JOINT RETRIEVAL OF CO AND VIBRATIONAL TEMPERATURE FROM MIPAS-ENVISAT

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ABSTRACT

MIPAS is a limb viewing fourier transform spectrometer operating in the infra-red. It scans the tangent altitude range 6-68 km at a vertical resolution of approximately 3km. CO has various natural and anthropogenic sources including forest fires and industry. In the troposphere, CO is the main sink of the principal oxidising agent - the hydroxyl radical - and so reduces its capacity for the removal of other atmospheric pollutants. In the stratosphere, its intermediate lifetime makes it useful as a tracer for stratospheric motions and processes of tropospheric-stratospheric exchange. However, the retrieval of CO from a limb sounding IR instrument is complicated because of non-LTE (non-local thermodynamic equilibrium) effects. Ordinarily, the internal vibrational energy level populations are controlled by collisions between molecules and follow the translational (kinetic) energy distribution of the ambient gas (LTE). However, if collisions are infrequent, radiative processes can lead to a non-Boltzmann distribution of the internal energy level populations (non-LTE). CO is strongly affected by non-LTE in the IR down to around 40km and modelling these processes is difficult. These effects are especially problematic in the limb viewing geometry due to the long path length viewed through the upper atmosphere. However, using a joint CO, vibrational temperature (T_v) retrieval it is possible to estimate the non-LTE effects without modelling the energy level populations. Instead, we retrieve a parameterisation of the non-LTE effects, T_v, directly from the emission spectra.

Key words: MIPAS, joint retrieval, carbon monoxide, vibrational temperature, non-LTE.

1. INTRODUCTION

Carbon monoxide has various natural and anthropogenic sources. It is produced primarily by the oxidation of methane and other hydrocarbons and is released as the product of incomplete combustion of fossil fuels and biomass as well as from other terrestrial sources. In the upper atmosphere CO is is produced by the photodissociation of CO_2. CO plays a central role in tropospheric chemistry via its reaction with the OH radical.

The hydroxyl (OH) radical, derived from ozone and water vapour, is the principal atmospheric oxidising agent and so CO concentrations have a direct impact on the oxidising capacity of the atmosphere. Removal of the hydroxyl radical reduces the capacity for the oxidisation and removal of other atmospheric pollutants.

The intermediate atmospheric lifetime of CO, which leads to strong vertical and horizontal concentration gradients makes CO useful as a tracer molecule for stratospheric motions and processes of tropospheric-stratospheric exchange.

There is, therefore, considerable interest in mapping its abundance on the global scale. According to IGOS (Integrated Global Observing Strategy) [3], which compiled a survey of instrument capabilities needed to advance our understanding of the Earth's atmosphere, an accuracy of down to 25% would be considered useful for CO in the upper-troposphere lower-stratosphere (UTLS) region. Our studies suggest that this should be possible using the MIPAS instrument.

A retrieval code (LMRTV) using sequential Levenberg-Marquardt Optimal Estimation [6] and the Reference Forward Model (RFM) [2] has been written to retrieve CO and T_v simultaneously from MIPAS spectra.

2. THE NON-LTE PROBLEM

The retrieval of CO is made difficult since its ro-vibrational energy levels are not in thermodynamic equilibrium with the ambient gas. Ordinarily, when collisions are frequent, a molecule's vibrational energy levels are determined by the kinetic, or translational, energy distribution of the gas and are described by Boltzmann statistics. However, at low pressures this assumption can break down. Under these conditions the vibrational energy levels may be principally controlled by other processes such as the radiation field and few collisions mean these states are maintained out of equilibrium with the surrounding gas. This situation is known as non-LTE. The CO

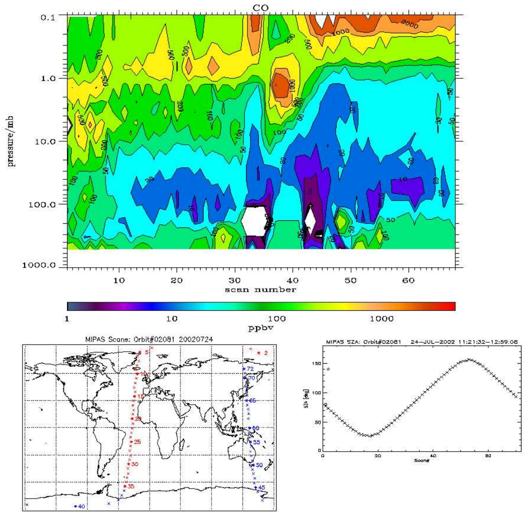

Figure 1. CO retrieval assuming LTE conditions. Unrealistic enhancements observed in daytime stratospheric and mesospheric regions. Silver squares denote a priori rather than retrieved values.

