Influence of line mixing on the retrievals of atmospheric CO$_2$ from spectra in the 1.6 and 2.1 µm regions

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Abstract

We present the first study of the influence of line mixing among CO$_2$ lines on the remote sensing retrieval of atmospheric carbon dioxide. This is done in the bands near 1.6 and 2.1 µm which have been retained by the Orbiting Carbon Observatory (OCO) and Greenhouse Gases Observatory Satellite (GOSAT) instruments. A purely theoretical analysis is first made, based on simulations of atmospheric spectra. It shows that line mixing cannot be neglected since disregarding this process induces significant errors in the calculated absorption coefficients, leading to systematic structures in the spectral fit residuals and airmass-dependent biases in the retrieved CO$_2$ amounts. These theoretical predictions are then confirmed by using atmospheric solar-absorption spectra measured by a ground-based Fourier transform spectrometer. Indeed, it is first shown that including line mixing in the forward model used for the inversion leads to a very significant reduction of the residuals in the 2.1 µm region. Secondly, the inclusion of line mixing reduces the dependence of the retrieved CO$_2$ on the airmass and greatly improves the consistency between values obtained independently from spectra in the 1.6 and 2.1 µm bands. These results open very promising prospects for various ground-based and space-borne experiments monitoring the carbon dioxide atmospheric amounts.

1 Introduction

Within the framework of Carbon Cycle science by Fourier Transform Spectroscopy (CC-FTS; Fu et al., 2008) and of the Total Carbon Column Observatory Network (TCCON; Wennberg et al., 2005), various instruments aim at accurately monitoring the carbon dioxide atmospheric amount. Among space-borne projects, the Orbiting Carbon Observatory (OCO; Crisp et al., 2004) and the Greenhouse Gases Observatory Satellite (GOSAT; Kuze et al., 2005) plan to use the CO$_2$ rovibrational transitions in the 2.06 µm and 1.61 µm (or, alternatively 1.57 µm) regions while the surface pressure and photon
path information will be obtained from the oxygen A-band near 760 nm. The objective is to identify the regional sources and sinks of CO$_2$ with a precision better than 1% (the aim is 0.3%). This puts very severe constraints on the quality of the spectroscopic data and forward spectral models used for both CO$_2$ and O$_2$, as discussed in Miller et al. 2005, for instance.

Concerning the O$_2$ A-band, recent laboratory studies show that calculating the absorption coefficient assuming that the lines are collisionally isolated leads to significant errors (Tran et al., 2006; Predoi-Cross et al., 2008). Indeed, both collisional line mixing (LM) and a Collision Induced Absorption contribution (CIA) (Hartmann et al., 2008) affect this region. Furthermore, it was demonstrated (Tran and Hartmann, 2008) that accounting for both processes is unavoidable if one wants to match the desired accuracy on retrievals of pressure from atmospheric spectra.

For CO$_2$, extensive laboratory experimental and theoretical studies have been devoted to LM effects. Numerous direct comparisons between measured and calculated atmospheric spectra have also been made in several spectral regions, as well as studies of the influence of LM on pressure, temperature and trace species retrievals as reviewed in Sects. IV.5 and VII.4 of Hartmann et al. (2008). For the $3^01^2_2-0^00^0$ (1.57 µm) and $3^01^3_2-0^00^0$ bands (1.61 µm) of $^{12}$C$^{16}$O$_2$, multispectrum fits of laboratory spectra have enabled the experimental determination of LM parameters at room temperature (Malathy Devi et al., 2007a, b; Predoi-Cross et al., 2007). Theoretical data are also available that can predict LM for any band of any isotopologue of CO$_2$ at any temperature (Niro et al., 2005c).

Some results are available concerning CIA (Chapt. VI of Hartmann et al., 2008), but the question of an eventual contribution of CO$_2$ CIA underlying the rovibrational transitions, as in O$_2$ (Tran et al., 2006), in the regions retained for the CO$_2$ monitoring remains open. Furthermore, the consequences of LM on the carbon dioxide amounts retrieved from atmospheric spectra have not been investigated yet. This paper presents the first study of this last problem.

