NON-LTE STUDIES FOR THE VALIDATION OF MIPAS L2 PRODUCTS

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1. INTRODUCTION

MIPAS is measuring the atmospheric limb emission in the mid-infrared to derive the geophysical parameters. This remote sensing technique is generally based on the assumption that the atmospheric compounds emit according to the Planck function at the local kinetic temperature, the so-called 'local thermodynamic equilibrium' or LTE, approach. It is known, however, that many of the vibrational levels of atmospheric constituents responsible for infrared emissions have excitation temperatures which differ from the local kinetic temperature [1]. These non-LTE populations can affect the limb radiances and hence potentially induce significant errors in the retrieved parameters. In this paper we describe the major efforts that have been carried out for evaluating the non-LTE effects in the geophysical parameters derived operationally from MIPAS spectra. Hence we focus only on the narrow spectral regions (microwindows) used for the retrieval of the operational species (pressure-temperature, O_3, H_2O, CH_4, N_2O, NO_2 and HNO_3) in the altitude range between approximately 10 to 60 km. Among these studies, we can distinguish those performed before having the data, and those carried out after. The first part comprises: (a) an assessment on the need to model non-LTE in the level 2 operational code; (b) the modelling of all known non-LTE processes and the evaluation of their impact on the error budget of the retrieved parameters; and (c) the effect of layers above the top-of-the atmosphere (TOA) in the level 2 code. The second part comprises: (a) an estimation of the uppermost atmospheric tangent height to be considered as the 'deep space' (zero-signal) spectra; and (b) the verification of the assumption of LTE in the level 2 code by: 1) inspecting the day/night difference spectra; 2) analysing the LTE residual spectra; and 3) performing non-LTE retrievals. The non-LTE effects analyzed here are based on the non-LTE information known before MIPAS data (with the only exception of NO_2). MIPAS data contain themselves a huge amount of information on non-LTE processes. Most of it, however, could not be used at this time since it requires a careful and detailed analysis.

2. THE CHOICE OF NON-LTE IN THE LEVEL 2 PROCESSOR

The inclusion of non-LTE emissions into a retrieval code has a high cost in computation time and requires a lot of effort for modelling and coding all non-LTE processes. This is true, in particular, because these are not only species-dependent but also depend on any vibrational level emitting in the infrared. Further, many cases require modelling of vibrational levels other than those whose emission is measured, because of the vibrational-vibrational collisional coupling between them. Thus, it is highly desirable that the code avoids the inclusion of non-LTE. Furthermore, MIPAS measurements are mostly concentrated in the stratosphere, where the non-LTE effects are generally weaker. Also, MIPAS has a great advantage in this sense: its high spectral resolution and wide spectral coverage enable us to select the ro-vibrational lines of the bands less affected by non-LTE and also avoid contamination from highly excited non-LTE emissions. With all this in mind, a preliminary study was carried out to determine the way non-LTE should be handled in the L2 operational code.

Four strategies were devised: a) to select microwindows where non-LTE is negligible and hence assume LTE in the code; b) to account for non-LTE in the forward model but do not compute non-LTE populations (i.e., use pretabulated values interpolated for the actual conditions); (c) to account for non-LTE in the forward model and calculate the non-LTE populations online with a non-LTE code; and d) to account for non-LTE and simultaneously retrieve from the data the non-LTE information. Mainly based on the considerations mentioned above, the result of the study was to assume LTE in the L2 operational code [2].

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3. NON-LTE EFFECTS ON RETRIEVED PARAMETERS: MODELLING

Once it was decided to assume LTE in the L2 operational code, a thorough study was carried out to include all known non-LTE processes in the selection of the operational microwindows. Introducing this information, the microwindows were selected so they provide the maximum information content, but keeping the non-LTE contribution to a minimum or being negligible [3].

