Non-LTE retrievals of CO_2 collisional rates and VMRs using limb emission high resolution spectra from MIPAS/ENVISAT

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Abstract

The MIPAS instrument on Envisat has a large spectral coverage (154.3 µm) measuring the most important IR emissions of CO_2, i.e., the 15 µm, 10 µm and 4.3 µm bands. Additionally, it has a very high spectral resolution (0.0625 cm^{-1}) [*Fischer et al., 2008*]. These characteristics makes it an ideal instrument for studying the non-LTE processes of CO_2 emissions and measuring the CO_2 VMR, as well as for the temperature retrieval. In this paper we focus on the retrieval of non-LTE collisional rates and CO_2 VMR using emission spectra at 10 and 4.3 µm in the mesosphere and lower thermosphere (MLT). The unprecedented spectral coverage and spectral resolution of MIPAS allow us to study in depth the nonLTE emission of CO_2 in the 4.3 µm, discerning the individual contributions to the limb emission of several tens of bands, including optically thick and thin bands in this altitude range. These measurements thus allow us to acquire unique information of the non-LTE processes driving the populations of the CO_2 vibrational levels which are applicable not only to MIPAS but also to other limb emission instruments like SABER. We present here new information about the non-LTE collisional processes as well as preliminary results of the daytime CO_2 VMR profiles in the MLT region.

1. Non-LTE modelling of CO_2 10 and 4.3 µm emissions

CO_2 daytime emissions at 4.3 µm are in non-LTE above around the stratopause, where solar pumping populates the ro-vibration energy levels more quickly than collisions thermalize them. Therefore, their accurate non-LTE modelling is crucial for the inversion of CO_2. We use the generic model GRANADA (Generic RAdiative traNsfer AnD non-LTE populations Algorithm, [*Funke et al., 2012*] for calculating the non-LTE populations of CO_2. The accuracy of the non-LTE populations is primarily limited by the uncertainties in the collisional rates.

Table 1.1: Main collisional processes and their respective rates analysed in this study.

Process	Parameters
$CO_2(v_1,v_2,v_3)+N_2 \leftrightarrow CO_2(v'_1,v'_2,v_3-1)+N_2(1)$	Kvv (FB, FH, SH, TH, FRH)
$CO_2(v_1,v_2,v_3)+N_2 \leftrightarrow CO_2(v_1',v_2',v_3)+N_2$	Fermi1; Fermi2
$CO_2(001)+N_2 \leftrightarrow CO_2(nv_1+mv_2)+N_2$	Kvt
$N_2+O(^1D) \rightarrow N_2(1)+O(^3P)$	ε K_{O1D}

Table 1.2: CO_2 bands at 10 and 4.3 µm used in this work.

Band	HITRAN transition
Fundamental band (FB)	00011→00001 (4.3 µm)
First hot (FH)	01111→01101 (4.3 µm)
Second hot 1 (SH1)	10012→10002 (4.3 µm)
Second hot2 (SH2)	02211→02201 (4.3 µm)
Second hot3 (SH3)	10011→10001 (4.3 µm)
Fundamental laser band (FLB)	00011→10002 (10 µm)
Third Hot 1 (TH1)	11112→11102 (4.3 µm)
Third Hot 2 (TH2)	03311→03301 (4.3 µm)
Third Hot 3 (TH3)	11111→11101 (4.3 µm)
Fourth Hot 1 (FRH1)	20013→20003 (4.3 µm)
Fourth Hot 2 (FRH2)	12212→12202 (4.3 µm)
Fourth Hot 3 (FRH3)	04411→04401 (4.3 µm)
Fourth Hot 4 (FRH4)	20012→20002 (4.3 µm)
Fourth Hot 5 (FRH5)	12211→12201 (4.3 µm)
Fourth Hot 6 (FRH6)	20011→20001 (4.3 µm)

The most important collisions in order to explain the emissions of the fundamental (FB), first hot (FH), second hot (SH), third hot (TH) and fourth hot (FRH) bands are summarized in Tables 1.1 and 1.2. The simulations have been performed with KOPRA [*Stiller et al., 2002*].