For this investigation, atmospheric transmission spectra are first calculated in both
the 2.06 µm and 1.61 µm bands, taking line mixing into account. This is done using the data and software of Niro et al. (2005c) which have been widely and successfully tested in other spectral regions. These (theoretical) transmission spectra, simulated for various observation zenith angles and spectral resolutions, are then fitted, in order to retrieve the CO₂ volume mixing ratio (vmr) xCO₂, using a model disregarding LM. It is shown that the subsequent errors on xCO₂ cannot be neglected if a precision better than 0.5% is needed. Disregarding LM also induces systematic residuals in the spectral fits and an airmass-dependent bias in the retrieved xCO₂.

In a second step, these theoretical results are unambiguously confirmed using ground-based atmospheric solar-absorption spectra recorded with a Fourier Transform Spectrometer (FTS) in Park Falls, Wisconsin. Indeed, fitting these spectra neglecting LM leads to residuals that are very similar to those predicted theoretically, and including LM in the forward model greatly improves the agreement between measured and fitted transmissions. Furthermore, taking LM into account leads to more precise values of the retrieved CO₂ atmospheric amount with less airmass dependence, and to a much better consistency between the CO₂ vmrs obtained in the 1.6 and 2.1 µm regions.

The remainder of this paper is divided into four sections. The theoretical approaches used to calculate atmospheric transmissions and to retrieve the CO₂ vmr are described in Sect. 2. These tools are then used for calculations and inversions of simulated atmospheric spectra in Sect. 3, where the influence of LM is studied for various airmasses and spectral resolutions. This demonstrates that LM has a significant influence, particularly in the 2.1 µm region, on both the retrieved CO₂ amount and the fit residuals. These predictions are confirmed, in Sect. 4, by treating atmospheric transmissions measured by a ground-based FTS. Concluding remarks and a discussion of future studies are made in Sect. 5.
2 Theoretical approach

2.1 Transmission spectra and fitting procedure

A series of atmospheric transmission spectra in the 1.6 and 2.1 \( \mu m \) spectral regions has been simulated, for various zenith angles (i.e. airmass values), based on a reference spectral-line-shape model (see Sect. 2.2) for the absorption coefficient \( \alpha^R \). A standard (mid-latitude spring) atmosphere was used, and the high resolution atmospheric transmissions have been computed from 0 up to 45 km using a step of 1 km. The \( \text{CO}_2 \) vmr was assumed independent of altitude and set to the nominal value of 380 ppm. These transmissions have been convolved by a \( \sin(2\pi \text{MOPD} \sigma)/(\pi \sigma) \) function in order to simulate the response of a FTS with Maximum Optical Path Differences (MOPD) of 2, 10 and 50 cm (spectral resolutions of 0.25, 0.05 and 0.01 cm\(^{-1}\), respectively). The resulting “experimental” transmissions \( \tau^E \) (simulating measured values) have then been fitted using an approximate \( \alpha^A \) spectral-shape model that neglects LM effects, leading to approximate transmissions \( \tau^A \). These fits were carried through a mean-square procedure, minimizing the quantity

\[
\frac{1}{N_p} \sum_{p=1}^{N_p} \left[ \tau^A(\sigma_p, x\text{CO}_2) - \tau^E(\sigma_p, 380 \text{ ppm}) \times (A\sigma_p + B) \right]^2,
\]

where \( \sigma_p \) denotes the wavenumber of the \( p \)th point in both the “experimental” and “approximate” spectra. In these fits, \( x\text{CO}_2 \) is adjusted together with a linear correction of the 100% transmission level described by the \( A \) and \( B \) parameters. The introduction of this correction is (generally) unavoidable when measured spectra are treated, since it enables eventual errors in the calibration (the solar extraterrestrial spectrum, the optics, the detector response, etc.) to be accounted for.

Finally, the spectral regions used here, which correspond to those retained for the OCO project, are “Band#1”, from 4765 to 4915 cm\(^{-1}\), and “Band#2”, from 6160 to...
6270 cm$^{-1}$. Also note that only absorption by CO$_2$ was included in the calculations whose results are presented in Sect. 3 (no other molecular species, no solar lines, etc.).

