutes which have developed retrieval codes to determine trace gases beyond the ESA key species. The formaldehyde distributions described in this paper were derived with the retrieval processor of the Institut für Meteorologie und Klimaforschung (IMK) and the Instituto de Astrofisica de Andalucia (IAA) (von Clarmann et al., 2003).

2 Formaldehyde spectral signatures

In the mid-infrared spectral region, formaldehyde shows weak emission lines between about 900 and 1850 cm^{-1} (Fig. 1) with the most prominent band centered around 1750 cm^{-1}. Due to the lowest instrumental noise level there, this region is used in the retrieval based on new spectroscopic data (Perrin et al., 2003; Sharpe et al., 2004) which are thought to be more accurate and contain more spectral lines compared to previous data. The challenge of the H_2CO retrieval is the very weak signal of the emission lines compared to the instrumental noise which is in the order of 3 nW/(cm^2 sr cm^{-1}) at the relevant spectral region.

Figure 2 (top) shows the simulated formaldehyde spectrum at 16.4 km tangent altitude for tropical atmospheric conditions. The spectrum is dominated by water vapor lines and minor ozone and nitric acid signatures. The H_2CO contribution is shown in Fig. 2 (bottom) which is given by the residual spectrum. The residual spectrum is the difference between the spectra at 16.4 km with and without formaldehyde considered in the simulation. For these conditions the formaldehyde contribution is below the

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instrumental noise of about 3 nW/(cm^2 sr cm^{-1}).

3 Retrieval setup

For the retrieval, 9 narrow spectral regions (microwindows) have been selected by visual inspection between 1700 cm^{-1} and 1750 cm^{-1}, which is the upper end of MIPAS channel C (see Table 1). The main criterion for the selection was high sensitivity to formaldehyde and low interference by other gases. Since the formaldehyde contribution is so small, the contribution of other gases still needs to be considered even after careful microwindow selection. Many gases need to be retrieved jointly in order to limit propagation of related errors in particular in the UTLS region. These interfering gases are: H_2O, O_3, HNO_3, $ClONO_2$, and PAN.

The retrieval procedure follows a scheme similar to that described by Rodgers (2000):

$$\boldsymbol{x}_{i+1} = \boldsymbol{x}_i + (\mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i + \mathbf{R})^{-1} \times [\mathbf{K}_i^T \mathbf{S}_y^{-1} (\boldsymbol{y} - \boldsymbol{F}(\boldsymbol{x}_i)) - \mathbf{R}(\boldsymbol{x}_i - \boldsymbol{x}_a)], \quad (1)$$

where $\boldsymbol{x}$ is the retrieval vector, $\mathbf{K}$ the partial derivatives of the spectra with respect to the retrieval vector (Jacobian), $\mathbf{S}_y$ the covariance matrix due to measurement noise, $\mathbf{R}$ the regularization or constraint matrix, $\boldsymbol{y}$ the measurement vector, $\boldsymbol{F}$ the forward model, $\boldsymbol{x}_a$ the a priori profile, and i the iteration index.

The retrieval is performed on a fine vertical grid with 1 km distance up to 44 km and 2 km above. Since the retrieval grid is finer than the tangent altitude spacing, the retrieval is stabilized by a first order Tikhonov smoothing constraint (Tikhonov, 1963):

$$\mathbf{R} = \alpha \mathbf{L}_1^T \mathbf{L}_1, \quad (2)$$

where α is the strength of the constraint and $\mathbf{L}_1$ the first order derivative matrix (as discussed by Steck, 2002), which smoothes the solution without biasing it towards the a priori profile. The regularization strength α is determined by finding a trade-off

between the number of degrees of freedom, which is given by the trace of the averaging kernel **A** (Rodgers, 2000)

$$\mathbf{A} = (\mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i + \mathbf{R})^{-1} \mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i \quad (3)$$

and the noise induced error (Steck, 2002)

$$\mathbf{S}_n = (\mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i + \mathbf{R})^{-1} \mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i (\mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i + \mathbf{R})^{-1}, \quad (4)$$

where $\mathbf{S}_n$ is the error covariance matrix due to instrumental noise. A regularization strength α of 10^4 was found optimum.