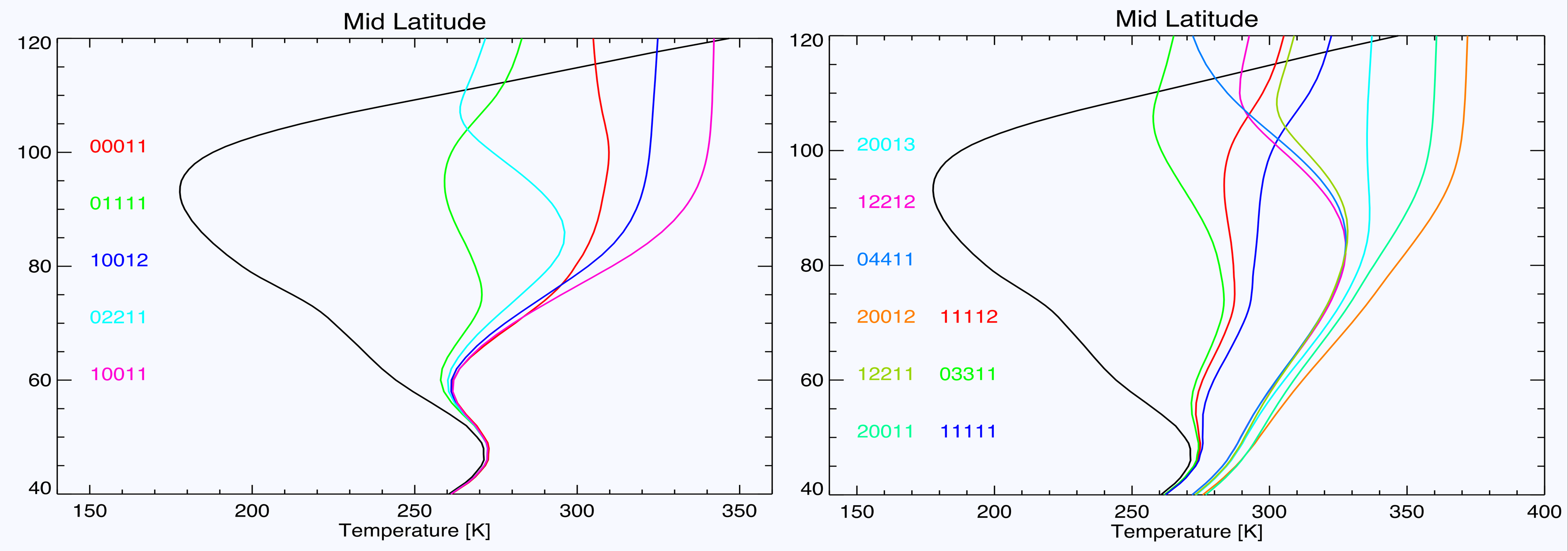

Fig1.1: Daytime vibrational temperatures profiles for the upper levels of the main CO_2 4.3 µm bands (see Table 1.2). The atmospheric conditions correspond to a reference atmosphere in April, 45ºN, SZA=44.5º.

The limb radiance spectra shows the complexity of the CO_2 emissions in non-LTE: there are tens of optically thick and thin contributing bands (Fig. 1.2).