2.2 Absorption coefficients

The reference spectral-line-shape used to compute $\alpha^R$ accounts for line-mixing processes between CO$_2$ transitions using the database and software of Niro et al. (2005c) where all needed equations can be found. These tools, and the model used to generate the line-mixing data in various CO$_2$ bands, have been extensively and successfully tested. This has been made using laboratory and atmospheric spectra, in a number of spectral regions (among numerous other references, see Rodrigues et al., 1999; Jucks et al., 1999; Niro et al., 2004, 2005a, b). These include various $Q$ branches as well as some $P$ and $R$ branches regions but not the bands (20$^0_0 1_3$←00$^0_0$ and 30$^0_1 3_3$←00$^0_0$) of interest here. Nevertheless, the model gives very satisfactory predictions (Rodrigues, 1998; Niro, 2003) for transitions of the same vibrational symmetry (namely $\Sigma$–$\Sigma$ corresponding to the stretching vibration for which the vibrational angular momentum $\ell_2$ is zero), giving a first argument in favour of our confidence in its quality. This confidence is further reinforced by the results plotted in Fig. 1, which are for two of the bands of interest for the OCO mission. Indeed, there is an excellent agreement between the theoretical values (Niro et al., 2005c) of the first order line-mixing coefficients $Y$ and those recently determined (Malathy Devi et al., 2007a, b; Predoi-Cross et al., 2007) from multispectrum analyses of measured laboratory spectra.

The approximate spectral-line-shape used to compute the absorption ($\alpha^A$) while retrieving the CO$_2$ vmr neglects line-mixing effects and so the absorption coefficient is simply the sum of individual line contributions with Voigt profiles. Remember that all spectroscopic parameters of the CO$_2$ data+software package of Niro et al. (2005c) have been taken from the 2000 edition of the HITRAN database (Rothmann et al., 2003, most recent one available at the time the package was built). These are not
the best ones presently available for the regions considered here (see Sect. 4) but this is of no consequences for the results presented in the next section since the reference and approximate models use exactly the same data. Note thatDicke and speed-dependence effects (Malathy Devi et al., 2007b; Predoi-Cross et al., 2007; Hartmann et al., 2008) have been neglected but again, since both approaches do, the conclusions regarding the influence of line mixing remain valid.

3 Theoretical results

Note that all the results presented below for the $3^0_0^1_3 \leftarrow 00^0_0$ band at 1.61 µm (Band#2) apply to the $3^0_0^1_2 \leftarrow 00^0_0$ band at 1.57 µm since these vibrational transitions have very similar spectral structures and integrated intensities (Predoi-Cross et al., 2007).

3.1 CO$_2$ volume mixing ratios

Results obtained for a MOPD of 50 cm are plotted in Fig. 2. They show that neglecting line mixing leads to significant errors on the retrieved CO$_2$ vmr in both spectral regions. The error depends on the airmass and is smaller in Band#2 than in Band#1 for reasons explained later. Note that the errors predicted in Band#1 are always larger than the 0.3% goal of the OCO mission.

The results in Fig. 3 demonstrate that the spectral resolution has only a small influence which is completely negligible for MOPD’s larger than 10 cm. This should be expected since, for MOPD>10 cm, the finite spectral resolution (<0.05 cm$^{-1}$) only slightly broadens the spectra features since the line contributions from the lower atmospheric layers have pressure-broadened widths of typically 0.18 cm$^{-1}$/atm (FWHM). Figure 3 also shows that the limited spectral resolution of the OCO and GOSAT experiments (typically 0.2–0.3 cm$^{-1}$, i.e. MOPD≈2 cm) does not significantly affect the quality of CO$_2$ retrievals with respect to LM.