As initial guess, the profile from the U.S. standard atmosphere 1976 is used. As a priori profile we use a zero profile to avoid any artificial structures in the formaldehyde profile not caused by the measurements. Thus, the linear retrieval equation (Rodgers, 2000)

$$\hat{\boldsymbol{x}} = \mathbf{A}\boldsymbol{x}_t + (\mathbf{I} - \mathbf{A})\boldsymbol{x}_a, \quad (5)$$

where $\hat{\boldsymbol{x}}$ is the estimated and $\boldsymbol{x}_t$ is the true H_2CO profile, simplifies for $\boldsymbol{x}_a = 0$ to $\hat{\boldsymbol{x}} = \mathbf{A}\boldsymbol{x}_t$. This means that in linear approximation the retrieved H_2CO profile is a smoothed version of the true profile.

All settings (microwindows, constraint, initial guess and a priori profiles) are chosen time and latitude-independent. This is again to ensure that all structures visible in the retrieved distributions originate from the measurements and are not artifacts due to any constraint.

4 Single profile retrieval and diagnostics

The retrieval procedure described above has been applied to real MIPAS measurements. Figure 3 shows an example for single profile retrieval of formaldehyde for MIPAS-Envisat orbit 8194 on 24 September 2003, at 14° S/46° W, which is right over Brazil. The profile shows maximum values in in the UTLS region of 180 parts per trillion

by volume (pptv) and near the stratopause of 140 pptv, which are both of reasonable size. However, the profile shows some oscillations and the retrieval error caused by measurement noise is rather large with values of about 70 pptv leading to percentage errors larger than 100% except for the altitude regions with maximum formaldehyde (about 60%).

A detailed error analysis is given in Fig. 4. Due to the small formaldehyde signatures and large instrumental noise, as discussed in Sect. 2, the measurement noise induced error (Fig. 4, solid blue) is the dominating error source with values between 70 and 115 pptv in the altitude region from 10 to 47 km. The error due to spectral shift (Fig. 4, solid red) exceeds 10 pptv at 40 km altitude and further increases with altitude. The systematic errors are dominated by errors due to uncertainties in spectroscopic data (Fig. 4, dashed blue) with maximum values of 24 pptv around 40 km altitude and 33 pptv at 10 km altitude. The altitude dependence of the error due to spectroscopic data is linked to the actual H_2CO profile shape and is nearly constant with altitude when expressed in percentage (about 20%). For single profile retrieval, however, this error becomes negligible compared to the noise error. Further errors due to gain calibration, instrumental line shape (ILS) and line-of-sight (LOS) uncertainties are mainly below 10 pptv for the complete altitude range.

The formaldehyde averaging kernel **A** (Fig. 5) shows sensitivity to the true profile from the UTLS region up to the stratopause. The dotted horizontal lines in Fig. 5 delimit the altitude region of every single degree of freedom with a total number of 3.9, which is given by the trace of **A**. The averaging kernels show that MIPAS is also sensitive to the UTLS region with about one piece of information. The vertical resolution is estimated at about 11 km. The averaging kernel also shows that there is basically no information in the retrieval above 60 km and below 10 km, although for this geolocation the lowest tangent altitude is at 7.9 km. This means that the atmosphere becomes optically opaque.

Figure 6 (solid line) shows the variation of the number of degrees of freedom along the complete orbit 8194. The number of independent pieces of information varies

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between 2 and 4.5 depending on latitude and number of cloud-free tangent altitudes (crosses). Near the southern winter pole (Fig. 6, about 270°), the number of tangent altitudes not affected by clouds is reduced to 13 due to polar stratospheric clouds. Together with the low temperatures in this region and the resulting low signal, the number of degrees of freedom has a minimum and is close to 2. The mean number of degrees of freedom for this orbit is about 3.5.

5 Global MIPAS formaldehyde data

The error analysis of the single profile retrieval has shown large random errors which are dominating the error budget. To reduce this error component and to receive more reliable data, averaging over a larger ensemble of data is the obvious way to go. Between 8 September 2003 and 1 December 2003, 30 days of data have been analyzed which cover about 420 orbits or more than 29 000 geolocations.