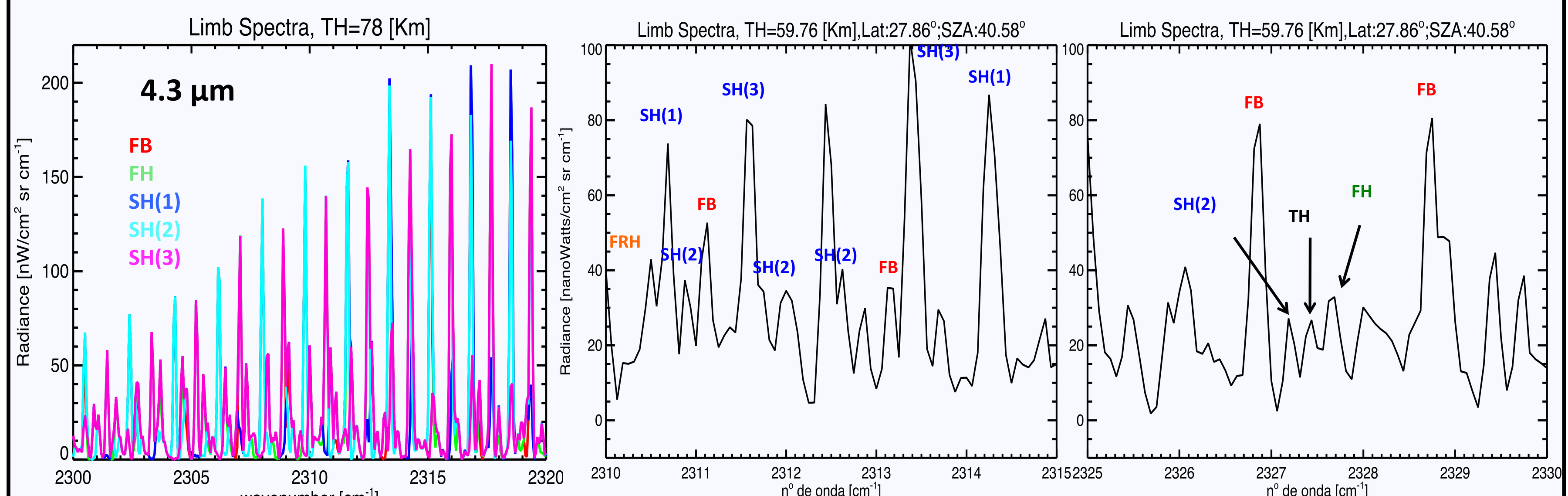

Fig. 1.2: Left: Radiance contributions of the individuals bands (FB, FH and SH's) at 4.3 µm at a tangent height of 78 km. (bands as in Table 1.2). Daytime measurement taken on January, 1 2009, 24ºS and 60ºE. Centre and right: Zoom of the MIPAS spectra showing the contribution of lines from several bands, as noted.

2. Retrievals of Non-LTE collisional rates: Results

In order to solve the whole system of coupled populations responsible for the CO2 4.3 µm emissions, a simultaneous retrieval of the non-LTE collisional parameters and CO_2 VMR is needed. The non-LTE retrievals of the collisional rates (Fig. 2.1) show stable results with virtually no latitudinal variation for all parameters.