Figures 2 and 3 show large differences between the errors induced by neglecting LM
when Band#1 and Band#2 are used. This can be explained noting that the integrated intensities of the lines in Band#1 are about 15 times larger that those in Band#2 in the HITRAN 2000 line list. As a result, the strong CO\textsubscript{2} transitions in the atmospheric spectra of Band#1 saturate, while this is not the case in Band#2 (see Figs. 6 and 7). The CO\textsubscript{2} vmr is thus essentially retrieved, in Band#1, from absorption in the troughs between the lines, where line mixing has the largest effects (see Fig. 6), as previously observed in the case of the O\textsubscript{2} A-band (Tran and Hartmann, 2008). This explanation is confirmed by the results in the main panel of Fig. 4, which show that the errors in Band#2 at very large airmasses (unrealistic but used for the demonstration) are qualitatively similar to those obtained in Band#1 for smaller airmasses. Furthermore, the insert in Fig. 4 demonstrates that, when the line intensities in Band#2 are multiplied by 15, the results obtained in Band#1 and Band#2 are quantitatively similar.

Finally, as should be expected, the error on the retrieved CO\textsubscript{2} depends on the extent of the spectral region retained for the fit. This is shown by Fig. 5 in the case of Band#1. Indeed, retaining only the central region (4820–4890 cm\textsuperscript{-1}) of the most intense band leads to much larger errors than when a broader range (4765–4915 cm\textsuperscript{-1}) is fitted. This can be understood from Fig. 6 which shows that the central region is the most affected by LM. This sensitivity to the fitting spectral range is significantly less pronounced in Band#2 since LM effects in this region are much weaker.

3.2 Transmissions and residuals

Typical transmission spectra in Band#1 and Band#2 for MOPD=50 cm and airmasses of 2, 4, and 10 are shown in Figs. 6 and 7. These plots also display the residuals (i.e. $\tau^E - \tau^A$) obtained from the fits (both the CO\textsubscript{2} vmr and a linear 100% transmission correction are adjusted on each spectrum) when line mixing is neglected. Figure 7 indicates that unambiguously demonstrating the influence of LM using measured atmospheric spectra in Band#2 will be difficult. Indeed, the transmission fit residuals induced by neglecting LM are very small (below 0.0025 for an airmass of 2) and will likely be masked by significantly larger errors due to measurement noise and imper-
fections of the forward model (not accurate enough spectroscopic data, pressure and temperature profiles, instrument function, etc.). The effects in Band#1 are larger (0.01 to 0.03) and can be observed in high quality measurements, as shown below.

These statements concerning the transmission fits residuals and the previous ones on the influence of LM of the retrieved CO₂ amounts are confirmed in the next section through treatments of measured atmospheric transmission spectra.

4 Experimental checks

In order to check the purely theoretical predictions of the preceding section, we have treated a few measured atmospheric spectra (larger scale tests will be made later as discussed in the conclusion). These were collected in Park Falls (Wisconsin) and obtained in solar absorption by a FTS with a MOPD of 45 cm (Washenfelder et al., 2006). The first set analyzed here consists of 140 spectra recorded on 22 December 2004 for solar zenith angles between 69° and 86°, thus sounding airmasses between 2.8 to 12.0. The second set, of 350 spectra, was recorded on 18 June 2008 for solar zenith angles between 22° and 84° corresponding to airmasses between 1.1 to 8. These two days involve very different surface temperatures (about −20°C and +20°C) and thus enable a test of the influence of temperature. In the fits, a 100% linear transmission correction was adjusted together with altitude-independent scaling factors for input vmr profiles of CO₂, H₂O, CH₄, plus the isotopologues HDO and ¹⁶O¹²C¹⁸O. The a priori CO₂ profiles are based on a simple seasonally-dependent empirical model fitted to in situ CO₂ measurements (Globalview, 2008). The a priori CH₄ profile is based on solar occultation balloon measurements by the JPL MkIV interferometer (Toon, 1991). The H₂O vertical distributions were provided, together with the pressure and temperature profiles, by the National Centers for Environmental Prediction (NCEP) re-analyses for the same dates and location. For the calculations, 71 atmospheric layers from 0 to 70 km (sufficient) were used and a number of solar lines were taken into account.