To assess the non-LTE effects in the microwindows selection, LTE and non-LTE synthetic spectra at MIPAS spectral resolution were computed. The computation of the non-LTE spectra requires, on one hand, new spectroscopic data, mostly of hot bands originating in high energetic levels, and, on the other hand, the non-LTE populations of the emitting levels of all molecules known to be (or likely to be) in non-LTE. From those spectra, retrievals were performed including all known sources of errors: instrumental, spectroscopic, contaminants, etc. The differences between the quantities retrieved from the non-LTE and from the LTE spectra were assumed as the errors induced by non-LTE. The non-LTE effects were evaluated for a set of reference atmospheres for temperature, species abundances, solar illumination and tropospheric conditions that covered both, typical and extreme atmospheric conditions (mid-latitude day- and night-time, polar winter and polar summer) for which the potential non-LTE effects vary from weakest to moderate to strongest [4].

The spectroscopic line parameters are usually taken from atmospheric spectral databases such as HITRAN [5]. This, however, lacks for some important hot bands parameters which, in some cases, are thought to contribute with significant atmospheric non-LTE emissions. Thus, the spectroscopic linelist used in these non-LTE studies was extended from HITRAN 96 with 199 bands of the ozone molecule involved in 17 polyads, and with 30 bands involved in 7 polyads of NO_2 [6]. These calculations represent a large increase in the number of spectral lines since the final dataset was approximately twice as large as the original HITRAN 96 data.

A global model was constructed for the computation of the non-LTE populations of many species and vibrational levels with the most updated information on non-LTE processes. Some existing models were updated with current information derived from recent satellite data (ISAMS, CLAES, CIRRIS-1A, etc.) and new models were also developed for species which were not studied before, e.g., N_2O, CH_4, NO_2, and HNO_3. A detailed description of the non-LTE models and the species and levels for which non-LTE populations were computed can be found in [4], and a recent update in [7].

As an additional output of this study, an extensive and comprehensive non-LTE spectra dataset was constructed, covering typical and extreme atmospheric conditions and the whole mid-IR spectrum, which is very valuable for assessing non-LTE effects in the real data. The details of the spectra calculations can also be seen in [4].

The deviation between modelled LTE and non-LTE radiances, which allows the estimation of non-LTE induced retrieval errors, was used lately for the selection of the microwindows dataset and occupation matrix of the L2 operational code, where they are kept, generally, much smaller than any other error source.

4. THE CHOICE OF THE TOP-OF-THE ATMOSPHERE (TOA)

One further point related to non-LTE effects is the selection of the 'top-of-the-atmosphere' in the forward model of the L2 operational code. It was originally selected as 120 km. To verify this, we calculated spectra, for all MIPAS bands, at the uppermost altitude of the retrieval (68 km) assuming the TOA at 120 km and extending it to 200 km. The difference spectra in band A shows maximum differences of 0.8 nW/(cm^2 sr cm^{-1}), much smaller than the noise, $\sim$50 nW/(cm^2 sr cm^{-1}. Bands AB and B show even smaller values. Band C, however, show values close to the noise at the shorter wavelengths edge of the band: values goes from 2 to 6 nW/(cm^2 sr cm^{-1}) at wavenumbers between 1700 and 1750 cm^{-1}. This emission comes from NO. For band D, it also shows that retrievals performed in this spectral region from emissions of NO, CO and CO_2 should set up the TOA altitude higher than 120 km. Thus, the use of a 120 km TOA is justified for retrieval of species operationally processed, if appropriate microwindows are chosen. In fact, the nominal selection of microwindows do not include any microwindow from within band D, so any problems with the effects of TOA are not expected to affect most of the data. For scientific analysis of additional species, such as NO, CO or CO_2, the atmospheric model has to be extended to altitudes higher than 120 km.

5. VERIFICATION OF LTE IN MIPAS DATA

5.1. Deep-space tangent height

The measurements taken to verify the deep space view (IF9) show a significant atmospheric contribution in band D in the NO 5.3 μm region at a tangent height of 185 km and even at 191 km. At 203 km, however, the signal of

NO disappears. The atmospheric signatures in bands A, AB, B, and C, are negligible even at lower tangent heights. Therefore, the nominal 210 km tangent height is high enough to be considered as the deep-space view. This first checking by looking at some particular spectra still needs to be extended to include some statistics of the space-view in the nominal measurements.

