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Implementation of CO₂ Q band line mixing computations into line-by-line atmospheric radiative transfer codes

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Abstract—In this paper, we discuss the computational difficulties of merging line-mixing models into line-by-line computations. We present the technical details of the upgrade of the High resolution Atmospheric Radiative Transfer Code into an accurate reference line-by-line code for line mixing computations in the Q branches of the CO₂. The implementation of line mixing was based on the model, database and software that were developed at the Laboratoire de Physique Moléculaire et Applications, and the HITRAN2K absorption line compilation. In the recent version of the line mixing database 306 vibrational bands of eight CO₂ isotopes are included and there are provisions for calculations using the first order and the more accurate relaxation operator method. The successful integration of the line mixing computations has been validated using airborne and ground-based high-resolution HIS radiance measurements. This validation exercise can also be regarded as the validation of the line mixing database for high resolution, nadir viewing thermal emission measurements.

Key-words: HITRAN, line mixing, HARTCODE.

1. Introduction

According to comparisons of the high-resolution spectral radiance simulations with measurements, ignoring the CO₂ Q band line mixing effects could be responsible for errors of about 20 per cent in the computed outgoing long wave spectral radiance (*Haskins et al.*, 1999). Line mixing is a term to describe the effect of the pressure on the closely packed absorption lines belonging to the same vibrational

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band. Whenever the line spacing is comparable to the pressure broadened half width, the lines will overlap and collision will broaden and mix the lines creating interference terms in the band shape. More detailed theoretical description and quantitative analysis of line mixing can be found in the literature, see for example *Armstrong (1982)*.

Here we shall focus only on the technical details of how line mixing may be implemented into a line-by-line (LBL) atmospheric radiative transfer code. In particular, how the Laboratoire de Physique Moléculaire et Applications, (LPMA), line mixing model, *Rodriguez et al. (1999)*, *Jucks et al. (1999)*, was implemented into the High-resolution Atmospheric Radiative Transfer Code, (HARTCODE), *Miskolczi et al. (1990)*, and *Rizzi et al. (2002)*.

The size of the most recent version of the LPMA distribution archive is about 17 MB (un-compressed), representing the situation of the database in May 2002. In the database the absorption line and line mixing parameters of 18708 CO₂ Q lines in the 468–6936 cm⁻¹ spectral range are organized into 918 files. The structure of the archive is very clear and compact, see *Fig. 1*. The SOFT_Q directory contains software that is ready for use for any homogeneous CO₂ path. In DATA_Q the BANDINF.DAT file gives a summary of the included vibrational transitions. Files S₁... S₃₀₆, Y₁... Y₃₀₆ and W₁... W₃₀₆ are the spectroscopic information, first order line mixing coefficients and the elements of the relaxation operator, subsequently. The TEST_Q directory contains precomputed cases for the consistency check of the full database. The sub-branches of the asymmetric CO₂ molecules are treated as separate bands. The number of the 'true' Q branches is 271. The LPMA database and software are not optimized for LBL radiative transfer computations in the atmosphere.

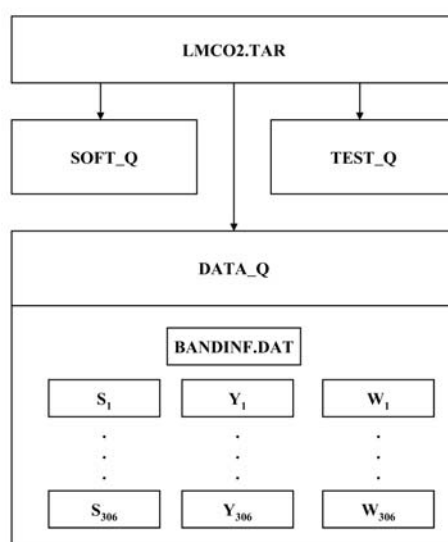


Fig. 1. Structure of the Laboratoire de Physique Moléculaire et Applications, (LPMA) CO₂ Q band line mixing archive.

HARTCODE is a general purpose software for optical depth, transmittance, radiance, and flux density computations in a spherically stratified refractive atmosphere using the LBL method. The schematic diagram of the code is presented in *Fig. 2*. The LAYER-1 section processes the input atmospheric profile and may output details of the slant path, layering and viewing geometry. The spectral quantities are read in the wave number loop, and this is the place where line mixing parameters will enter. LAYER-2 module computes the monochromatic optical depth over an appropriate wavenumber grid which is necessary for the wavenumber integration. This part of HARTCODE has been substantially modified to accommodate line mixing computations. In the LAYER-3 module the spectral mean quantities of the output parameters are computed for any required viewing geometry. HARTCODE uses a unique input absorption line file, which is prepared by a preprocessing code. This file is shaped for fast and efficient use with a given radiative transfer problem.