In a first step, the CO₂ absorption was calculated, for all lines, taking LM into account.
or not, with the tools of Niro et al. (2005c). The results show a noticeable improvement of the fit residuals when LM is taken into account but significant discrepancies remain. An analysis shows that this is due to the fact that the spectroscopic data of Niro et al. (2005c) where extracted from the 2000 edition (Rothmann et al., 2003) of the HITRAN database. As demonstrated by recent studies (Toth et al., 2008), the line intensities, positions, and broadening parameters thus used are not very accurate. A careful update of the data of Niro et al. (2005c) should thus be made for all bands and the software must be changed in order to take pressure-induced shifts into account. This is a relatively large task which is beyond the scope of the present paper but which will be carried in the coming year (see Sect. 5).

In order to better treat the spectra considered here, an alternative solution that is easy and quick to implement has been used. It uses Voigt profiles for most lines (see below) and has the advantage of using a very carefully built spectroscopic database which includes the shifts and the most recent experimentally determined individual line parameters. In particular, for CO$_2$, the data of Toth et al. (2008) is used. The line-mixing contribution (i.e., only the dispersive part due to the first order line-mixing coefficient $Y$, cf. Eq. 7 of Niro et al., 2005c) was then calculated with the tools of Niro et al. (2005c) for the strongest vibrational band in the considered region (i.e. $20^1_3\leftarrow00^0$ or $30^1_3\leftarrow00^0$). Taking LM into account for this single band only is sufficient since the influence of LM in the other ones, which are much weaker, is negligible. While doing this, the LM results were scaled by a constant factor (0.9 for Band#1, 1.00 for Band#2) correcting for the difference between the HITRAN 2000 line intensities and the more precise values of Toth et al. (2008). A constant pressure shift was assumed.

Before presenting the results obtained concerning the residuals in Band#1 and the retrieved CO$_2$ vmr, let us mention that the fits in Band#2 confirm the predictions of Sect. 3.2. Indeed, as expected from Fig. 7, the residuals of the fits of measured transmissions in Band#2 do not enable any reliable detection of LM effects. The latter lead to changes which are significantly smaller than errors due to imperfection of the forward model (spectral and atmospheric state) and measurement noise. For instance,
the rms of the residuals in the 6180–6260 cm$^{-1}$ interval for a zenith angle of 74.85° (about 0.002) only reduces by 1% when LM is included in the forward model.

The situation in Band#1 permits a more severe test of the spectral model, as shown by Fig. 8. Indeed, first, the residuals obtained neglecting LM show structures very similar, both in shape and magnitude, to the predictions of Fig. 6. Second, when LM is included, the residuals are significantly reduced, confirming that LM does have an influence and showing that its spectral effects are correctly taken into account. For a zenith angle of 82.45°, the rms of the fit of transmissions in the 4820–4890 cm$^{-1}$ interval is reduced by a factor of nearly 2.5 (from 0.0067 to 0.0027) thanks to the inclusion of LM in the retrieval. Note that, whereas Fig. 8 shows that the agreements in the $R$ branch and in the trough between $P$ and $R$ branches are now practically perfect, this is not the case for the central part of the $P$ branch near 4840 cm$^{-1}$. Although taking LM into account significantly reduces the residuals, some remain for which we do not have a clear explanation yet. A defect of the LM model (i.e. of the $Y$ values) seems very unlikely in view of Fig. 1 and of the fact that line-mixing coefficients were constructed with a self consistent approach (Niro et al., 2004) for both the $R$ and $P$ branches which have very similar structures.

The results concerning the CO$_2$ amount for the two days studied are displayed in Fig. 9. Three remarkable features can be pointed out. (i) The first is that including LM does reduce the CO$_2$ vmr in both Band#1 and Band#2, the effect being larger in the first region than in the second, a finding which confirms the predictions of Sect. 3.1. (ii) The second point is that including LM makes the results obtained in Band#1 and Band#2 much more consistent (to within about 1%) and much less dependent (particularly in Band#1) on the airmass (the variation reduces to ±0.5%). Note that the experimental results also quantitatively confirm the influence of the airmass on the error induced by neglecting LM shown in Figs. 2 and 5. (iii) Last but not least, the retrieved values of $x$CO$_2$ are very close to those deduced from in situ measurements also made at Park Falls. This being obtained for the two days studied shows that the effects of temperature are correctly taken into account. Note that the missing points and the scatter in the
results for the winter day are due to the presence of clouds around midday.

