CO₂ LINE MIXING IN MIPAS LIMB EMISSION SPECTRA
AND ITS INFLUENCE ON RETRIEVAL OF ATMOSPHERIC
PARAMETERS

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Abstract—Aboard the European ENVISAT polar platform, the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) i.r. spectrometer will scan across the limb in order to record high resolution emission spectra. In the course of the definition of micro-windows for retrieval of line of sight, temperature and trace constituents, the spectral and altitudinal regions where CO₂ Q-branch line mixing has to be considered have been identified. Line-by-line modelling of spectra was performed taking account of line mixing and resulting spectra were compared to those calculated within purely Lorentzian pressure broadening. The accuracy of the Rosenkranz approximation was tested and found to be sufficient in most spectral regions. The impact of CO₂ Q-branch line mixing on the retrieval was compared to typical random errors due to spectral noise. Systematic errors due to the neglect of line mixing proves to play no important role for the temperature, pressure and trace constituents retrieval in spectral regions of more than 2 cm⁻¹ distance to CO₂ Q-branch centres. Apart from a few exceptions retrieval errors due to the neglect of line mixing are negligible for the spectral regions assigned for on-line processing of MIPAS measurements. © 1998 Elsevier Science Ltd. All rights reserved

1. INTRODUCTION

The MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) i.r. spectrometer will be part of the core payload for the European Polar Platform ENVISAT (Environmental Satellite) which is to be launched in 1999. High resolution (0.05 cm⁻¹, apodized) limb radiance spectra will be obtained covering several broadband spectral intervals between 685 and 2410 cm⁻¹. Data of MIPAS measurements will be used for the retrieval of several atmospheric quantities such as temperature and trace constituents. The significantly higher spectral resolution compared to previous instruments leads to an increased sensitivity of the retrieval to the spectral line shapes so that physical effects such as line mixing (also called collisional narrowing) will be detectable. Especially CO₂ Q-branch line mixing will affect radiance spectra in the spectral region covered because of the high CO₂ volume mixing ratio and narrow line spacing. The effect of CO₂ Q-branch line mixing in the v₂ fundamental band has already been reported by Strow et al. Line mixing was found to lower atmospheric brightness temperature by as much as 3 K. Another investigation on the impact of line mixing on the retrieval of CCl₄ volume mixing ratio in a spectral range around 790 cm⁻¹ including the 11101 → 10002 CO₂ Q-branch has shown that the neglect of line mixing maps into an error of volume mixing ratio in the order of 30-50%. In order to improve the retrieval of atmospheric quantities CO₂ Q-branch line mixing could be included in the forward model. This, however, leads to increased computational effort during data analysis. Alternatively, sets of spectral micro-windows can be defined where line mixing effects plays no significant role. This paper investigates the effect of line mixing on limb emission spectra in the altitude range which will be covered by MIPAS by comparing exact modelling of the line shape to calculations without consider-

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ation of line mixing. Furthermore the accuracy of the less time-consuming line mixing model in the Rosenkranz approximation is compared to the exact model. As neglect of line mixing leads to systematic radiance errors, related retrieval errors of target quantities were assessed.

2. THEORETICAL FORMULATION OF THE LINE SHAPE

Within the impact approximation, the absorption coefficient taking account of line mixing depends on the frequency-independent complex relaxation matrix \( \mathbf{W} \) introduced by Ben-Reuven. Its diagonal elements are related to pressure broadening, while non-diagonal elements are related to line mixing. \( \mathbf{W} \) is calculated using the EPGL (Exponential Power Gap Law) model introduced by Strow et al. It is assumed that the relaxation matrix elements have the same functional form as the rotational state-to-state cross sections within a single vibrational state \( \mathbf{K}_{j,k} \) which are modelled using an empirical energy-gap scaling law,

\[
\mathbf{K}_{j,k} = a_1 \left( \frac{\Delta E_{j,k}}{B_0} \right)^2 \exp \left( -a_3 \frac{\Delta E_{j,k}}{k_B T} \right)
\]

for \( j > k \). \( \Delta E_{j,k} = E_j - E_k \) is the energy gap between the rotational states \( j \) and \( k \), \( B_0 \) the rotational constant, \( k_B \) the Boltzmann constant and \( T \) the kinetic temperature. Detailed balance gives the rates for energetically downward transitions \( j < k \). The temperature dependent parameters \( a_1 \), \( a_2 \) and \( a_3 \) of this exponential power gap law are determined by a least squares fit to the following sum rule:

\[
\mathbf{W}_{ij} \approx -\frac{1}{2} \left[ \sum_{k\neq j} \beta(v_i,j,k)\mathbf{K}_{j,k} + \sum_{k\neq j} \beta(v_i,j,k)\mathbf{K}_{j,k} \right]
\]

where \( \mathbf{W}_{ij} \) is given by the Lorentzian half width. The sums are over all rotational states of the initial vibrational level denoted by \( v_i \) and the final vibrational level denoted by \( v_f \). \( \beta \) is a symmetry factor which takes into account the propensity differences between \( e_f \leftrightarrow e_f \) and \( e_f \leftrightarrow f_e \) state to state transitions and depends on the vibrational excitation and the angular momentum exchange of the involved states. The values of \( \beta \) were determined empirically by Strow et al. The non-diagonal elements of \( \mathbf{W} \) are given by \( \mathbf{W}_{j,k} = -\mathbf{K}_{j,k} \).