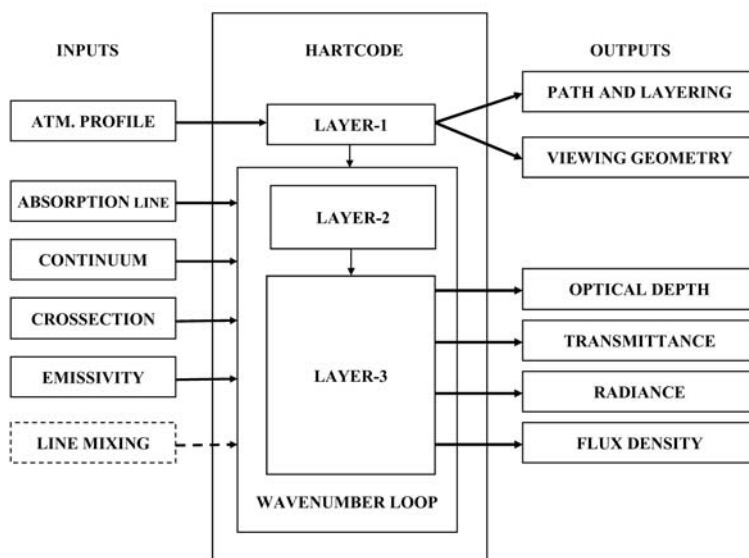


Fig. 2. Schematic structure of the High-resolution Atmospheric Radiative Transfer Code, (HARTCODE).

In this work the input absorption lines were taken from the *HITRAN2K* database (2002). This compilation contains over a million transitions of 38 different absorbers, but the CO₂ Q lines are identical to those of present in the 1996 edition, *Rothman et al.* (1998). The *HITRAN2K* database contains several improvements, among others, improved water vapor line parameters, which are important when comparing simulated and measured radiance spectra. Regarding the CO₂, we have

altogether 60802 transitions, out of these 11694 are Q lines of 328 Q bands. Although, in its original form, the HITRAN2K absorption line file is suitable for line-by-line computations, for efficient use and for line mixing computations it must be re-shaped.

Implementation of line mixing into HARTCODE was taken in two steps. First the LPMA and HITRAN2K databases were treated to make them suitable for direct HARTCODE access. Next, the subroutines to compute line-mixing with the first order or the relaxation operator method were added, together with the necessary changes in some existing HARTCODE modules.

2. Modifications related to the LPMA and HITRAN2K databases

In HARTCODE the grid structure for wave number integration over a given resolution is non-uniform, and is set up by using the absorption line positions present in the input line file. The LPMA and HITRAN2K databases were created by using different sources of theoretical and experimental spectroscopic data, therefore, the first step was to solve line compatibility problems between the two databases. HITRAN2K contains several Q-bands which are not included in the LPMA, while most of the coincidental Q bands contain more absorption lines in the LPMA than in the HITRAN2K. In *Fig. 3* the absorption lines in the coincidental Q bands are plotted in the 500–1000 cm^{-1} spectral range. Apparently, most of the excessive LPMA Q lines are weak. In case the wave number grid points are generated using the HITRAN2K lines, grid points would be missing for these weak lines. On the other hand, merging thousands of very weak LPMA Q lines into the input line file would introduce unnecessary computational burden, which should be avoided. However, the line mixing computation of the monochromatic absorption coefficient requires all rotational lines of a given vibrational transition that were included in the development of the LPMA parameterization.

The simple practical solution to the above problem is to use two properly organized and filtered data file. The first one is an ordinary line file and it should contain all transitions of all absorbers that have significant contributions to the absorption coefficients. Also, it should contain a kind of complex flag which identifies the Q bands for which line mixing coefficients are available in the LPMA database. This first file will control the setup of the wavenumber grid. The second file contains all LPMA Q lines and the line mixing coefficients sequentially organized into blocks by the minimum wave number of the rotational lines in the contributing vibrational bands. To create these two files the HARTCODE line preprocessing software was modified. The modified code is performing the following tasks:

- Checks the original HITRAN2K data file for unhandled transitions.
- Determines the coincidental Q bands and supplies flags for the related transitions.
- Re-organizes the LPMA database into a blocked sequential file.
- Merges the LPMA database to the HITRAN2K.
- Applies filters on the combined database and creates the final absorption line file.