5.1 Zonal means

Zonal mean formaldehyde data is shown in Fig. 7. Averages have been taken for latitude bins of 5° leading to about 500 to 1000 profiles per bin. This means a reduction of the random error by a factor of about 20 to 30. For the averaging only altitudes are used which are within the cloud-masked tangent altitude range and where the corresponding diagonal value of the averaging kernel is above a given threshold (0.03).

In the upper tropical tropopause region, mean values exceed 60 pptv. These larger values are attributed mainly to biomass burning emission. MIPAS has detected enhanced values also in other gases like PAN (Glatthor et al., 2007), C_2H_6, and ozone (von Clarmann et al., 2007) which are attributed to biomass burning events. Due to the very weak emission lines, MIPAS can measure enhanced formaldehyde mainly in the tropical troposphere, where lower tropospheric air is transported to higher altitudes.

In the upper stratosphere a prominent maximum is visible at around 40 km altitude

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with values of about 130 pptv in the tropics. The stratospheric values in the southern hemisphere are smaller than in the tropics but much larger compared to the northern hemisphere. This is likely connected with the southern polar vortex and its breakup. In the northern winter upper stratosphere low temperatures cause an extremely low signal, which makes the formaldehyde retrieval even more difficult and prone to error propagation. These degraded retrievals are characterized by unrealistic negative mixing ratios.

5.2 Diurnal variations

Since MIPAS is measuring the atmospheric emission, the zonal mean data (Fig. 7) can be divided into day- and nighttime measurements. Daytime measurements (Fig. 8) show enhancements in the stratosphere with maximum values of more than 150 pptv. For nighttime measurements (Fig. 9), formaldehyde stratospheric maximum values are reduced to values below 100 pptv. Since there are slightly more daytime than nighttime measurements available, the combination of all measurements gives a maximum of 130 pptv which is slightly shifted towards daytime results. In the southern polar nighttime lower stratosphere, the values are larger than for daytime which is likely connected to the special chemistry in the polar vortex.

While photochemistry plays the dominating role particularly in the upper stratosphere, in the upper troposphere also transport is important to understand the formaldehyde mixing ratios and may outweigh the diurnal variations there.

6 Comparison with other satellite instruments

6.1 Comparison with ACE-FTS

ACE-FTS is operating in the infrared between 750 and 4400 cm^{-1} at a spectral resolution of 0.02 cm^{-1} (Bernath et al., 2005). ACE-FTS is a solar occultation instrument

measuring a maximum of 15 sunrises and 15 sunsets a day. The altitude range spans from the upper troposphere to the mesosphere at an average vertical resolution of 4 km.

Table 2 shows the comparison between ACE-FTS and MIPAS measurements between 12 and 20 km. The ACE-FTS values are measured in a biomass burning plume on 8 October 2005 (Coheur et al., 2007), while MIPAS values are zonal averages for 10° N between 8 September 2003 and 1 December 2003. The 10° N bin for MIPAS was chosen to match, at least partly, the high ACE-FTS tropical values measured in a biomass burning plume. The general agreement between ACE-FTS and MIPAS is good with values between 15 and 31 pptv for an altitude range of 16 to 20 km. At 12 km altitude both instruments show enhanced values at a similar magnitude (71 and 92 pptv). Due to the poor vertical resolution of MIPAS formaldehyde profiles, the large upper tropospheric values are smeared over a wide altitude range.

6.2 Comparison with Odin-SMR

Odin-SMR is a limb-viewing instrument aboard the Odin satellite launched on 20 February 2001 into a 600 km sun-synchronous orbit (Murtagh et al., 2002). The formaldehyde analysis is based on a weak rotational transition line at 576.7083150 GHz (Ricaud et al., 2007). The signal-to-noise ratio is increased by averaging about 1000 spectra within vertical layers of 2 km width leading to profile retrieval in the upper stratosphere.

For the comparison, the period from 19 to 20 September 2005 was taken. The values in Table 3 are averaged values within three latitude bands: 90° S–45° S, 30° S–30° N, and 45° N–90° N. For comparison, MIPAS zonal mean values are also averaged for the latitude bands given above but for the previously mentioned period in 2003. Additionally to the measured values, Table 3 also contain values from the three-dimensional chemical-transport model Reprobus (Lefèvre et al., 1994; Ricaud et al., 2007) which are monthly averages.