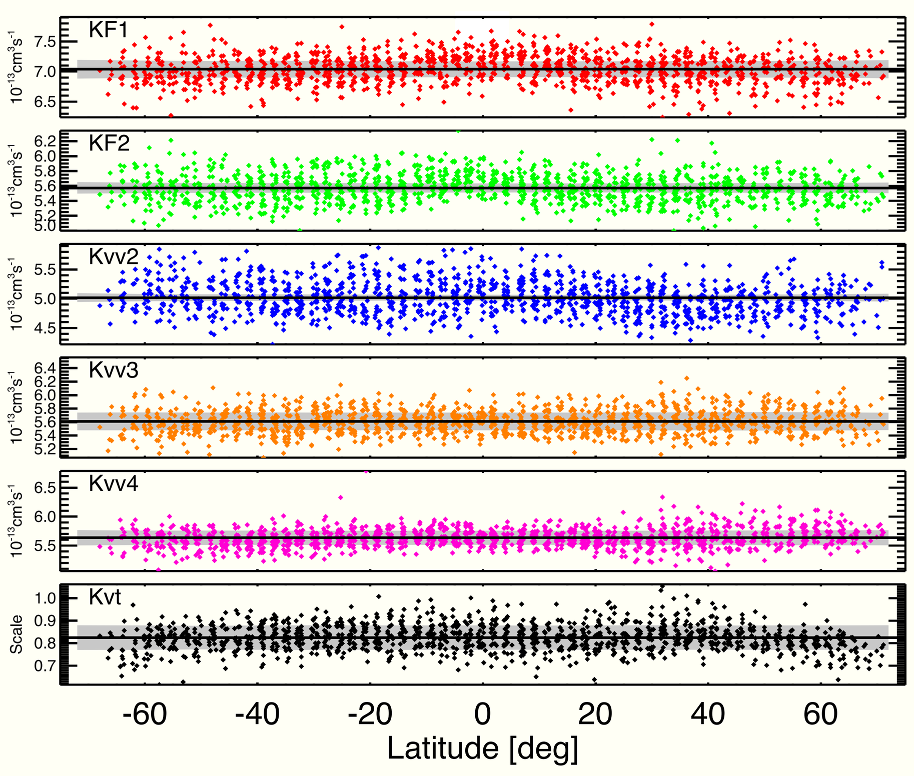

Fig. 2.1: Latitudinal distribution of non-LTE collisional rates retrieved for 4 days (January, 22; March, 25; June, 3 and September, 11 of 2010) in daytime conditions. Each point represent a single scan. The mean value from all scans is represented by solid lines. The grey shaded areas represent the noise error in the retrieved rates [Jurado-Navarro et al., 2015].

Rate	Standard values (previous works)	Mean retrieved
Fermi1	2.0×10^{-11} [*López-Puertas & Taylor, 2001*]	7.04×10^{-13}
Fermi2	2.4×10^{-12} [*López-Puertas & Taylor, 2001*]	5.57×10^{-13}
Kvv (SH)	5.0×10^{-13} [*Nebel et al., 1994*]	5.02×10^{-13}
Kvv (TH)	5.0×10^{-13} [*Sharma & Wintersteiner, 1985*]	5.61×10^{-13}
Kvv (FRH)	5.0×10^{-13} [*Sharma & Wintersteiner, 1985*]	5.64×10^{-13}
Kvt factor	1.0 [*Funke et al., 2012*]	0.90
ε K_{O1D} factor	1.0 [*Funke et al., 2012*]	1.1

Table 2.1: Non-LTE collisional rates (units of cm^3s^{-1}): retrieved (mean values at 300 K) and the standard values considered in previous studies [Jurado-Navarro et al., 2015].

3. Retrievals of Non-LTE collisional rates: Temperature dependence and residuals

The use of currently accepted temperature dependence for some rates resulted in very large residuals in the spectra. New temperature dependences have been derived.