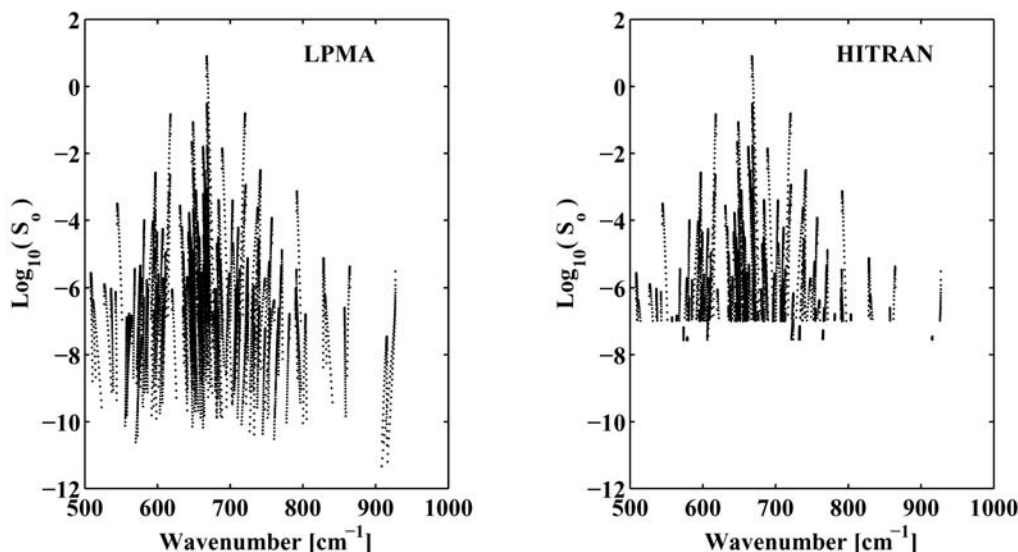


Fig. 3. Intensity distributions of the LPMA and HITRAN2K Q lines in the coincidental Q bands. S_0 [$\text{cm}^{-1} (\text{atm}\cdot\text{cm}_{\text{STP}})^{-1}$] is the line intensity at 296 K.

As an example of the operation of the pre-processing code, some numerical results for a spectral radiance simulation problem in the $450\text{--}3550 \text{ cm}^{-1}$ spectral range, using a vertical path through the whole USS 76 atmosphere are given. In this case the filters were set to keep only those transitions which contribute more than 10^{-2} percent to the total Voigt monochromatic absorption coefficients at the line centers. As a result, there remained 98994 transitions in the final absorption line file (with 21336 CO_2 and 8740 coincidental CO_2 Q lines), and 11968 transitions in the LPMA line mixing file. Ten other molecular species, H_2O , N_2O , CO , CH_4 , O_2 , NO , SO_2 , NO_2 and N_2 were also contributing to the final number of transitions. These line files were used at the validation of the line mixing model with the High-resolution Interferometer Sounder (HIS) measurements.

In case of interest, a complete set of five FORTRAN line processing routines are available from the authors. These codes may be used to process the LPMA database with different HITRAN editions or other absorption line archives.

3. Modifications in HARTCODE

Major modifications of the HARTCODE were needed for two reasons. Firstly, the nature of the computation of the line mixing with the first order or relaxation operator method requires the interruption of the strict sequential reading of the input absorption line file, and jump into a reading sequence, based on the positions and widths of the vibrational bands. Since Q bands have complex overlapping structure, the treatment of the ordinary lines and the flagged Q lines is rather complex. Secondly, the mathematical representations of the line mixing computations require the efficient evaluation of the complex probability function and library routines for handling complex operators. A summary of the equations relevant to the line mixing computations is given in the Appendix.

Introducing the line mixing option into the HARTCODE resulted in significant increase of the size of the code. The new version of HARTCODE contains about 1700 more program lines. Eleven subroutines have been added. The first six are performing the following tasks: read the LPMA Q line file; evaluate the complex probability function; compute the population, first order line mixing coefficients, Lorentz half widths and relaxation matrix elements for the current temperature and pressure; compute the absorption coefficients; compute the equivalent Q lines. The other six routines are from the LPMA Mathematical Library and their tasks are to diagonalize and invert complex operators. Some of the above routines are the slightly modified versions of the codes available in the SOFT_Q directory of the LPMA distribution archive. During the implementation major efforts were devoted to resolve the synchronized reading of the two absorption line files and to develop consistent line wing cut-off concept for the coincidental Q lines.

As an illustration, the effect of the code modifications is shown in *Figs. 4* and *5*, where monochromatic layer optical depth computations are compared with– and without applying line mixing. In *Fig. 4* the unmodified code results are presented. In *Fig. 5* the difference between the two curves at the top shows the effect of the line mixing on the total optical depth. The maximum difference is about 50 per cent and it occurs at around 618.5 cm^{-1} . The set of curves at the middle of *Fig. 5* represents the optical depth from the LPMA Q lines and the bottom set of curves are the contributions from the other molecules and non-LPMA Q lines. Each curve in the sets shows the variation of the optical depth of an atmospheric layer between the altitudes of 0 and 20 km. In this spectral interval of 1 cm^{-1} width 1332 grid points were used for the wavenumber integration.