The absorption coefficients \( k(\nu) \) were calculated by using two different approaches. First, calculations were performed using a numerical diagonalization procedure (DND) which leads to the following expression for the absorption coefficient:

\[
k(\nu) = \frac{8\pi^2 \nu}{3\hbar c} \left[ 1 - \exp \left( -\frac{\hbar \nu}{k_B T} \right) \right] \frac{N_\nu}{\pi} \sum_i \frac{\mathrm{Im} \mathbf{A}_i \Re \mathbf{A}_i + \mathrm{Im} \mathbf{A}_i (\nu - \Re \mathbf{A}_i)}{(\nu - \Re \mathbf{A}_i)^2 + (\mathrm{Im} \mathbf{A}_i)^2}
\]

with

\[
\mathbf{\Omega}_i = \sum_j \mathbf{T}_{ij} \mathbf{T}_{kj}^{-1} \rho_k \partial_k
\]

Here \( \nu \) is the wavenumber, \( \hbar \) the Planck constant, \( c \) the velocity of light, \( N_\nu \) the number density of the absorbing gas, \( \rho_k \) the density of the initial state of the transition \( k \), \( d_i \) and \( d_j \) the dipole matrix elements of the transitions \( i \) and \( j \), respectively. The transformation matrix \( \mathbf{T} \) and the diagonal matrix of eigenvalues \( \mathbf{\Lambda} \) are determined by the relation

\[
\mathbf{\Lambda} = \mathbf{T}^{-1} \partial (\nu_0 \nu P \mathbf{W}) \mathbf{T}
\]

with the vector of line centre wavenumbers \( \nu_0 \) and the total pressure \( P \). Since \( \mathbf{T} \) and \( \mathbf{\Lambda} \) depend on the relaxation matrix \( \mathbf{W} \) which is temperature dependent and on the total pressure \( P \) the calculation of \( \mathbf{W} \) and the determination of \( \mathbf{T} \) and \( \mathbf{\Lambda} \) is necessary for each atmospheric layer. A polynomial temperature parameterization of the parameters \( a_1, a_2 \) and \( a_3 \) of Equation (1) is used.
for the implementation in the forward code, based on the precalculated parameters $\alpha_i, \beta_i, \gamma_i$ and $\delta_i$:

$$a_i(T) = \left( \frac{T_0}{T} \right)^{0.75} \left[ \alpha_i + \beta_i(T - T_0) + \gamma_i(T - T_0)^2 + \delta_i(T - T_0)^3 \right] \quad \text{for} \quad i = 1 \quad (6)$$

$$a_i + \beta_i(T - T_0) + \gamma_i(T - T_0)^2 + \delta_i(T - T_0)^3 \quad \text{for} \quad i = 2, 3$$

with $T_0 = 200$ K.

The Rosenkranz approximation\(^6\) (RK) which only considers first order line mixing errors requires less computational effort. Within this approximation $k(v)$ can be written as

$$k(v) = \frac{8\pi^3 v}{3hc} \left[ 1 - \exp \left( -\frac{hv}{k_BT} \right) \right] \frac{N_i}{\pi} \sum_i \rho_i d_i^2 \left( \frac{P_{\nu(i)}^L + (v - v_i)P_{\nu(i)}^R}{(v - v_i)^2 + (P_{\nu(i)}^L)^2} \right) \quad (7)$$

Here $v_i$ is the centre wavenumber of line $i$ and $\alpha_{Li}$ are the Lorentzian half widths. The first-order line mixing coefficients $Y_i$ are given by

$$Y_i = 2 \sum_{j \neq i} \frac{\mathbf{W}_{ij}}{v_i - v_j} \quad (8)$$

with the dipole matrix elements $d_i$ and $d_j$. The temperature dependences of $Y_i$ are parameterized similar to Equation (6) using the precalculated parameters $\alpha_i, \beta_i, \gamma_i$ and $\delta_i$ with $T_0 = 200$ K. The Rosenkranz approximation is only accurate for relatively low pressures. Errors of 2% in the absorption coefficients compared to calculations using the DND approach occur at Q-branch centres for pressures of 100 hPa and increase up to 12% at 500 hPa.