5.2. Comparison of Day/Night spectra

We have checked, in a qualitative way, the non-LTE effects by looking at day/night difference spectra at the uppermost tangent height ($\sim$68 km) of the nominal measurements. In order to maximise the signal and distinguish non-LTE features from noise we co-added 32 daytime spectra and 30 nighttime spectra of orbit #504. This is important to 'validate' the non-LTE processes that have been included in the selection of microwindows. For vibrational bands close to LTE, non-LTE is difficult to be discriminated from temperature variability. That is also true for compounds that have a significant day/night variability, e.g., O_3 in the upper stratosphere and mesosphere, NO_2, etc. In general, the non-LTE emissions look as expected from previous simulations. E.g., CO_2 emission in the 15 μm region is very close to LTE; CO_2 emissions in the 10 and 4.3 μm regions are much enhanced at daytime; O_3 emission in band AB shows a larger nighttime signal than in the daytime, thus reflecting both the warmer nighttime temperature of this orbit and the larger concentration of O_3. H_2O also shows non-LTE features similar as expected, in this case showing clearly the much larger non-LTE contribution of the first hot band than that of the fundamental band.

One exception in the estimation of non-LTE seems to be NO_2. The co-added spectra do not show the hot bands contribution predicted by the model, even for the first hot band. Although it is difficult to discriminate non-LTE effects because of the large diurnal variability of NO_2, it seems that the non-LTE excitation of the NO_2 ν_3 bands by photochemical processes in the daylight stratosphere is smaller than the predictions [6]. See more details below in Section 5.4.

Another exception seems to be CH_4. MIPAS data suggests than CH_4 is in non-LTE above around 60 km. For this species no evidence of non-LTE has been reported so far. In the L2 error analysis, non-LTE for CH_4 was included following a theoretical prediction with processes similar to those in H_2O. The non-LTE effects seen in MIPAS data are in qualitative agreement with the predictions.

5.3. Residuals spectra

One further aspect of checking the non-LTE effects in the L2 retrieved products is to analyse the residual spectra (difference between the measured spectra and the adjusted spectra resulting in the L2 retrieval). A way of analysing it quantitatively and statistically is to correlate these residuals with the non-LTE residuals, obtained as the difference between the synthetic non-LTE and LTE spectra computed for an *a priori* atmosphere. This, however, give us an estimation of the upper limit effect of non-LTE since with this method non-LTE cannot be discriminated from other error sources such as spectroscopic data (strengths), temperature, etc.). We have analysed the residuals only in the microwindows used for the retrievals and at the tangent heights where they are used (occupation matrix). The analysis was done separately for day and night residuals, since non-LTE in some bands is expected to be significantly dependent on illumination conditions, and also for different latitudes (6 latitude bands) and tangent heights only above 42 km. Three periods of data were analized corresponding to July, August and orbits 2081–2083.

In general, non-LTE residuals are of similar magnitude than predicted. non-LTE in the pressure-temperature retrieval is slightly smaller than anticipated. We believe this is due to the lower collisional rate of $CO_2(v_2)$ by atomic oxygen used in the non-LTE climatology. Using a faster rate, as atmospheric radiance measurements suggest (we should note that, on the contrary, laboratory data indicates values lower than that used in the climatology), drives the population of the $CO_2(v_2)$ levels to be closer to LTE, as this analysis suggests.

Non-LTE effects in O_3 and H_2O are similar to those predicted.

The effects of non-LTE in CH_4 seems to be larger than those predicted by about a factor of 2. No evidence of non-LTE on CH_4 has so far been reported. Non-LTE errors in L2 error budget were computed using a CH_4 non-LTE model with similar processes as for H_2O. It seems that the model underestimates these effects significantly. Further work on the characterisation of non-LTE in CH_4, in particular by using the upper atmospheric data, is clearly needed.

Non-LTE in N_2O is larger than predicted. However the contribution of non-LTE to the N_2O total error budget is very small [8]. Therefore, even if they are larger than expected they are not significant.