For southern hemispheric latitude region, MIPAS and Reprobus values agree quite well (Table 3, left columns) with values between 47 and 67 pptv between 37 and 49 km

altitude. In the northern hemisphere (Table 3, right columns), large differences are observed. This apparent disagreement is attributed to seasonal variation; contrary to Odin and Reprobus data, the MIPAS average, which spans from 8 September to 1 December includes polar winter data which push the seasonal mean towards much lower values (Fig. 7). For tropical conditions (Table 3, middle columns), where the stratospheric maximum is mostly pronounced, MIPAS values are again in good agreement with both Odin-SMR and Reprobus.

7 Summary and conclusions

We have demonstrated that high spectral resolution measurements of MIPAS on Envisat are sensitive to formaldehyde. These emission lines are weak compared to the instrumental noise, nevertheless vertical distributions from the upper troposphere to the stratopause have been derived on basis of most recent spectroscopic data. Formaldehyde single profile retrieval is formally possible, however with a large noise error (more than 60%), which is the dominant error source. The number of degrees of freedom for single profile retrieval ranges from 2 to 4.5 depending on latitude and number of cloud-free tangent altitudes.

For the period from 8 September 2003 to 1 December 2003, 30 days of data have been analyzed which cover 420 orbits or more than 29 thousand geolocations. To reduce the large noise error component, profiles have been averaged leading to a reduction by a factor of 20 or more. In the upper tropical troposphere, enhanced formaldehyde values of about 70 pptv were measured which have been attributed to biomass burning emission. In the stratosphere, formaldehyde production and destruction is dominated by photochemical reactions. Zonal mean profiles show a prominent maximum in the upper tropical stratosphere with values up to 130 pptv, which are decreasing towards the poles. Zonal mean values in the upper tropical stratosphere show differences between day and night of up to 50 pptv.

Comparison with other satellite instruments (ACE-FTS and Odin-SMR) show good

agreement. High formaldehyde values in the tropical UTLS region are confirmed by ACE-FTS and in the upper stratosphere by Odin-SMR.

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Table 1. Microwindows for MIPAS formaldehyde retrievals.

MW	begin (cm^{-1})	end (cm^{-1})
1	1701.3	1702.9
2	1708.7	1710.0
3	1720.2	1722.0
4	1722.8	1723.1
5	1727.8	1729.5
6	1730.6	1731.8
7	1735.7	1736.7
8	1738.2	1739.1
9	1744.7	1746.7

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Table 2. Comparison with ACE-FTS measurements. (1) ACE-FTS values are measured in a biomass burning plume on 8 October 2005. (2) MIPAS values are zonal mean values for 10° N between 8 September 2003 and 1 December 2003.

altitude (km)	ACE-FTS(1) (pptv)	MIPAS(2) (pptv)
20	23	19
18	23	15
16	31	22
14	37	61
12	92	71

Table 3. Comparison with Odin-SMR measurements for 3 latitude bands: 90° S–45° S, 30° S–30° N, and 45° N–90° N. Odin-SMR values are averaged for the period 19 to 20 September 2005, Reprobus values are averaged for September 2005, and MIPAS values are averaged for the period 8 September 2003 to 1 December 2003. All formaldehyde values are in pptv.

altitude	90° S–45° S			30° S–30° N			45° N–90° N		
(km)	Odin-SMR	Reprobus	MIPAS	Odin-SMR	Reprobus	MIPAS	Odin-SMR	Reprobus	MIPAS
49	28	61	47	83	91	76	40	49	6
45	59	67	61	76	122	95	43	53	16
41	43	62	65	88	132	104	42	50	23
37	96	49	63	45	109	100	108	48	28