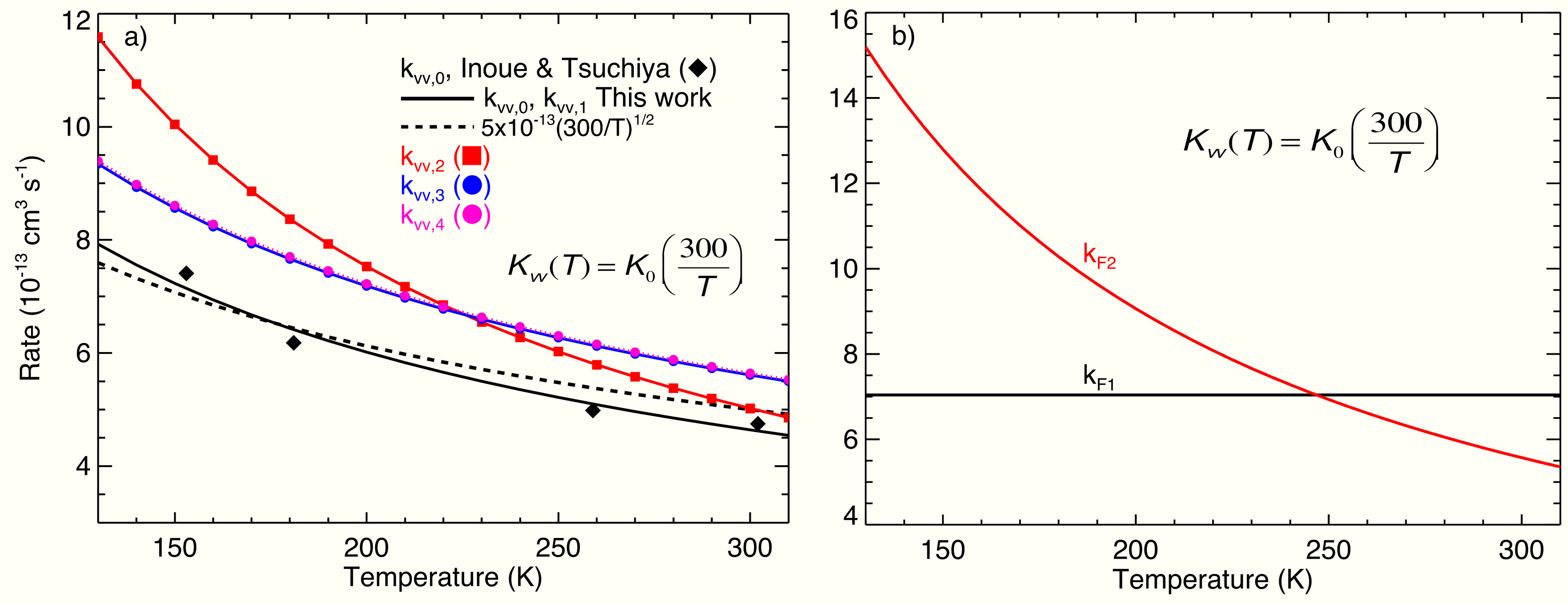

Fig. 3.1: Temperature dependence of the different rates used in this work. (a) $k_{vv,0}$ of the fundamental and first hot bands (solid black line), fitted to the values from Inoue & Tsuchiya 1975 (black diamonds) with **α**=0.64; $k_{vv,2}$ for the second hot (solid red line) with **α**=1, and; $k_{vv,3}$ for the third hot (solid blue line) and $k_{vv,4}$ for the fourth hot (solid pink line) both with **α**=0.60; dashed black line represents the temperature dependence of the Kvv's rates from previous works (standard values). (b) Fermi1 (black line) with **α**=0 and Fermi2 (red line) with **α**=1.0 [Jurado-Navarro et al., 2015].

Examples of observed and simulated MIPAS spectra at 4.3 and 10 µm are shown in Fig. 3.2. The agreement of simulated and observed spectra in the 4.3 µm region is within 5% (blue line in left bottom panel). In the 10 µm region it is slightly worse (≈10%) but within the noise (right bottom panel).