The differences between the a priori values of $x_{\text{CO}_2}$ and those retrieved from the atmospheric spectra (Fig. 9), and the fit residuals remaining in Fig. 8, may originate from various sources. Among these one finds, of course, (small) errors on the spectroscopic data used and particularly those on the integrated intensities of the lines. In fact, slight inconsistencies (of the order of one percent) between the values of these parameters in the $20^01_3 \leftarrow 00^00$ and $30^01_3 \leftarrow 00^00$ bands are likely responsible for the small difference between the $\text{CO}_2$ vmrs deduced in Band#1 and Band#2. Another source of possible error is the assumed known atmospheric state, both in terms of the a priori $\text{CO}_2$ vmr distribution used and of the $P+T$ vertical profile. Indeed, a relative error $\Delta P/P$ on the surface pressure directly translates into fit residuals and errors on $x_{\text{CO}_2}$.

Let us emphasize that the results of Figs. 8 and 9 have been obtained without ad-hoc adjustment of any spectroscopic parameters since only vmrs and a 100% transmission base line have been adjusted. They are thus meaningful and successful tests of the spectroscopic data and spectral shape models.

5 Conclusion and future studies

The results presented in this paper unambiguously demonstrate, for the first time, that line mixing among $\text{CO}_2$ lines must be accounted for if one wants to achieve the 0.3% accuracy on retrieved $x_{\text{CO}_2}$ required by the OCO project. A theoretical analysis and tests made using spectra measured by a ground-based FTS show that, when a forward model neglecting LM is used, significant and consistent residuals remain in the fits of atmospheric transmissions. Furthermore, treating the measured spectra taking LM into account almost reduces the residuals to within the noise level. Last but not least, including LM in the fit of measured transmissions makes the $\text{CO}_2$ vmrs retrieved in Band#1 and Band#2 very consistent, less dependent on the airmass, and in good agreement with values deduced from in situ measurements. These are very promising results in view of the improvement of routinely made retrievals of carbon dioxide atmo-
spheric amounts from ground-based or space-borne spectra. Note that they also imply that the forward model used for the analysis of OCO or GOSAT data must faithfully represent the airmass-dependence of LM to a high accuracy. Otherwise, due to the unavoidable fact that the airmass generally increases poleward, errors in the representation of LM will cause a latitude dependent bias in retrieved $x$CO$_2$. This in turn will generate spurious latitude-dependent sinks of CO$_2$ in inversion modeling.

For future and larger scale studies, the CO$_2$ database and software of Niro et al. (2005c) must be updated and improved, for all bands and isotopologues. In fact, there is evidence that the spectroscopic data used, taken from the 2000 edition of the HITRAN database (Rothmann et al., 2003), are far from being the best presently available. The pressure-induced line shifts, disregarded up to now, must also be taken into account as well as the broadening of CO$_2$ lines by H$_2$O (Sung et al., 2009), which may have an influence for humid atmospheres. This requires changes and extensions of the data files and some modifications of the software, a substantial task that will be completed in the coming year. Note that this update is of interest not only for CO$_2$ retrievals in the bands considered in this paper, but also for other remote sensing problems using longer wavelengths where LM among CO$_2$ lines must be properly taken into account. These include determinations of trace species amounts and of vertical profiles of the pressure and/or temperature, as discussed in Sect. VII.4 of Hartmann et al. (2008). Finally, the influence of Dicke narrowing and of the speed dependence of the broadening coefficient (Malathy Devi et al., 2007b; Predoi-Cross et al., 2007; see also Chapt. III of Hartmann et al., 2008) on the quality of retrievals is still to be studied. If proved to be important, these effects will have to be included in the forward model. In addition to these problems, the question of an eventual contribution of CIA by CO$_2$ in the regions considered in this paper should be studied.