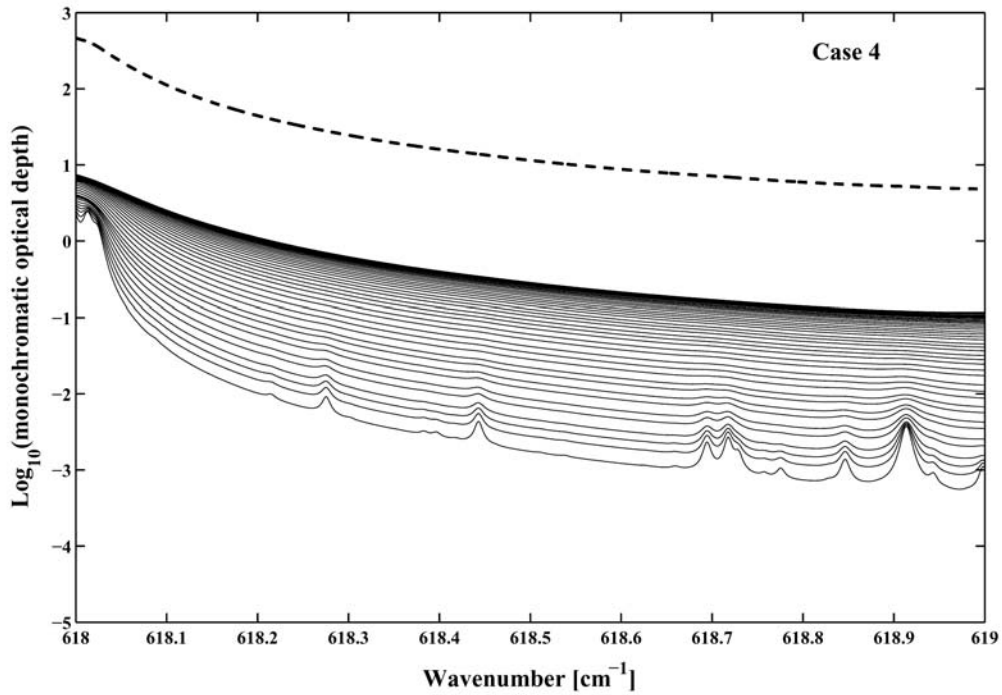


Fig. 4. Monochromatic optical depth of the atmospheric layers at different altitudes. Computed for the UWITRA93 case 4 without line-mixing. Dashed line is the total optical depth through the 20 km vertical path.

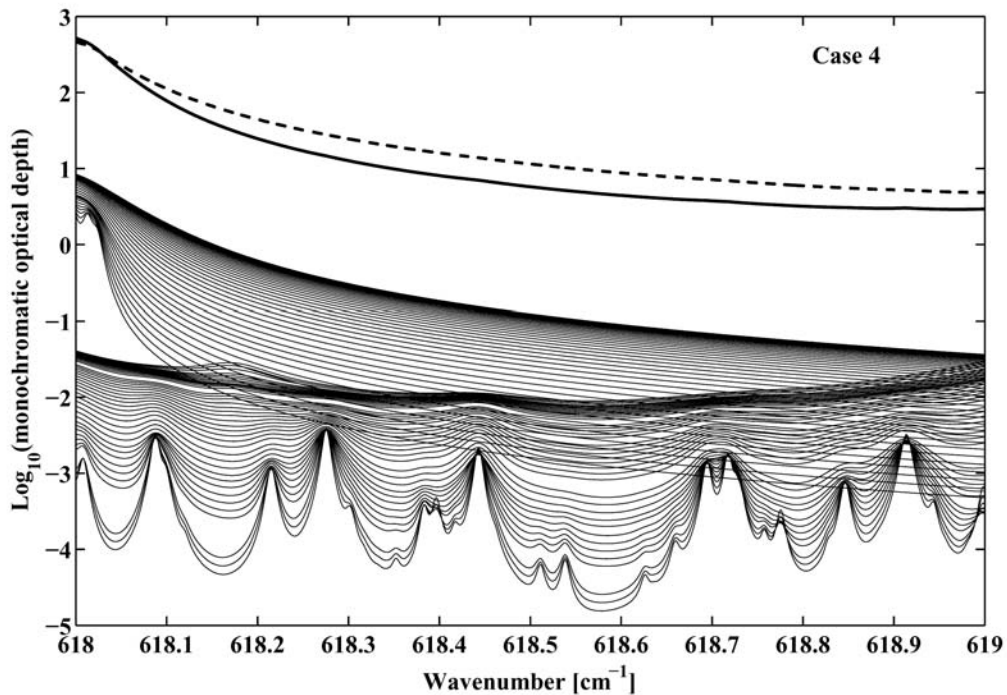


Fig. 5. Monochromatic optical depth of the atmospheric layers at different altitudes. Computed for the UWITRA93 case 4 with line-mixing. The top two lines are the total optical depths with- and without line-mixing. The two set of curves are the results of the separation of the absorption lines into LMPA Q lines and other absorption lines.