For the altitude range studied here both line shapes must be convolved with a Doppler shape in the line centre region ($\Delta v = 2$ cm\(^{-1}\)) to obtain

$$k(v) = \frac{8\pi^3 v}{3hc} \left[ 1 - \exp \left( -\frac{hv}{k_BT} \right) \right] \frac{N_i}{\pi} \sum_i \sqrt{\ln 2} S_i \left[ \text{Re} W(x_i,y_i) + \text{Im} W(x_i,y_i) \right] \quad (10)$$

$$S_i = \rho_i d_i^2, \quad x_i = \frac{v - v_i}{\sigma_D}, \quad y_i = \frac{\sigma_{Li}}{\sigma_D}, \quad \text{for RK}$$

$$S_i = -\text{Re} \Omega_{ii}, \quad x_i = \frac{v - \text{Re} \Lambda_{ii}}{\sigma_D}, \quad y_i = -\text{Im} \Lambda_{ii}, \quad \text{for DND}$$

where $\sigma_D$ is the Doppler half width and $W(x_i,y_i)$ is the complex probability function which can be resolved numerically by means of the Humlicek algorithm.\(^{11}\)

In order to satisfy detailed balance all Q-branch lines of a given band for which relaxation matrix elements have been calculated are used in the forward calculation even if some of them are located outside the microwindow under consideration. Farther away than 10 cm\(^{-1}\) from all Q-branch lines line mixing is disregarded because of the dominating influence of far wing effects caused by the finite duration of collisions. An empirical $\chi$-factor as introduced by Le Doucen et al., Cousin et al., and Menoux et al.\(^{14}\) is used instead for all CO\(_2\) lines in order to consider the sub-Lorentzian behaviour of the line wings.

### 3. SIMULATED MIPAS/ENVISAT SPECTRA

Line mixing parameters were determined for seven prominent CO\(_2\) Q-branches (see Table 1) within the spectral regions of the MIPAS detector channels. LTE (Local Thermodynamical Equilibrium) spectra were simulated for a non-scattering atmosphere for geometries as expected to be recorded by MIPAS/ENVISAT by using the SCAIS (Simulation Code for Atmospheric
Table 1. Altitude range of spectral radiance errors due to the neglection of line mixing dominating the NESR in the spectral regions around Q-branches

<table>
<thead>
<tr>
<th>Spectral region (cm⁻¹)</th>
<th>Transition</th>
<th>Interfering trace constituents</th>
<th>ΔZ₂₁₆₆ₑₛₑ (km)</th>
<th>Z₂₁₆₆ₑ (km)</th>
<th>ΔZ₂₁₆₆ₑ (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>719-724</td>
<td>10001 ← 01101</td>
<td>H₂O, O₃, N₂O, NO₂, HCN, C₂H₂, N₂O₅</td>
<td>6-50</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>740-745</td>
<td>11101 ← 02201</td>
<td>H₂O, O₃, HNO₃, NO₂, HCN, C₂H₂, N₂O₅</td>
<td>6-35</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>789-794</td>
<td>11101 ← 10002</td>
<td>H₂O, O₃, HNO₃, C₂H₂, C₂H₅, CCl₄</td>
<td>6-30</td>
<td>6</td>
<td>6-15</td>
</tr>
<tr>
<td>1923-1935</td>
<td>11102 ← 00001</td>
<td>H₂O, O₃, NO, COF₂</td>
<td>6-20</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>2074-2079</td>
<td>11101 ← 00001</td>
<td>H₂O, O₃, CH₄, OCS, CO</td>
<td>6-10</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>2090-2095</td>
<td>12201 ← 01101</td>
<td>H₂O, O₃, CH₄, OCS, CO</td>
<td>6-10</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>2127-2132</td>
<td>20001 ← 01101</td>
<td>H₂O, O₃, NO₂, CH₄, OCS, CO</td>
<td>6-10</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

1Altitude range where errors due to the neglection of line mixing exceed NESR.
2Altitude of maximum of errors due to the neglection of line mixing.
3Altitude range where the error due to Rosenkranz approximation < NESR.

Infrared Spectra) line-by-line algorithm modified for line mixing calculations. An infinitesimal field of view (FOV) of the instrument was assumed. High resolution spectra were apodized to a final spectral resolution of 0.05 cm⁻¹. Calculations were performed for spectral ranges covering the CO₂ Q-branches listed in Table 1 for tangent altitudes from 6 to 65 km. In order to consider nonlinear effects in the radiative transfer, relevant interfering species were taken into account. For the atmospheric model of pressure and temperature the US Standard atmosphere was used. The volume mixing ratio (vmr) vertical profiles of trace gases used were typical for mid-latitudes and reflect the accumulation of anthropogenic trace constituents in the atmosphere as observed in 1991. Geometry and refraction effects were included using a ray tracing algorithm, and Curtis–Godson mean values for pressure, temperature and volume mixing ratios were calculated within each layer of a 44-layer model. Line parameters were taken from the 1992 HITRAN database. Three different radiance spectra have been calculated for each spectral interval and tangent altitude for reason of intercomparison: first, line mixing was considered as DND approach; second, line mixing was considered within the Rosenkranz approximation; and third, calculations were performed based on a simple Voigt line shape.