The effects of non-LTE in NO_2 is smaller than anticipated, which is in consonance with the results of the retrievals of NO_2 non-LTE parameters (see Section 5.4 below).

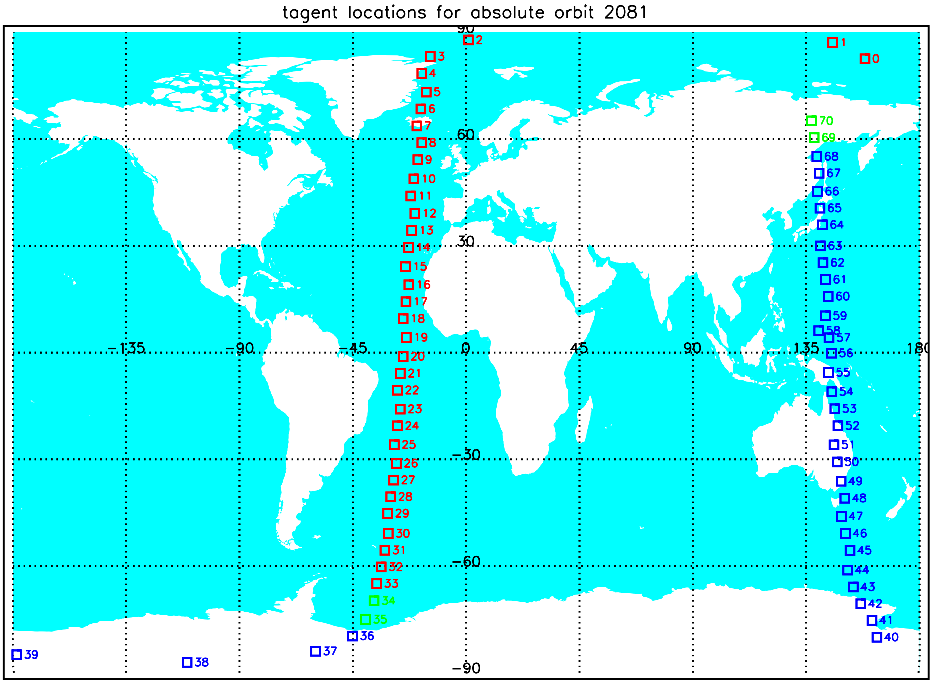

Figure 1. Tangent height geolocations for the scans of orbit #2081 taken on 24 July 2002. The numbers correspond to the scans and are used as the x-axis in the following figures. Red numbers correspond to daytime conditions and blue to nighttime. In green are for twilight.

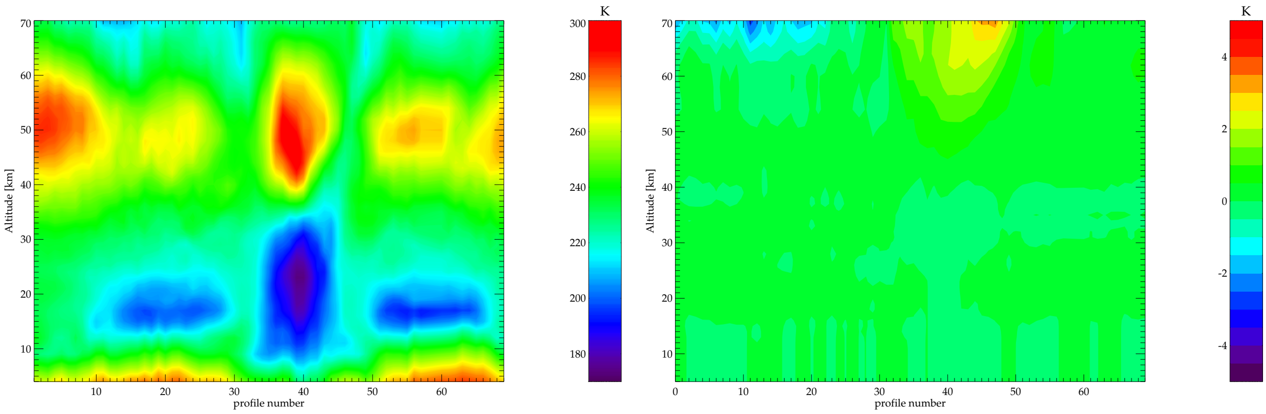

Figure 2. Non-LTE kinetic temperatures (left) and non-LTE–LTE temperature differences (right) for orbit #2081.