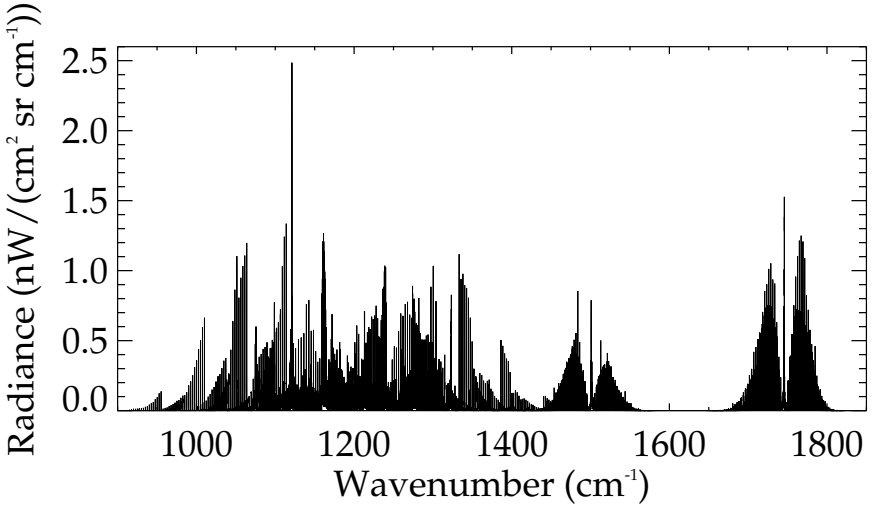

Fig. 1. Simulated H_2CO spectrum at 16.4 km tangent altitude with only H_2CO in the atmosphere for tropical conditions; based on new spectroscopic data (Perrin et al., 2003).

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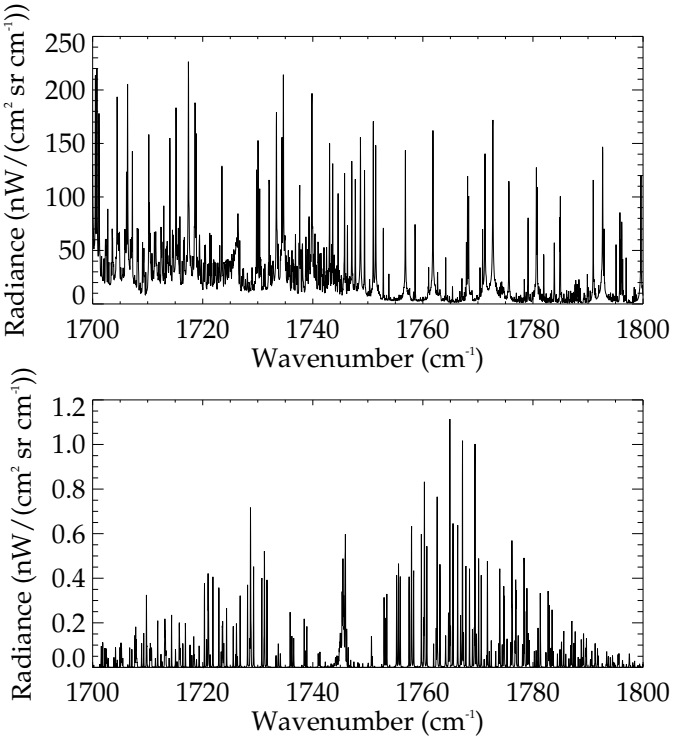

Fig. 2. Top: Simulated spectrum at 16.4 km tangent altitude; tropical conditions, all gases inclued. Bottom: Formaldehyde contribution only (note the different scale).

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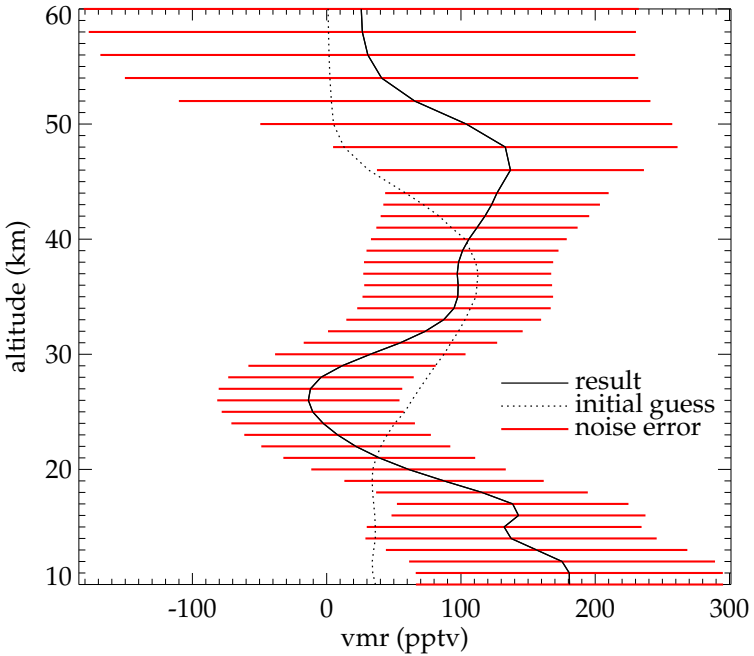