4. SPECTRAL LINE MIXING ERRORS IN Q-BRANCH REGIONS

The results of the radiance calculations for the spectral bands under investigation are summarized in Table 1. The spectral errors due to incorrect line shape modelling were compared to the spectral random errors due to the instrumental noise level (NESR—Noise Equivalent Spectral Radiance, see Table 2). Figures 1, 2 and 3 show spectral regions and magnitudes of spectral radiance errors due to the neglection of CO₂ Q-branch line mixing (line mixing errors) for the bands 10001 ← 01101, 11101 ← 02201 and 20001 ← 01101 which serve as instructive examples.

Due to its dependence on pressure, one would expect the errors due to the neglection of line mixing to decrease with increasing tangent height. This expected behaviour can be observed for all transitions except the first two in Table 1. For the bands 10001 ← 01101 (719-724 cm⁻¹) and 11101 ← 02201 (740-745 cm⁻¹), the radiance errors show a maximum close to 30 and 20 km altitude, respectively. The reason for this behaviour is the atmosphere being optically thick for low tangent altitudes around the Q-branch centre, moving the atmospheric layers which contribute mainly to the spectral signal to higher altitudes than the tangent height. The line mixing effect competes with saturation effects in the spectra, leading to the observed maximum in the errors for stratospheric tangent altitudes.

Apart from the immediate vicinity of the Q-branch centre the radiance in the spectra calculated under consideration of line mixing is decreased for tangent heights above the tropopause.

Table 2. Guaranteed NESR for MIPAS/ENVISAT

<table>
<thead>
<tr>
<th>Wavenumber range (cm⁻¹)</th>
<th>685-970</th>
<th>1020-1170</th>
<th>1215-1500</th>
<th>1570-1750</th>
<th>1820-2410</th>
</tr>
</thead>
<tbody>
<tr>
<td>NESR (non-apodized) [nW/(cm² sr cm⁻¹)]</td>
<td>50</td>
<td>40</td>
<td>20</td>
<td>6</td>
<td>4.2</td>
</tr>
<tr>
<td>NESR (apodized) [nW/(cm² sr cm⁻¹)]</td>
<td>35</td>
<td>28</td>
<td>14</td>
<td>4.2</td>
<td>2.94</td>
</tr>
</tbody>
</table>
Fig. 1. Line mixing effects for the transition 10001 - 01101. The left panel shows the radiance and the radiance difference ($L_{\text{without line mixing}} - L_{\text{with line mixing}}$) for tangent altitudes 8, 17 and 35 km. The other panels show the maximum difference in radiance for tangent altitudes between 6 and 60 km (middle) and for each tangent height the spectral region where the line mixing error exceeds the NESR of the apodized spectra and the spectral location of the maximum line mixing error (diamond) (right).

Radiance unit [r.u.] is defined as [W/(cm²sr cm⁻¹)].
Fig. 2. Line mixing effects for the transition 11101 \rightarrow 02201. The left panel shows the radiances and the radiance difference ($L_{\text{without line mixing}} - L_{\text{with line mixing (DNDP)}}$) for tangent altitudes 6, 14, and 23 km. The other panels show the maximum difference in radiance for tangent altitudes between 6 and 60 km (middle) and for each tangent height the spectral region where the line mixing error exceeds the NESR of the apodized spectra and the spectral location of the maximum line mixing error (diamond) (right). Radiance unit [r.u.] is defined as [W/(cm²sr cm⁻¹)].
Fig. 3. Line mixing effects for the transition 20001—01101. The left panel shows the radiance and the radiance difference \((L_{\text{without line mixing}} - L_{\text{with line mixing}})\) for tangent altitudes 6, 8 and 14 km. The other panels show the maximum difference in radiance for tangent altitudes between 6 and 60 km (middle) and for each tangent height the spectral region where the line mixing error exceeds the NESR of the apodized spectra and the spectral location of the maximum line mixing error (diamond) (right).

Radiance unit [r.u.] is defined as \(\text{W/(cm}^2\text{sr cm}^{-1})\)
and increased for lower heights, compared to spectra calculated without considering line mixing (see Fig. 1). This is caused by the spectra being optically thick for tangent heights near the tropopause. The reduction of the absorption coefficients due to line mixing moves the altitude of the maximum of the contribution function downwards, i.e., to warmer regions for tangent heights below the tropopause, and to colder regions above the tropopause.