4. Validation

To validate the newly implemented line mixing algorithm for atmospheric applications, we selected the UWITRA93 data set *Knuteson* (1993). Since HARTCODE was participating in the 1993 ITRA exercise, the atmospheric profiles and the radiance measurements were ready for immediate use, see *Figs. 6* and *7*. In the data set there are two up-looking (ground based), and two down-looking (airborne) measurements. The unapodized spectral resolution of the HIS instrument in the band 1, ($600\text{--}1080\text{ cm}^{-1}$) is about 0.3 cm^{-1} . HARTCODE radiances, with- and without applying first order line mixing computations, were computed with 0.005 cm^{-1} spectral resolution. The relative differences in the downward radiances, (cases 1 and 2), are about 20 to 50 percent, but for Q bands closer to the window region it may exceed 80 per cent, see *Fig. 8*. The line-mixing effects on the upward radiances, (cases 3 and 4), are considerably less, and remain below 20 per cent. This is mainly due to the significant contributions to the radiances from the surface.

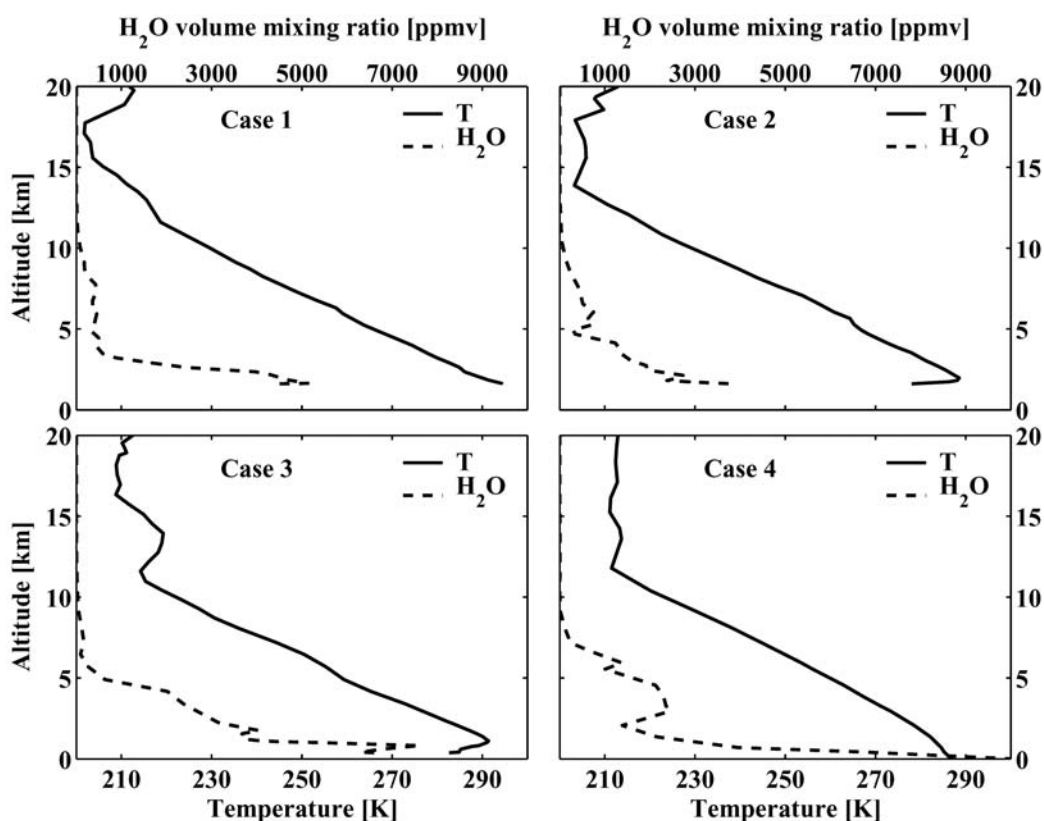


Fig. 6. Temperature and H₂O volume mixing ratio profiles of the UWITRA93 data set. Cases 1 and 2 were used for the ground based HIS measurements and cases 3 and 4 were used for the aircraft measurements.