Fig. 3. Formaldehyde retrieval result (solid) (orbit 8194, 24 September 2003, 14° S/46° W) with error bars (red) and initial guess (dotted).

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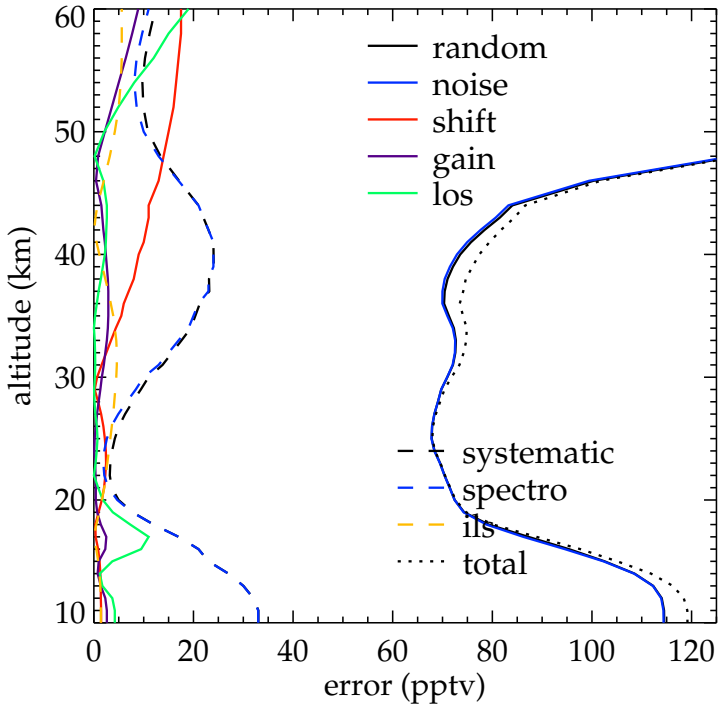

Fig. 4. Error analysis of formaldehyde retrieval (24 September 2003, 14° S/46° W). Error sources from top to bottom: total random error (solid black), measurement noise (solid blue), spectral shift (solid red), gain calibration uncertainty (solid purple), line-of-sight (LOS) uncertainty (solid green), total systematic error (dashed black), spectroscopic data uncertainties (dashed blue), instrumental line shape (ILS) (dashed yellow), and total error (dotted black).

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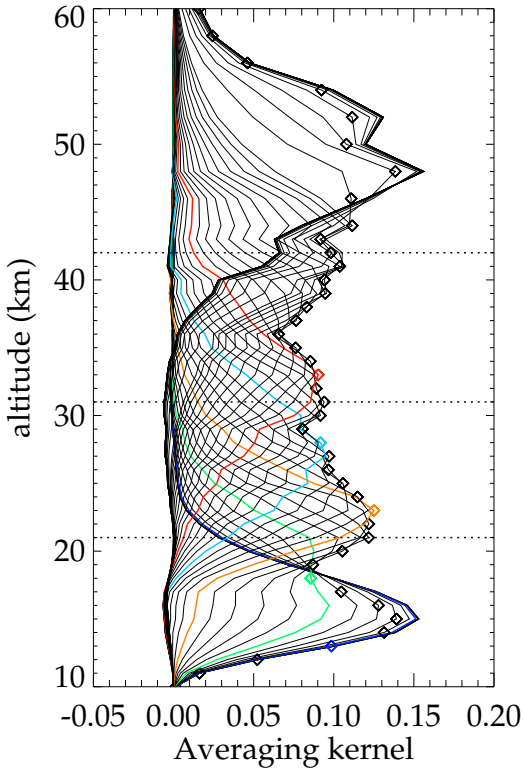

Fig. 5. Formaldehyde averaging kernels, some altitudes are highlighted in colors, dotted horizontal lines delimit the altitude regions characterized by one degree of freedom each, which is derived from sum of the diagonal elements of the averaging kernel matrix (diamonds).