5.4. Non-LTE retrievals

Non-LTE retrievals have been performed for orbit 2081 (see Fig. 1) for temperature-LOS (line of sight) and for O_3, H_2O, CH_4, and NO_2 volume mixing ratios (vmr). The retrievals were performed with the jointly developed IMK–IAA non-LTE processor [9, 10] for the microwindows and occupation matrices used in the operational L2 processing. The non-LTE processor uses a forward non-LTE model which calculates online the non-LTE populations of the species at work in each iteration for the retrieved temperature profile (option (d) described in Section 2). We should note that we do not retrieve simultaneously non-LTE information but use that currently known from all previous experiments and reported in the literature. One exception is the non-LTE chemical excitation of the $NO_2(v_3)$ levels, which has been retrieved from MIPAS spectra and is discussed in detail below.

The results for the combined retrieval of temperature and line of sight (altitude registration) are shown in Fig. 2. The left panel shows the temperature retrieved under non-LTE conditions and the right panel the non-LTE–LTE differences. The non-LTE model for CO_2 implemented here uses the fast collisional rate of $CO_2(v_2)$ by atomic oxygen, opposite to the moderate value used in the non-LTE climatology.

The results show that non-LTE induces kinetic temperature (T_k) differences smaller than $\pm$1K below $\sim$60 km. The non-LTE temperatures are cooler than those retrieved under LTE in $\sim$1–2 K for daytime around 70 km. On the contrary, non-LTE T_k's are warmer in 3–7 K for the polar night (scans $\sim$35–45). These results are in agreement with expectations. The cooler non-LTE temperatures in the daytime are due to the larger non-LTE populations obtained after the relaxation of solar absorption at 4.3 and 2.7 μm. The warmer temperatures in the polar night mesosphere result from the under-LTE populations of the $CO_2(v_2)$ levels that occur for this warm region (see left panel).

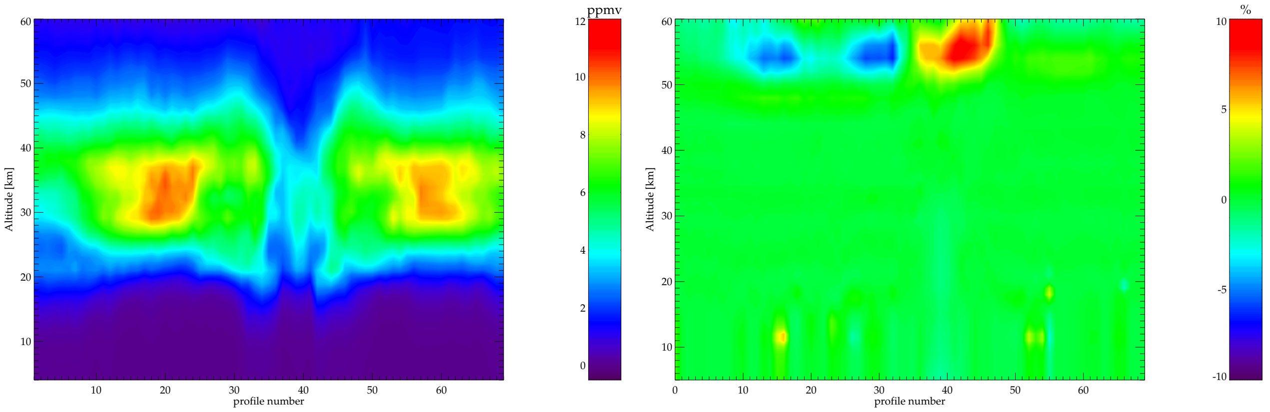

Figure 3. Non-LTE O_3 vmr (left) and non-LTE–LTE O_3 vmr differences for orbit #2081.