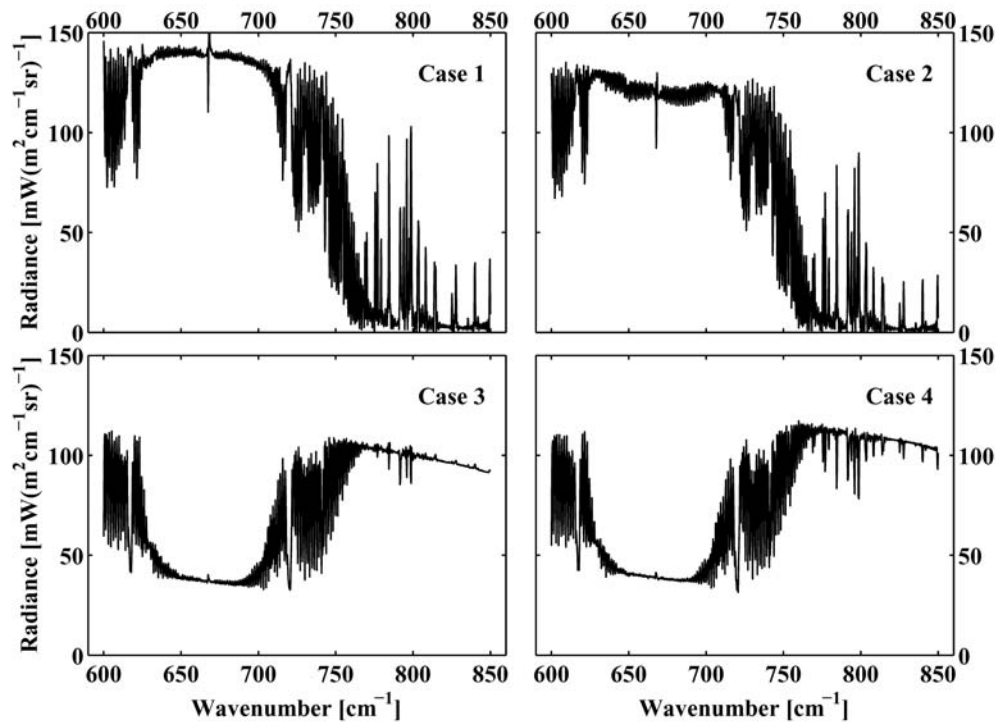


Fig. 7. High-resolution Interferometer Sounder radiance measurement in band I for the UWITRA93 cases. These radiances were used for the validation of the line-mixing model and its implementation into HARTCODE. The spectral resolution is 0.36 cm^{-1} .

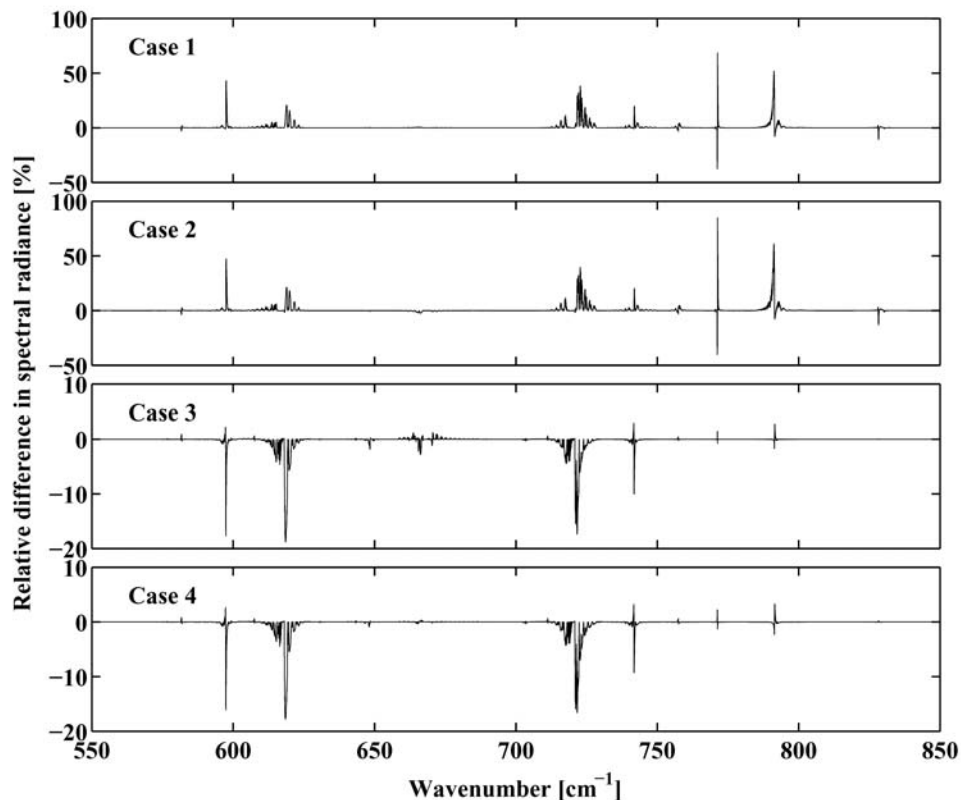


Fig. 8. Effect of line-mixing on the high-resolution simulated spectra. UWITRA93 cases, 0.005 cm^{-1} spectral resolution. The relative difference is defined as $100 \cdot (R - R_x) / R_x$, where R is the radiance without line-mixing and R_x is with line-mixing.