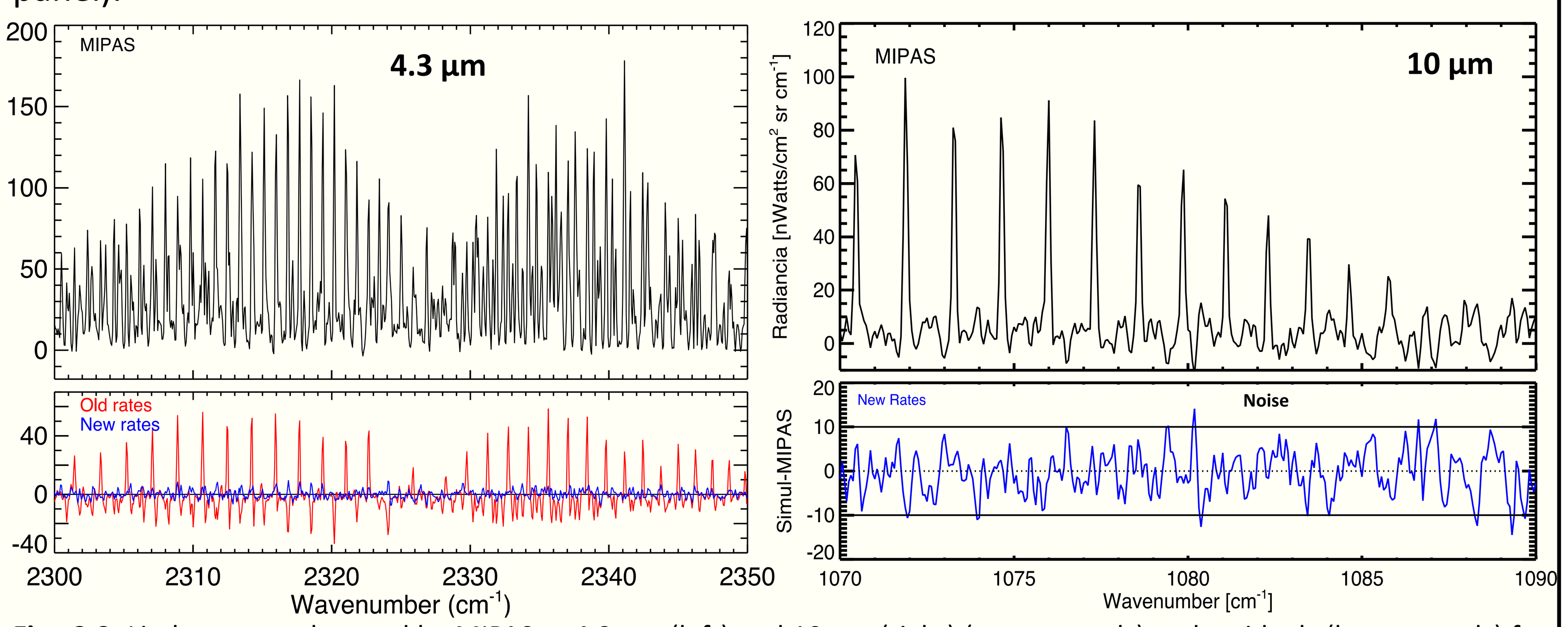

Fig. 3.2: Limb spectra observed by MIPAS at 4.3 µm (left) and 10 µm (right) (upper panels) and residuals (lower panels) for the standard (previous works, red) and retrieved rates (blue). Left: the P and R branches of the CO_2 SH bands are visible. The right plot shows the fundamental laser band emitting near 10 µm. Daytime measurements taken on January, 1 2009, 24ºS, 60ºE at tangent heights of 70 km (left) and 63 km (right).