The other spectral bands all behave similar showing the line mixing error monotonously decreasing with increasing altitude, due to the lower intensities of these bands. As in these cases radiance contributions originating from low altitudes reach the instrument, the errors due to the Rosenkranz approximation become comparable to the NESR in one particular case. This only affects a narrow region around the Q-branch centre since the asymptotic behaviour \((v - v_{Q\text{-branch}} > 0)\) is the same for the RK and the DND line shapes. Errors of the Rosenkranz approximation exceed NESR only in the centre region of the 11101 \(\leftrightarrow\) 10002 Q-branch for tangent altitudes below 15 km (errors of 1.4 \(\times\) NESR for 8 km tangent height).

5. ESTIMATION OF THE P/T- AND VMR-RETRIEVAL ERRORS

The assessment of systematic errors and random errors due to the instrumental noise level (NESR) was performed for a retrieval scenario where an instrumental offset and a continuum contribution in the absorption coefficients due to aerosols, clouds, etc. had to be determined simultaneously with the target parameter. Spectral line mixing errors were calculated by using the RK line mixing model since its accuracy was found to be sufficient for the spectral ranges under investigation. The retrieval error due to the neglection of line mixing was estimated linearly using a formalism as proposed by Clarmann et al.19:

\[
\Delta_{\text{sys}} = (A^T A)^{-1} A^T (L_{\text{without line mixing}} - L_{\text{line mixing (RK)}})
\]  

where \(A\) is the Jacobian matrix, containing the partial derivatives of the measured spectral radiances \(L_m (m = 1, \ldots, \text{max number of spectral measurements})\) with respect to the atmospheric state parameters \(P_n (n = 1, \ldots, \text{max number of parameters})\), i.e., pressure or temperature or vmr and offset and continuum, \(A^T\) is transposed, \(L_{\text{line mixing (RK)}}\) is the vector of spectral radiances under consideration of line mixing, \(L_{\text{without line mixing}}\) the vector of spectral radiances under neglection of line mixing, and \(\Delta_{\text{sys}}\) the resulting \(\text{max dimensional vector of retrieval errors of the atmospheric state parameters. The relevance of this error can be compared to the random error represented by the square root of the diagonal elements of the retrieval covariance matrix}

\[
S_x = (A^T A)^{-1} A^T \Sigma A (A^T A)^{-1}
\]  

The microwindows under investigation were chosen from the microwindow data base for pressure-temperature and 5 key species retrievals (O\(_3\), H\(_2\)O, CH\(_4\), HNO\(_3\), N\(_2\)O) as proposed for the MIPAS/ENVISAT on-line processing.20 Since line mixing is only calculated in a spectral range of 10 cm\(^{-1}\) around the CO\(_2\) Q-branches, only microwindows inside of this area were considered for this analysis.

6. RETRIEVAL ERRORS DUE TO THE NEGLCTION OF LINE MIXING

Retrieval errors due to the neglection of line mixing were estimated for sixty microwindows defined for pressure, temperature and vmr retrieval. Since microwindows for CH\(_4\), HNO\(_3\), and N\(_2\)O retrievals are not located in regions where CO\(_2\) Q-branch line mixing is relevant, only H\(_2\)O and O\(_3\) microwindows were considered for the vmr retrieval error analysis. All calculated retrieval errors are the results of a simultaneous 3-parameter retrieval (pressure or temperature or vmr, offset, continuum). In general, the retrieval error due to line mixing was found to be very low for the microwindows proposed for on-line processing.

Microwindows for pressure and temperature retrieval were investigated in the vicinity of the Q-branches located at 720 cm\(^{-1}\), 740 cm\(^{-1}\), 791 cm\(^{-1}\) and 1932 cm\(^{-1}\). Except for four microwindows at 733–742 cm\(^{-1}\), O-branch lines are not located within these microwindows. Only one of
Table 3. Table of P/T-microwindows where the temperature retrieval error due to line mixing $\Delta T_{\text{lm}}$ exceeds 5% of the temperature retrieval error due to noise $\Delta T_{\text{noise}}$. 'Prior.' means the position in the priority list of best microwindows in Ref. 20

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Microwindow</th>
<th>Frequency range (cm$^{-1}$)</th>
<th>$\Delta T_{\text{lm}}$ (K)</th>
<th>Relative to $\Delta T_{\text{noise}}$ (%)</th>
<th>Prior.</th>
</tr>
</thead>
<tbody>
<tr>
<td>08</td>
<td>PT 40A</td>
<td>795.000–795.550</td>
<td>-0.055</td>
<td>5.910</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>PT 40A</td>
<td>795.000–795.550</td>
<td>-0.099</td>
<td>5.331</td>
<td>4</td>
</tr>
<tr>
<td>23</td>
<td>PT 25A</td>
<td>711.175–715.375</td>
<td>0.174</td>
<td>21.520</td>
<td>1</td>
</tr>
<tr>
<td>26</td>
<td>PT 32A</td>
<td>751.000–751.175</td>
<td>0.326</td>
<td>9.055</td>
<td>9</td>
</tr>
<tr>
<td>47</td>
<td>PT 29A</td>
<td>740.725–740.850</td>
<td>-0.111</td>
<td>7.589</td>
<td>7</td>
</tr>
</tbody>
</table>