To model the HIS measurements, the HARTCODE radiances were evaluated using the FFT method, which involves interpolation, smoothing, fast Fourier transform, truncation, zero filling and inverse Fourier transform. Here we used linear interpolation for 2^{19} discrete wavenumber points. Since unapodized radiances can have zero or negative values, relative errors can not be computed. In *Fig. 9* the differences in the simulated and measured radiances are displayed. The upper curves in case 1 and 2 and the lower curves in case 3 and 4 are the differences without line mixing. The other four curves in the plots (they are vertically offset by ± 10 units for better view) show the differences when the line mixing effect was considered. Here we are not going into the quantitative details of the comparison our purpose is merely to show that the LPMA line mixing model works properly within HARTCODE. Apparently, there are large improvements by introducing the line-mixing, actually bringing the differences close to the instrument noise. Line-mixing computations with the relaxation operator method produced very similar results, (not shown here), but with considerably longer computing time. Obviously, line mixing computation has a price. The computer time necessary to run a case was increased by a factor of three for the first order method, and a factor of six for relaxation operator method. Note, that one single HARTCODE run in the $450\text{--}3500\text{ cm}^{-1}$ spectral range, (with 0.005 cm^{-1} resolution and using 80 atmospheric layers), without line mixing takes about 15 minutes on a 2.8GHz HP PC.

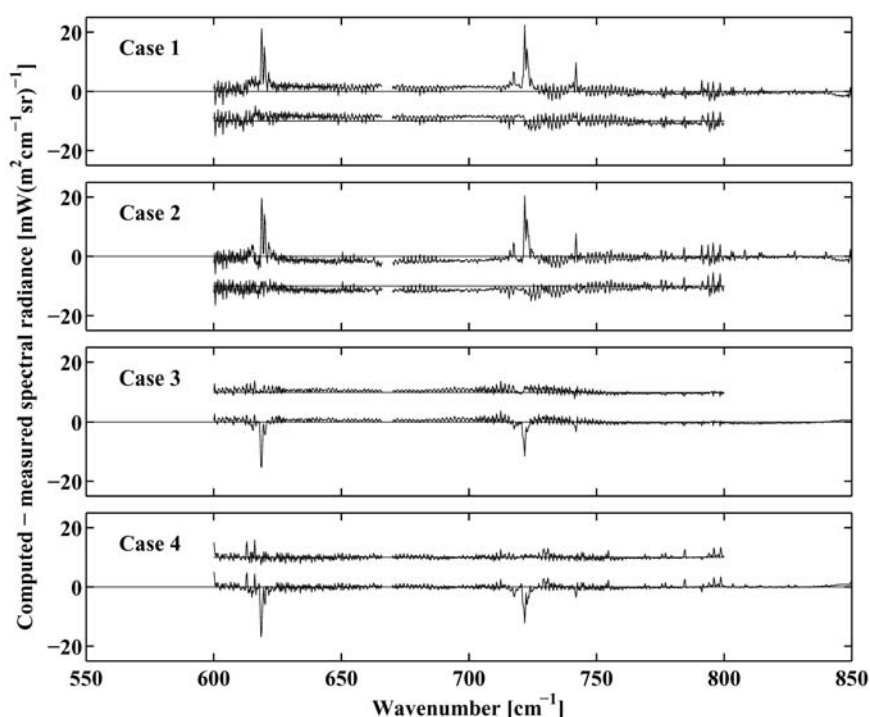


Fig. 9. Effect of line-mixing on the simulation errors. The longer curves in the plots were computed without line-mixing. The shorter curves, with ± 10 units vertical offsets, are the errors when line-mixing was considered in the calculations.

5. Conclusions

Here we have demonstrated that the LPMA line mixing model can be effectively implemented and used within a line-by-line atmospheric radiative transfer code. The key to the LPMA data base was to make it suitable for simultaneous sequential processing with the HITRAN2K absorption line file. It appears that the development of an interface code which is unique for the LPMA database, (or for any other line mixing database with different structure), is always necessary. The excellent documentation of the LPMA archive made this job relatively easy. Once this code is developed the use of further editions of the HITRAN database with different CO₂ lines, or using a new LPMA edition (with better line mixing parameters, but with the same structure) will be a matter of re-running the software. The increased computer time of the LBL calculations has little importance when the accuracy is the primary concern.