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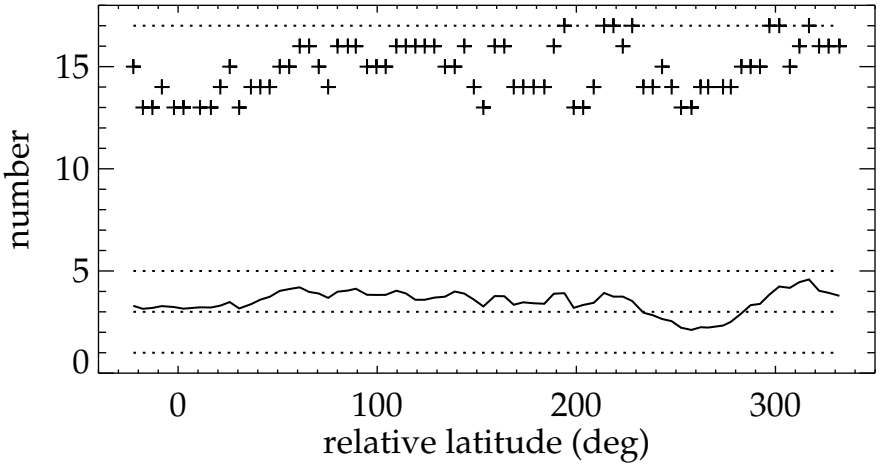

Fig. 6. Degrees of freedom (solid line) and number of cloud-free tangent altitudes (crosses) along orbit 8194 (24 September 2003). The values on the abscissa have the following meaning: 0° and 180° correspond to the equator, 90° to the north pole, and 270° to the south pole. Dotted lines are for guidance only.

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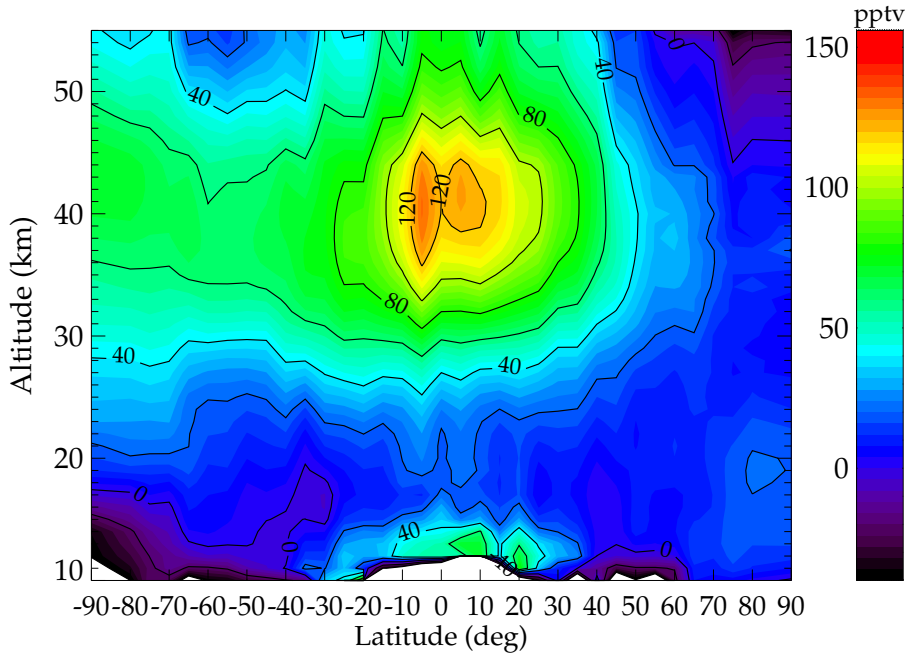

Fig. 7. Zonal mean of formaldehyde for the period 8 September 2003–1 December 2003. Zonal averages are taken for 5° latitudinal bins. White areas mean no data available or values are outside the plotting range.