these four microwindows includes the Q-branch centre at 741.7 cm$^{-1}$ and is therefore strongly affected by line mixing. For all other microwindows the influence of line mixing is very low and retrieval errors due to line mixing are less than a fifth of the retrieval error due to noise. The maximum retrieval error due to line mixing is 0.33 K for temperature and 1.1% for the pressure retrieval. For altitudes higher than 47 km retrieval errors are less than 0.1 K or 0.1% of pressure.

The influence of line mixing on the water vapour retrieval was tested for six microwindows in the region around the Q-branch located at 1932 cm$^{-1}$. Due to a sufficient large distance to the Q-branch centre deviations in the retrieved H$_2$O vmr are less than 0.1% of the vmr and less than 1% of the noise-induced retrieval error for all tangent altitudes. O$_3$ vmr retrievals were investigated in the vicinity of the Q-branches at 720 cm$^{-1}$, 740 cm$^{-1}$, 791 cm$^{-1}$, 2080 cm$^{-1}$, 2093 cm$^{-1}$, and 2129 cm$^{-1}$. Retrieval errors due to the neglection of line mixing of more than a tenth of the noise-induced retrieval error occur only in microwindows around the 720 cm$^{-1}$ Q-branch for altitudes between 20–38 km. Maximum retrieval errors due to the neglect of line mixing of 13.2% O$_3$ vmr are found in a microwindow at 722.0–722.125 cm$^{-1}$ which is located 1.3 cm$^{-1}$ apart from the Q-branch centre.

Tables 3, 4 and 5 show a compilation of microwindows where retrieval errors due to the neglect of line mixing exceed 5% (for P/T) and 10% (for O$_3$ vmr) of the noise-induced error.

7. DISCUSSION OF SPECTRAL AND RETRIEVAL ERRORS FOR SAMPLE MICROWINDOWS

7.1. P/T-microwindow at 741.45–741.75 cm$^{-1}$

Figure 4 shows the P/T microwindow (741.45–741.75 cm$^{-1}$) which contains the centre of the 11101 $\rightarrow$ 02201 Q-branch. The whole spectrum is highly saturated up to 17 km resulting in small radiance errors due to the neglection of line mixing. Above 17 km the optical path becomes transparent for the immediate vicinity of the Q-branch centre at 741.70–741.75 cm$^{-1}$ and radiance is strongly overestimated by neglection of line mixing, due to a lower absorption coefficient. Maximum radiance errors appear at 23 km. The averaged radiance differences are approximately 1% of the radiance signal averaged over the microwindow at this tangent height. For higher altitudes the errors become lower due to the pressure dependence of line mixing. Above 45 km radiances are slightly underestimated at the Q-line centres with low angular momentum values. Below 20 km no retrieval error due to noise could be assessed as the spectra are no longer sensitive to the retrieval parameters, i.e., all retrieval errors become infinite. Above 20 km the neglection of line mixing leads to an underestimation of pressure and temperature of 4 K and 12% pressure (at 32 km) at maximum. For altitudes above 32 km errors are directly compensated by overestimation of pressure and temperature. Between 20 km and 32 km

Table 4. Same as Table 3, but for the pressure retrieval error due to line mixing $\Delta P_{\text{lm}}$.

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Microwindow</th>
<th>Frequency range (cm$^{-1}$)</th>
<th>$\Delta P_{\text{lm}}$ (%)</th>
<th>Relative to $\Delta P_{\text{noise}}$ (%)</th>
<th>Prior.</th>
</tr>
</thead>
<tbody>
<tr>
<td>08</td>
<td>PT 40A</td>
<td>795.000–795.550</td>
<td>-0.170</td>
<td>6.883</td>
<td>12</td>
</tr>
<tr>
<td>23</td>
<td>PT 25A</td>
<td>711.175–715.375</td>
<td>1.103</td>
<td>22.423</td>
<td>1</td>
</tr>
<tr>
<td>26</td>
<td>PT 32A</td>
<td>751.000–751.175</td>
<td>-0.212</td>
<td>7.035</td>
<td>4</td>
</tr>
<tr>
<td>47</td>
<td>PT 29A</td>
<td>740.725–740.850</td>
<td>-0.167</td>
<td>6.334</td>
<td>9</td>
</tr>
</tbody>
</table>
the background radiation, which is an additional retrieval parameter, is responsible for compensation, and pressure and temperature errors are caused mainly by the anticorrelation of the retrieval parameters. Here, spectral errors due to the neglect of line mixing are better compensated by a change of the background radiation than a pressure or temperature change. The maximum of the retrieval error is located at the altitude region with the lowest correlation between spectral errors due to the neglect of line mixing and spectral derivatives with respect to pressure and temperature (see Fig. 6(a)). Only at the tangent height of 20 km spectral correlations between radiance errors due to the neglect of line mixing and derivatives with respect to pressure and temperature are strong enough to lead to an overestimation of pressure by 30% and temperature by 1 K.