The effects of non-LTE on the retrieved O_3 are shown in Fig. 3. The non-LTE–LTE differences in O_3 vmr are very small (<2–3%) below $\sim$50 km. The retrieved O_3 under non-LTE between 50–60 km is significantly smaller (-10%) at daytime and is larger (5–10%) in the warmer polar winter. The latter effect is caused by the underpopulation of the O_3 v_3 levels in the warm lower mesosphere, an effect similar to that shown in temperature and described above. The lower non-LTE O_3 vmr in the daytime side is not caused by a direct local non-LTE effect but by the propagation in the retrieval of the lower O_3 vmr retrieved at higher altitudes under non-LTE.

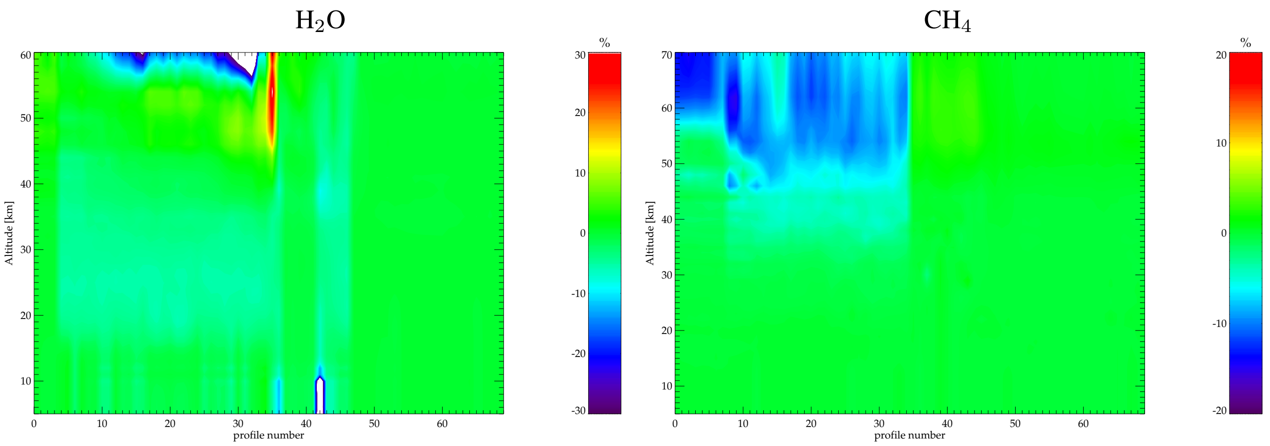

Figure 4. Non-LTE–LTE differences in the retrieved H_2O vmr (left panel) and CH_4 (right panel) for orbit #2081. Note the different colour scale in the H_2O and CH_4 figures.

The results of the H_2O vmr non-LTE retrievals are shown in the left panel of Fig. 4. The non-LTE–LTE differences in the retrieved H_2O vmr are negligible in the whole altitude interval at nighttime. At daytime, there are significant differences above about 55 km, reaching differences of $\sim$30% at 60 km, with smaller non-LTE values, and also, in the 20–35 km region with differences of about –10%. The differences at heights above 55 km are due to the larger non-LTE populations of the $H_2O(010)$ level in the daytime. Those at lower heights (20–35 km) are not due to local non-LTE populations but induced in the retrieval method by the smaller H_2O non-LTE vmr values above 55 km. The retrieved non-LTE H_2O vmr can, on the other hand, be larger than in LTE ($\sim$20%) in the lower mesosphere under polar winter conditions; when the lower mesosphere is rather warm.

The results of the CH_4 vmr non-LTE retrievals are shown in the right panel of Fig. 4. The non-LTE effects are negligible at nighttime. At daytime, however, the theoretical non-LTE model predicts smaller CH_4 vmr in about 10–15% above about 50 km. These effects might be even larger, as suggested by the residual analysis (Section 5.3). Further work on the analysis of non-LTE in CH_4 using the upper atmospheric data is needed.