molecule is affected particularly strongly by non-LTE since the solar radiation contains strong CO features which act to pump the vibrational energy levels of atmospheric CO into excited states. This effect is important in the stratosphere and above. Collisional excitation between CO and other molecules in non-LTE also plays a role. Figure 1 shows what happens if we do not account for non-LTE effects. Day and night-time VMR appear significantly different even though CO concentrations should have no diurnal variation.

A useful parameterisation of the non-LTE populations is vibrational temperature, T_v, see equation 1. This is equivalent to the kinetic temperature (T_k) that would be needed to produce the observed non-LTE radiance. When inserted into the Boltzmann exponential factor it gives the observed populations of a level m with energy E_m. Only the fundamental vibrational transition CO(1–0) is important in consideration of the joint retrieval.

$$T_{vm} = \frac{E_m}{k \ln\left(\frac{n_0 g_m}{n_m g_0}\right)} \qquad (1)$$

In non-LTE the populations of the states are determined by a mixture of collisional interactions and the exchange of quanta. The former can involve both vibrational-translational and vibrational-vibrational exchanges, and both can involve a multiplicity of levels and of exchange partners. When all of these are considered, it is no simple matter to perform reliable calculations of the middle atmosphere temperature structure [5]. This difficult problem is already being tackled and the Advanced MIPAS Level 2 Data Analysis (AMIL2DA) processor uses such a population model in its retrieval scheme [4].

However, there is a way we can avoid needing to model the non-LTE temperature structure explicitly. This is achieved by retrieving T_v directly from the emission spectra. The forward model used is the RFM. This model does not calculate the non-LTE populations. However, if the T_v profiles are known, it is able to calculate the non-LTE radiance. We can therefore treat T_v as another parameter to be retreived from the spectra. Apart from the relative simplicity of this approach, there are several advantages to performing a joint retrieval. Firstly, we constrain the vibrational temperature structure using observations, which is often considered preferable to following a modelling approach, especially when the physics is complicated. In addition, the retrievals run much faster. Processing a single scan using the AMIL2DA processor may take around 40 minutes. However, using this joint retrieval method a single scan takes less than 5 minutes.

3. THE CHALLENGES OF A JOINT RETRIEVAL

There are large amounts of CO above the top tangent altitude (68 km). This CO is mainly produced by the photodissociation of CO_2;

$$\mathrm{CO_2} + hv \rightarrow \mathrm{CO} + \mathrm{O}(^1\mathrm{D}) \qquad (2)$$

Large amounts of CO in this region means sensitivity to CO lower down, where mixing ratios are lower, may be reduced.

We are unable to sample the atmosphere directly at these altitudes. However, in a limb viewing geometry, it is essential that we are able to take some account of the atmospheric state in this region. T_v may differ by more than 100 K from T_k in this region and so may have a significant impact on the observed spectra.

An additional difficulty relates to the fact that perturbations to CO and T_v in the forward model are indistinct to some extent. We therefore need to ensure that both parameters can infact be retrieved independently.

4. THE RETRIEVAL METHOD

CO and T_v are retrieved simulataneously. The retrieval code (LMRTV) uses Levenberg-Marquardt Optimal Estimation [6]. This method uses prior knowledge about the expected atmospheric state and estimates the most probable state based on this *a priori* information in conjunction with the emission measurements. We use the retrieved kinetic temperature (T_k) profile as our *a priori* estimate of the T_v profile. Climatological values of CO are used as *a priori* for the VMR retrieval.

The *a priori* is updated sequentially through the profile. In a limb viewing geometry, the spectra obtained at each tangent height are affected by the atmosphere above. Therefore, if we begin the retrieval using spectra obtained at the top of the profile, it is useful to update our *a priori* knowledge about this part of the atmosphere when we retrieve from spectra obtained lower down the profile.