Once an improved version of the software and associated data is built, it would be of interest to treat numerous atmospheric spectra (various zenith angles, instrument altitudes, hot and cold atmospheres, 1.57, 1.61, and 2.06 µm bands, narrow and broad spectral regions), in order to carry a study similar to that presented in this paper, but
of much broader scope. In doing this, much attention has to be paid to the accuracy of the knowledge of the $P+T$ profile of the sounded atmospheres. In fact, any error, particularly on the pressure profile, directly translates into residuals in the fits of measured transmissions and in bias on the retrieved CO$_2$ vmr. From this point of view, carrying simultaneous fits in the O$_2$ A-band in order to determine (check) the surface pressure, as done in Tran and Hartmann (2008), may add useful information.

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Fig. 1. Comparison of room temperature CO$_2$-air first order LM coefficients from the theoretical database of Niro et al. (2005c) (___) with experimental values obtained from multispectrum fits of laboratory spectra in Refs. (Malathy Devi et al., 2007a, b) (*), and (Predoi-Cross et al., 2007) (**). Values are plotted vs. the rotational quantum number $m$ ($m = -J_i$ for $P$ lines, $m = J_i + 1$ for $R$ lines) and the error bars on these plots correspond to the one standard deviations given in Malathy Devi et al. (2007a, b) and Predoi-Cross et al. (2007) multiplied by 2 in order to represent the full confidence interval.
Fig. 2. Relative errors, induced by neglecting LM, on the CO$_2$ vmrs deduced from fits of spectra with a 50 cm MOPD for various airmasses. The CO$_2$ vmr and a linear 100% transmission have been adjusted. ___ and _ _ _ are values obtained in Band#1 (4765–4915 cm$^{-1}$) and Band#2 (6160–6270 cm$^{-1}$), respectively.
Fig. 3. Influence of the spectral resolution on the errors on CO$_2$ vmr retrieved neglecting line-mixing effects. The results are for MOPD's of 2 cm (---), 10 cm (---) and 50 cm (---). The upper (full lines) and lower (dashed lines) sets of three curves refer to Band#1 (4765–4915 cm$^{-1}$) and Band#2 (6160–6270 cm$^{-1}$), respectively.

\[
\frac{\langle x_{CO_2}^{\text{FIt}} - x_{CO_2}^{\text{Ref}} \rangle}{x_{CO_2}^{\text{Ref}}} \times 100\%
\]

\(x_{CO_2}^{\text{FIt}}\): Retrieved CO$_2$ vmr from the fits
\(x_{CO_2}^{\text{Ref}}\): Reference CO$_2$ vmr
Fig. 4. Relative errors on the CO$_2$ vmrs deduced from fits, neglecting line-mixing effects, of spectra with a 50 cm MOPD for various airmasses. The main plot gives results obtained in Band#2. In the insert can be compared results obtained in Band#1 (___) with those obtained in Band#2 (—_) after multiplying the Band#2 line intensities by 15.
**Fig. 5.** Relative errors, induced by neglecting LM, on the CO$_2$ vmr deduced from fits of spectra with a 50 cm MOPD for various airmasses. ____ and ___ are values obtained in Band#1 by fitting the full region between 4765 and 4915 cm$^{-1}$ and by restricting the fits to the 4820–4890 cm$^{-1}$ interval, respectively.
Fig. 6. Transmissions (top) and fit residuals (bottom, due to neglecting LM) obtained in Band#1 for MOPD=50 cm and airmasses of 2, 4, and 10. The narrow peaks in the residuals near 4770 and 4807 cm\(^{-1}\) are due to \textit{Q} branches which, being narrow, are significantly affected by LM (Rodrigues et al., 1999).
Fig. 7. Same as Fig. 6 but for Band#2.
Fig. 8. Residuals obtained from fits of ground-based atmospheric solar-absorption spectra in Band#1 for various airmasses. The panels on the left and right hand sides display results obtained without and with the inclusion of LM, respectively.
Fig. 9. Scaling factor, applied to the a priori CO$_2$ vmr profile deduced from in situ measurements, see text, retrieved in Band#1 (left panels) and Band#2 (right panels) versus the Universal Time of the measurement obtained with (blue) and without (red) the inclusion of LM in the forward model. The upper and lower plots are for 22 December 2004 and 18 June 2008, respectively.