The scientific community engaged with molecular spectroscopy and atmospheric radiative transfer, has long time been awaiting for readily available line mixing parameters and algorithms that are included into the further editions of the HITRAN database. Regarding the number of existing line mixing models and parameterizations, see for example *Hoke et al.* (1994), *Strow et al.* (1994), *Timofejev et al.* (1997), the evaluation, selection and implementation could take a long time. Meanwhile, as the most recent and most comprehensive CO₂ line-mixing archive, the LPMA model may be used alternatively.

Acknowledgement—We are very grateful to *J.-M. Hartmann* for the most recent version of the LPMA line mixing archive, to *R. O. Knuteson* for the HIS measurements and the related documentation.

APPENDIX

Formulas relevant to line-mixing computations

Line intensity definition in HITRAN (in units of cm⁻¹(molecules cm⁻²)⁻¹):

$$S_i^0 = \Pi_i(T_0) D_i^2 \nu_i (1 - \exp(-c_1 \nu_i / T_0)).$$

Voigt monochromatic absorption coefficient for non-LPMA Q lines and for other CO₂ lines:

$$k_\nu(p, T) = X_{\text{CO}_2} \frac{T_S p}{p_S T} L_0 \sum_{i=1}^N S_i^0 \frac{(1 - e^{-c_1 \frac{\nu_i}{T}}) F_i(T_0)}{(1 - e^{-c_1 \frac{\nu_i}{T_0}}) F_i(T)} \sqrt{\frac{\ln 2}{\pi}} \frac{e^{-c_1 E_i \frac{T_0 - T}{T_0 T}}}{c_3 \sqrt{\frac{T}{M_i}} \nu_i} [V(x, y)]^{RE}.$$

First order line mixing absorption coefficient for LPMA Q lines:

$$k_v^F(p, T) = A_v(p, T) \sum_{i=1}^N B_v^i(T) \left([V(x, y)]^{RE} - Y_i(T) [V(x, y)]^{IM} \right).$$

Absorption coefficient for the equivalent Q lines:

$$k_v^R(p, T) = A_v(p, T) \sum_{i=1}^N \frac{([SE_i]^{RE} [V(x, y)_i]^{RE} - [SE_i]^{IM} [V(x, y)_i]^{IM})}{c_3 \sqrt{\frac{T}{M_i}}},$$

where

$$A_v(p, T) = X_{CO_2} \frac{T_s p}{p_s T} L_0 (1 - e^{-c_1 \frac{\nu}{T}}) \sqrt{\frac{\ln 2}{\pi}},$$

and

$$B_v^i(T) = \Pi_i(T_0) \frac{F_i(T_0)}{F_i(T)} D_i^2 \frac{e^{-c_1 E_i \frac{T_0 - T}{T_0 T}}}{c_3 \sqrt{\frac{T}{M_i}}}.$$

List of symbols

$\Pi_i(T_0)$	Population at temperature T_0
D_i	Dipole moment
ν_i	Resonance wavenumber, cm^{-1}
c_1	1.4387686
T_0	296.00 K
X_{CO_2}	CO ₂ volume mixing ratio
T_s	273.15 K
p_s	1013.25 hPa
T	Temperature, K
p	Pressure, hPa
L_0	2.68710×10^{19}
ν	Wave number, cm^{-1}
N	Total number of the Q lines of all contributing bands
$F_i(T), F_i(T_0)$	Partition functions of the CO ₂ isotope
E_i	Ground state energy
c_3	3.58128×10^{-7}
M_i	Molecular weight of the CO ₂ isotope
$V(x, y)_i$	Complex probability function
$x = (\nu - \nu_i) (\ln 2)^{1/2} / \alpha_D$	Real part of the argument of V
$y = \alpha_L / \alpha_D (\ln 2)^{1/2}$	Imaginary part of the argument of V
$\alpha_D = c_3 (T/M_i)^{1/2} \nu$	Doppler half width
$\alpha_L = \alpha_0^i (p/p_s) (T_0/T)^\Gamma$	Lorentz half width
Γ	Temperature coefficient of the i th transition
α_0^i	Lorentz half width at T_0 and p_s

$xx = (H^R + v_i^* - v)(\ln 2)^{1/2} / \alpha_D$	Real part of the argument of V for the equivalent lines
$yy = H^I (\ln 2)^{1/2} / \alpha_D$	Imaginary part of the argument of V for the equivalent lines
H^R	Positions of the equivalent lines
H^I	Half width of the equivalent lines
SE_i	Complex intensities of the equivalent lines
v_i^*	Population-averaged wave number.

The superscripts *RE* and *IM* refers to the real and imaginary part of the V complex probability function and $Y_i(T)$ is the first order line mixing coefficient. The sums in the above equations are extended to all the lines of all contributing Q bands at a particular wavenumber. Detailed explanation of H^R and H^I can be found in *Rodriguez et al.* (1999).

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