7.2. \( O_3 \) microwindow at 722.0–722.125 cm\(^{-1}\)

The \( O_3 \) microwindow at 722.0–722.125 cm\(^{-1}\) (Fig. 5(a)) contains only one \( O_3 \) line and is affected by \( CO_2 \) Q-branch line mixing of the 10001 ← 01101 band. The radiance in the line wings is underestimated due to the neglect of line mixing (2% of the mean radiance signal) for the 8 km tangent height, because the region where the bulk of the signal originates from is shifted upwards to colder regions. For higher tangent altitudes the neglect of line mixing leads to an overestimation of the radiance signal. Strongest spectral deviations (8% of the mean radiance signal) are found around 20 km altitude still located in the line wings. An increased \( O_3 \)-vmr increases radiance slightly for lower tangent heights, becoming more relevant with altitude. Due to the very low sensitivity below 20 km all retrieval errors are amplified drastically resulting in line mixing and noise errors up to 200%. All spectral derivatives with respect to the fitted parameters are highly correlated to the line mixing residuals above 15 km (see Fig. 6(b)). Since line mixing/vmr correlation is slightly lower than the other correlations above 20 km the \( O_3 \) vmr plays the role of a corrective factor similar to the \( P/T \)-microwindow. For high tangent heights (above 50 km) the radiance signal becomes comparable to the NESR leading to very high noise-induced retrieval errors.

7.3. \( O_3 \) microwindow at 2130.0–2131.5 cm\(^{-1}\)

The \( O_3 \) microwindow in Fig. 5(b) is located at 2130.0–2131.5 cm\(^{-1}\) and contains several strong \( O_3 \) lines. The neglect of the 20001 ← 01101 Q-branch line mixing leads to an overestimation of radiance for low tangent heights (0.8% of the mean radiance signal at 8 km tangent height) monotonously becoming lower with higher altitudes. Radiance is overestimated by changing \( O_3 \) vmr to higher values but not as strong as for the first \( O_3 \) microwindow (due to a higher degree of saturation). Since the radiance signal is only a few times stronger than NESR for all altitudes, noise-induced retrieval errors are very high and fall below 30% only at 45 km altitude. The radiance differences due to the neglect of line mixing and the derivatives with respect to \( O_3 \)-vmr are strongly correlated, leading to a similar correlation between retrieval errors and radiance errors (see Fig. 6(c)). The maximum retrieval error due to the neglect of line mixing

Table 5. Table of \( O_3 \) microwindows where the \( O_3 \)-vmr retrieval error due to line mixing \( \Delta \text{vmr}_{\text{lm}} \) exceeds 10% of the retrieval error due to noise \( \Delta \text{vmr}_{\text{noise}} \). "Prior." means the position in the priority list of best microwindows in Ref. 20.

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Microwindow</th>
<th>Frequency range (cm(^{-1}))</th>
<th>( \Delta \text{vmr}_{\text{lm}} ) (%)</th>
<th>( \Delta \text{vmr}_{\text{noise}} ) (%)</th>
<th>Prior</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>O3 7A</td>
<td>724.250–724.450</td>
<td>4.078</td>
<td>16.907</td>
<td>28</td>
</tr>
<tr>
<td>23</td>
<td>O3 6A</td>
<td>722.675–722.900</td>
<td>5.174</td>
<td>27.802</td>
<td>2</td>
</tr>
<tr>
<td>29</td>
<td>O3 5A</td>
<td>722.000–722.125</td>
<td>–13.200</td>
<td>43.053</td>
<td>38</td>
</tr>
<tr>
<td>32</td>
<td>O3 7A</td>
<td>724.250–724.450</td>
<td>3.040</td>
<td>15.455</td>
<td>19</td>
</tr>
<tr>
<td>38</td>
<td>O3 6A</td>
<td>722.675–722.900</td>
<td>–1.529</td>
<td>12.030</td>
<td>7</td>
</tr>
</tbody>
</table>
Fig. 4. Results of the retrieval error calculation for a P/T-microwindow. The left panel shows the radiance spectra for tangent heights 8, 20, 35 and 50 km. The right panels show the altitude dependence of errors due to the neglect of line mixing: Arithmetic mean value of spectral radiance difference due to the neglect of line mixing \((E_{\text{without line mixing}} - E_{\text{with line mixing}})\) (solid) and arithmetic mean radiance deviations due to an increased temperature of 5 K (dotted) and due to an increased pressure of 10% (dashed) relative to the arithmetic mean radiance of the spectrum at the left; errors in the temperature retrieval due to the neglect of line mixing (solid) and noise (dotted) in the middle; errors in the pressure retrieval due to the neglect of line mixing (solid) and noise (dotted). Tangent heights are indicated by diamonds at the right. Radiance unit [r.u.] is defined as \([W/(cm^2sr cm^{-1})]\).
Altitude dependence of errors due to the neglect of line mixing