4. Retrieved CO_2 VMR

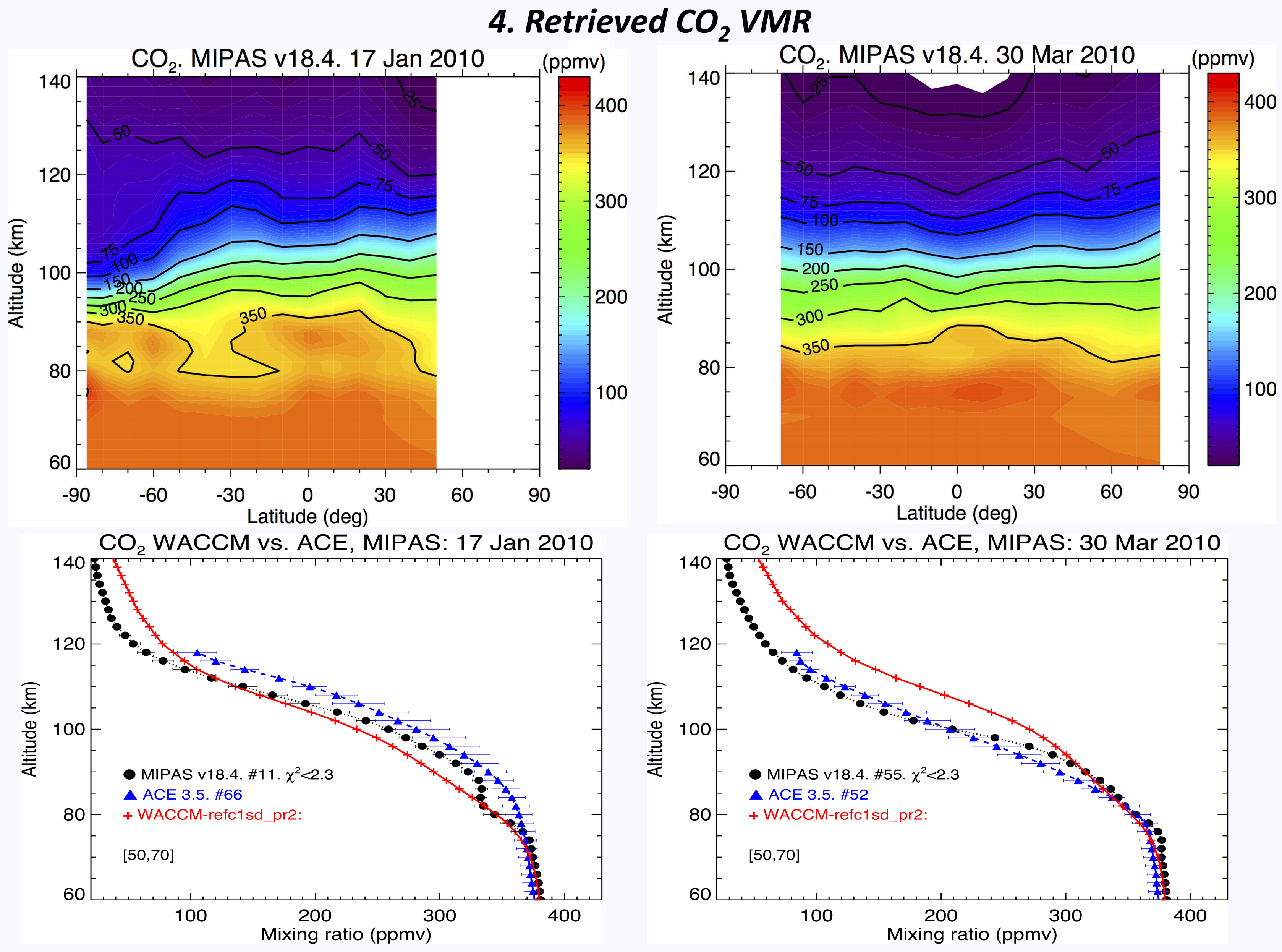

Fig. 4. Retrieved CO_2 VMR for solstice conditions (17 Jan 2010) (left panels) and equinox (30 March 2010) (right). Upper panels show zonal mean plots and lower panels mean profiles for 50-70ºN comparing with WACCM and ACE. In solstice MIPAS is generally smaller than ACE but close to WACCM. In equinox MIPAS is in very good agreement with ACE (and both are larger than WACCM).

5. Conclusions and Future Work

- A new set of non-LTE collisional rates affecting the populations of the CO_2 states emitting near 10, 4.3 and 2.7 µm has been derived from MIPAS spectra. Some of these rates are very different (factors of 1-10) from the values currently used, present a different temperature dependence, and hence have a significant impact on the modelling of these emissions as measured by wideband instruments (e.g. SABER).
- The retrieved CO_2 VMRs derived from MIPAS spectra using these new rates agree very well with ACE for equinox conditions and reasonable well for solstice outside the polar summer conditions. At latitudes near the polar summer, MIPAS is smaller than ACE above ~80 km, while it is larger than WACCM (Kzz*2). Global distributions of CO_2 for the MIPAS MA/UA measurements (2007-2012) are currently being retrieved.

6. References

Fischer et al., ACP, 2008.; Funke et al., JQSRT, 2012; Inoue, G., and Tsuchiya, S., J. Phys. Soc. Jpn. 38, 870, 1975; Jurado-Navarro et al., JGR, submitted, 2015. López-Puertas & Taylor, World Scientific Pub., Singapore, 2001; Nebel et al., JGR, 99, 1994; Sharma & Wintersteiner, JGR, 90, 1985; Stiller et al., J.Q.S.R.T, 72, 2002.

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