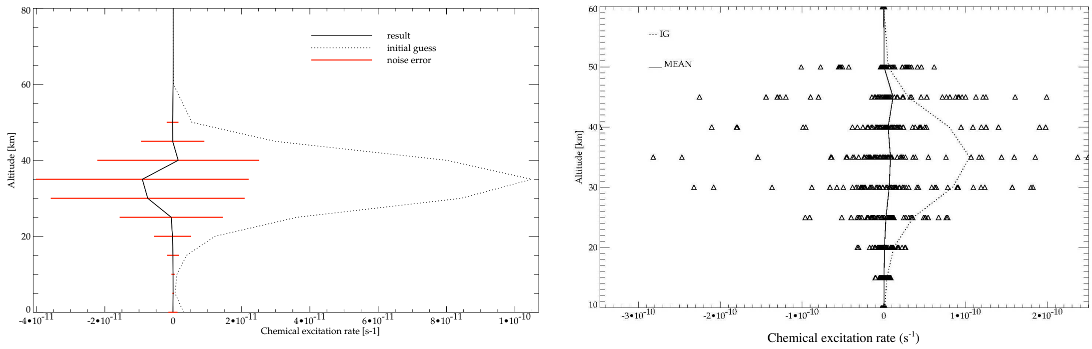

Figure 5. Chemical excitation rate for the production of NO_2 retrieved from MIPAS orbit #2081 for a single scan (left) and for all scans (right).

Non-LTE effects in NO_2 were predicted to be significantly large. Non-LTE evidences from previous experiments were unclear or contradictory. For this reason we first attend to retrieve non-LTE information from the MIPAS spectra themselves. We performed retrievals of the chemical excitation of the $NO_2(v_3)$ levels [1, 6] with the retrieval code mentioned above [9, 10] and using option (d) described in Section 2. Fig. 5 shows two examples of retrievals. The left panel shows the chemical excitation retrieved in one particular scan (#2), and gives us an idea of the accuracy of the retrieved rate. The right panel shows the profiles for all successful retrievals of orbit 2081 together with the mean and the a priori used. The results show clearly that, although the retrieved errors are rather large, the chemical excitation is much smaller, by about a factor 10, than that previously assumed in the non-LTE climatology (the a priori in the figures).

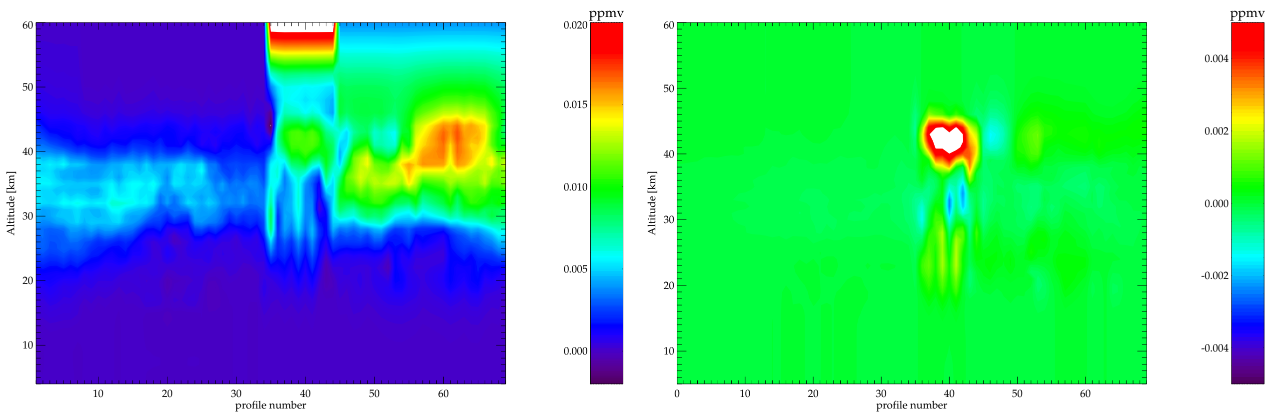

Figure 6. Non-LTE NO_2 vmr (left) and non-LTE–LTE NO_2 vmr differences (right) for orbit #2081.