5. RESULTS

5.1. Sensitivity analysis

Retrieval precision is calculated using an *a priori* uncertainty of 100% for CO and 10K for T_v as;

$$\mathbf{S_x} = (\mathbf{k^T S_y^{-1} k} + \mathbf{S_a^{-1}})^{-1} \qquad (3)$$

where $\mathbf{S_x}$ is the retrieval precision covariance, $\mathbf{S_y}$ is the instrument noise covariance, $\mathbf{k}$ is the forward model jacobian and $\mathbf{S_a}$ is the *a priori* uncertainty covariance.

Figure 2 shows the expected precision. We obtain retrieval random errors for CO of better than 70% at most altitudes and better than 25% in the UTLS.

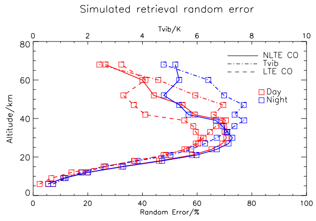

Figure 2. Retrieval precision for LTE CO and joint CO, T_v retrievals.

5.2. Retrievals from real data

Pressure and temperature aswell as contaminant species, principally O_3, N_2O, CH_4 and H_2O, were retrieved from the spectra using MORSE (MIPAS Orbital Retrieval using Sequential Estimation) [1]. It is also necessary to retrieve an aerosol continuum term for low altitude sweeps, which is caused by thin cloud and aerosol. The lowermost retrievals are sometimes lost due to the presence of thick cloud. Sweeps are set to the *a priori* value in these cases. Retrievals assuming LTE using MORSE and results from the new joint retrieval using LMRTV for a daytime scan is shown in figure 3. A T_v climatology is derived from the AMIL2DA non-LTE populations model. The T_v profiles look roughly as expected. The retrieval of CO appears to be improved using the new joint retrieval.

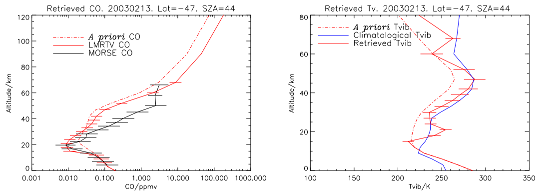

Figure 3. Retrieved profiles from orbit 10226 assuming LTE (MORSE) and non-LTE (joint retrieval, LMRTV) for a daytime scan.

Figure 4 shows coincident day and nighttime scans from 6th June 2003. We expect CO to look similar. T_v climatologies are derived from the AMIL2DA model. Day and nighttime retrievals using LMRTV are more similar than those derived using MORSE.

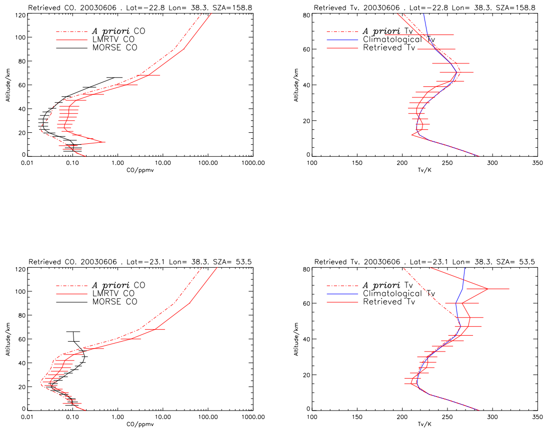

Figure 4. Retrieved profiles from coincident scans for day and nighttime assuming LTE (MORSE) and assuming non-LTE (joint retrieval, LMRTV).

Figure 5 shows orbit#06616 processed using MORSE assuming LTE and using the joint retrieval LMRTV. The joint retrieval removes the unrealistic enhancements in CO VMR.