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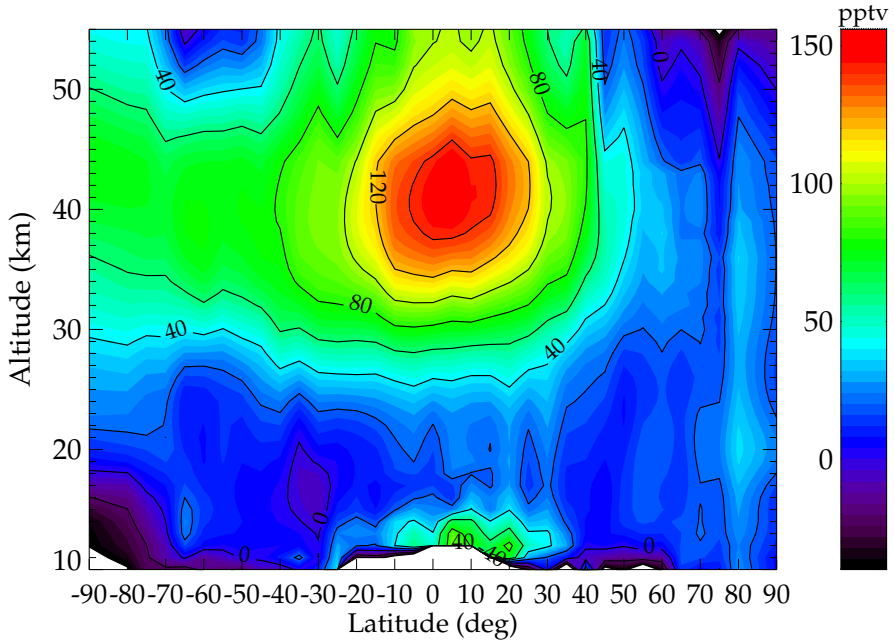

Fig. 8. Zonal mean of daytime formaldehyde for the period 8 September 2003–1 December 2003. For more details see Fig. 7.

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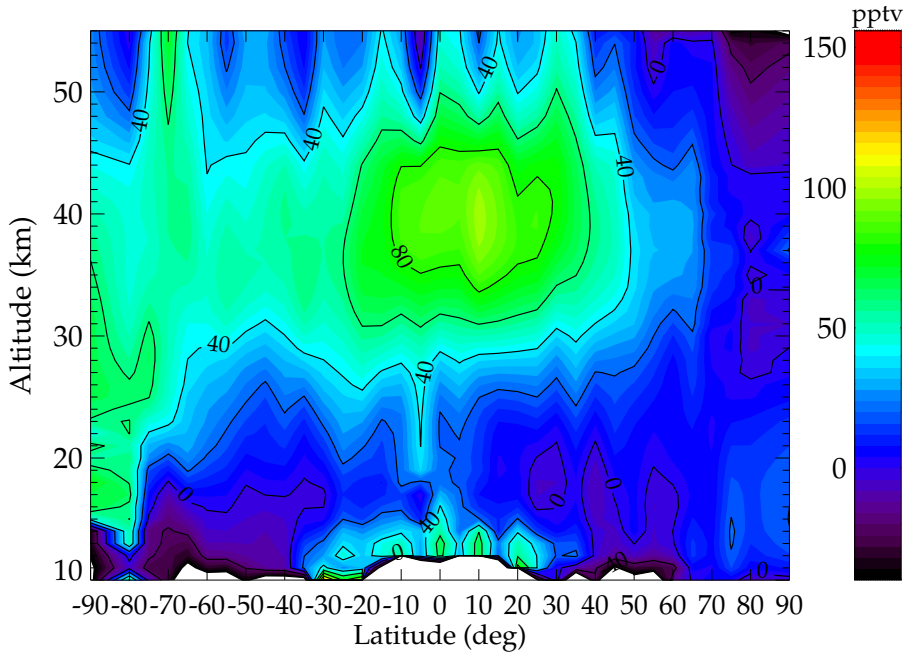

Fig. 9. Zonal mean of nighttime formaldehyde for the period 8 September 2003–1 December 2003. For more details see Fig. 7.

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