Fig. 5(a)—caption opposite.
Fig. 5. Results of the retrieval error calculation for two O₃-microwindows at 722.0–722.125 cm⁻¹ (a) and 2130.0–2131.5 cm⁻¹ (b). The left panels show the radiance spectra for tangent heights 8, 20, 35, and 50 km. The other panels show the altitude dependence of errors due to the neglection of line mixing: arithmetic mean value of the radiance difference due to the neglection of line mixing (\(L_{\text{without line mixing}} - L_{\text{with line mixing}}\)) (solid) and arithmetic mean radiance deviations due to an increased vmr of 0.1% (2130.0–2131.5 cm⁻¹) and 10% (722.0–722.125 cm⁻¹), respectively (dotted), relative to the arithmetic mean radiance of the spectrum in the middle; vmr retrieval errors due to the neglection of line mixing (solid) and noise (dotted) at the right. Tangent heights are indicated by diamonds. Radiance unit [r.u.] is defined as [W/(cm² sr cm⁻¹)].
Fig. 6. Correlation coefficients between radiance differences due to the neglect of line mixing and partial spectral derivatives with respect to offset [Im,Off], continuum [Im,Con], pressure [Im,P] and temperature [Im,T] for the P/T-microwindow of Fig. 4-(a) and vmr [Im,vmr] for the O₃-microwindows of Fig. 5(a)-(b) and 5(b)-(c). Tangent heights are indicated by diamonds.
at 8 km tangent height is about 30% of vmr but still 5 times smaller than the noise-induced retrieval error.

8. DISCUSSION AND CONCLUSIONS

Within the presented investigation, the effect of CO$_2$ Q-branch line mixing on MIPAS/ENVISAT limb emission spectra was studied. Two different approaches to model CO$_2$ Q-branch line mixing were used, the numerical diagonalization approach (DND) and the Rosenkranz approximation (RK). Line mixing effects in CO$_2$ Q-branches were found to be visible in atmospheric limb emission spectra for altitudes from 6 to 60 km. Deviations between spectra calculated with and without consideration of line mixing are strongest in a close area around the Q-branch centres (~2 cm$^{-1}$). The nonlinearity of radiative transfer destroys the straight pressure dependence of radiance errors due to the neglect of line mixing which is existent for the absorption coefficients. Therefore line mixing effects in atmospheric limb spectra are not restricted to low altitudes and not necessarily decreasing with increasing altitude. The neglect of line mixing leads not necessarily to an overestimation of radiance in the vicinity of Q-branches but could even manifest in an opposite behaviour. The Rosenkranz approximation is sufficiently accurate in all cases except for the Q-branch centre region of the 11101 $\rightarrow$ 10002 band for altitudes below 15 km.

Retrieval errors were estimated for the current selection of microwindows for pressure-temperature and 5 key species retrievals (O$_3$, H$_2$O, CH$_4$, HNO$_3$, N$_2$O) of the MIPAS/ENVISAT on-line processor. A similar assessment will be applied in future to the selection of microwindows for further 23 trace constituents. In general the influence of line mixing on pressure, temperature and vmr retrievals is weak (for pressure, temperature, O$_3$ and H$_2$O) or not significant (for CH$_4$, HNO$_3$ and N$_2$O) for the microwindows investigated in this study. If there is a need of using microwindows including CO$_2$ Q-branches or being located at their immediate vicinity, it is recommended to integrate line mixing routines in the forward calculation. The behaviour of retrieval errors due to the neglect of line mixing depend on the nonlinearity of radiative transfer, visible in the radiance differences, and on the correlations between the partial derivatives with respect to the simultaneously fitted retrieval parameters and the radiance differences due to the neglect of line mixing. Therefore no general conclusions on the altitude dependence being valid for all microwindows under investigation can be drawn; each microwindow must be investigated in detail. In principle, these retrieval errors disappear in a sufficiently great distance to the Q-branch, but there are some exceptions.

Keeping in mind that nonlinearity of radiative transfer could lead to an amplification of line mixing errors, it might be possible that even P- and R-branch coupling—which has been disregarded up to now—could be significant in some microwindows. P- and R-branch line mixing is difficult to model due to the necessity of including far wing effects caused by the finite duration of molecular collisions. This has not yet been investigated but remains an interesting topic for future research.

REFERENCES