5.3. Vibrational temperature of CO isotopologues

The non-LTE characteristics of the weak isotopic lines are not well understood but may affect the CO retrieval. CO isotopologues in the Earth's atmosphere in order of abundance are:

$$^{12}C^{16}O \quad ^{13}C^{16}O \quad ^{12}C^{18}O \qquad (4)$$

By averaging 1050 spectra from a single day, isotopic

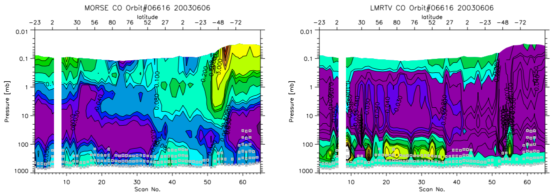

Figure 5. Orbit#06616 from 6th June 2003 processed using MORSE (CO only LTE) and LMRTV (joint CO, T_v, non-LTE). Colour scales are same in each plot. Silver boxes indicate a priori rather than retrieved values.

lines are become visible in both the day and nighttime spectra.

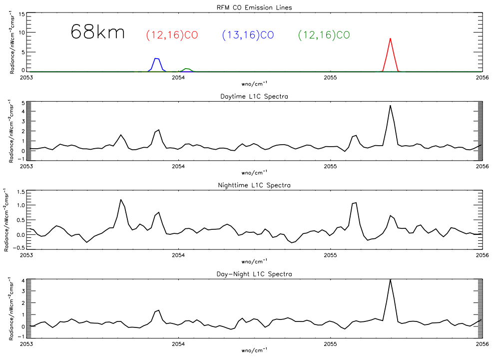

Figure 6. RFM simulated isotopic lines and averaged day and nighttime MIPAS spectra from 1st January 2003 at 68 km. Day-night difference is shown in bottom panel.

Figure 7 shows the observed radiances plotted against the RFM modelled LTE radiances in the spectral range 2060–2070 cm^{-1}. Contaminants have been removed. At 68 km the observed radiances are enhanced with respect to their LTE values due to non-LTE effects. The non-LTE enhancement differs between isotopologues. However, at 33 km, where we expect the non-LTE effects to be less pronounced, the observed radiances for each isotopologue are more similar and closer to the modelled LTE radiances.

If we assume that the atmosphere is optically thin then we may derive T_v profiles from equation 5;

$$\frac{R_{non-LTE}}{R_{LTE}} = \frac{\exp\left(\frac{h\nu}{kT_k}\right) - 1}{\exp\left(\frac{h\nu}{kT_v}\right) - 1} \tag{5}$$

Figure 8 shows the T_v profiles obtained. For the 1st and 3rd most abundant CO isotopologues, the daytime T_v derived using this method are quite close to

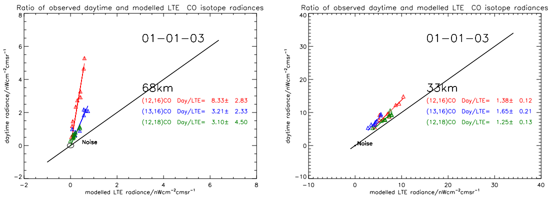

Figure 7. Observed daytime radiance plotted against modelled RFM radiance at 68 and 33 km in the spectral region 2050–2060 cm^{-1}.

the AMIL2DA T_v climatology. However, the 2nd most abundant isotopologue differs significantly at 60 km, which requires further investigation. The nighttime T_v are slightly different from the climatological T_v. These results suggest that the less abundant isotopologues may in general have slightly higher T_v.

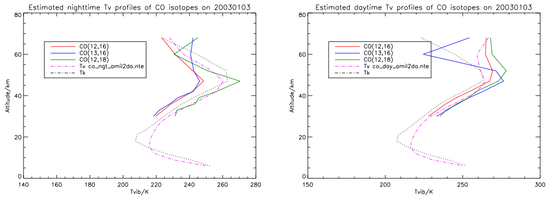

Figure 8. Day and nighttime vibrational temperature profiles derived for the CO isotopologues.

6. CONCLUSIONS AND FUTURE WORK

If we do not attempt to account for non-LTE, we retrieve unrealistically high values of CO in the daytime at high altitudes. However, we can perform a joint CO, T_v retrieval to account for these non-LTE effects. This does not significantly degrade retrieval precision below around 21 km and random errors of better than 25% are possible in the UTLS. The joint retrieval produces T_v that is reasonably consistent with expected values and the retrieval of CO appears to be improved. Investigations into the CO isotopologues suggest that they may have slightly different T_v and we have been able to make an estimate of their T_v profiles. Further validation work is required. MORSE is currently being configured to be able to perform a joint CO, T_v retrieval.

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