Including this new chemical excitation rate in the NO_2 non-LTE model, we performed retrievals of NO_2 under non-LTE. The results are shown in Fig. 6. The left panel shows the non-LTE NO_2 vmr retrieved values and the right panel the non-LTE–LTE differences. The resulting non-LTE effects are very small ($<5\%$). The difference found for the scans in the day/night transition are not caused directly by non-LTE $NO_2(v_3)$ populations but by the large effect that the a priori profile and the number of measurements (altitude grid points) included in the retrieval have on the retrieved NO_2 vmr at the upper altitudes. In summary, we conclude that non-LTE effects in NO_2 is very small.

6. CONCLUSIONS

(a) The operational products of MIPAS are mostly focused in the stratosphere where non-LTE effects are less important. Also, its high spectral resolution and wide spectral coverage allow us to discriminate from LTE and non-LTE. Since the inclusion of non-LTE is very computationally expensive and require a great effort in non-LTE modelling, we assumed LTE in the operational level 2 retrieval code.

(b) A thorough non-LTE modelling was carried out to incorporate our current knowledge of non-LTE in the selection of the operational microwindows. The non-LTE errors derived from these calculations are presented in reference [8].

(c) The use of a 120 km TOA is justified for retrieval of species operationally processed. For scientific analysis of additional species, such as NO, CO or CO_2 in bands C and D, the atmospheric model has to be extended to higher altitudes.

(d) The analysis of non-LTE in the day/night spectra show, in general, the major expected non-LTE features. Exceptions are NO_2, for which the non-LTE effects seem to be significantly smaller than predicted, and CH_4, for which non-LTE seems to be larger than theoretically predicted. The latter needs a detailed analysis for an accurate assessment.

(e) The analysis of a set of measurements of the deep space view shows that there is no discernible atmospheric signal at the setup height of 210 km. For some isolated cases of high geomagnetic activity, some atmospheric signal might be present at that height, particularly at high latitudes. These analyses should be extended to other scans.

(f) The analysis of non-LTE from the residuals spectra suggests than non-LTE is, in general, in accordance with predictions. The two exceptions mentioned above for NO_2 and CH_4 are also seen in this analysis.

(g) Non-LTE retrievals for temperature, O_3, H_2O and CH_4 for orbit #2081 show that non-LTE errors are small below about 50 km. There can be however, significant errors (underpredictions) for considering LTE in the retrievals of temperature for polar-winter-like atmospheric conditions (cold stratopause and warm lower mesosphere) above about 50 km.

The non-LTE retrievals in O_3 show that non-LTE effects are small ($\leq$5%) below 50 km but can be significant (5–15%) between 50 and 60 km, particularly in the daytime and polar winter conditions.

The non-LTE retrievals for H_2O show that non-LTE is negligible below about 55 km, but can be significant above, in the daytime and polar winter conditions, reaching differences of up to –30% at 60 km. They can also induce differences of about –10% at 20-35 km at daytime.

Non-LTE in CH_4 is negligible except above 50 km at daytime, where they can induce errors of about –15%. The residual analysis and the upper atmosphere measurements suggest that they might be even larger.

The non-LTE chemical excitation rate of NO_2 seems to be significantly smaller than predicted (at least a factor of 10 smaller). Hence, non-LTE in NO_2 is very small.

Non-LTE effects are strongly linked with the *a priori* profiles and the number of measurements included in the retrieval. Care should be taken to distinguish direct non-LTE effects from those induced through the use of the *a priori* and the number of measurements (altitude grid points) included in the retrieval.

(h) The analysis and retrievals of the upper atmosphere spectra are very useful to gain new information on non-LTE processes and, hence, to evaluate more accurate their effects. Their analysis is therefore of high importance to better assess non-LTE effects in the operational products.

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