Line mixing

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Abstract: The treatment of line mixing within the algorithm is briefly described. KOPRA supports two different approaches, first, the exact treatment by means of a direct diagonalization method (DND) and second, Rosenkranz's fist order approximation. In all cases, a parameterization of the relaxation matrix is calculated externally and read in by the code. A description of the input data format is given.

1 Introduction

The significantly higher spectral resolution of modern instruments leads to an increased sensitivity to the spectral line shapes so that physical effects affecting line shapes such as line mixing (also called collisional narrowing) will be detectable. Especially CO_2 Q-branch line mixing will affect radiance spectra in the spectral region covered because of the high CO_2 volume mixing ratio and narrow line spacing. The effect of CO_2 Q-branch line mixing in the ν_2 fundamental band has already been reported by Strow and Reuter [1]. 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 CCl_4 volume mixing ratio in a spectral range around 790 cm^{-1} including the $11101 \leftarrow 10002$ CO_2 Q-branch has shown that the neglection of line mixing maps into an error of volume mixing ratio in the order of 30 - 50 %[2]. The effect is not only observed in CO_2 Q-branches, but also in P- and R-branches of the strong ν_3 fundamental band of CO_2 as well as in Q-branches of other gases such as N_2O and CH_4.

Line mixing occurs when collisions between a radiating molecule and broadening gas leads to a population transfer between the ro-vibrational molecular states and a redistribution of spectral intensity within a band. The intensity of the effect increases with pressure since it is proportional to the broadening gas density. KOPRA offers two different treatments of line shape calculation under consideration of line mixing. The direct diagonalization method (DND) enables exact line mixing calculation while the less time consuming Rosenkranz approximation is only valid for low atmospheric pressures. Therefore the DND approach is recommended for optical pathes through low altitude regions with high pressures such as for ground based observational geometries. The determination of the collisional induced population transfer between the ro-vibrational molecular states expressed by the so-called relaxation matrix is not performed within the code. A parametrisation of relaxation matrix data for the most prominent CO_2 bands is calculated by an external code and read in as input data. Furthermore, the line mixing treatment of KOPRA can easily be extended to other molecules by providing the corresponding input data. KOPRA also supports the calculation of P- and R-branch coupling, provided that input data exists.

2 Theory

2.1 The relaxation matrix W

Within the impact approximation, the absorption coefficient taking account of line mixing depends on the frequency-independent complex relaxation matrix **W** introduced by Ben-Reuven [3]. Its diagonal elements are related to pressure broadening, while nondiagonal elements are related to line mixing. **W** could be calculated using the EPGL (Exponential Power Gap Law) model introduced by Strow et al. [1],[4] and Tobin [5]. 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 modeled using an empirical energy-gap scaling law,

$$\mathbf{K}_{j,k} = a_1 \left(\frac{|\Delta E_{j,k}|}{B_0} \right)^{a_2} exp\left(-a_3 \frac{|\Delta E_{j,k}|}{k_B T} \right) \tag{1}$$

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:

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

where $\mathbf{W}_{jj}$ 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. β is a symmetry factor which takes into account the propensity differences between $e,f \leftarrow e,f$ and $e,f \leftarrow f,e$ state to state transitions and depends on the vibrational excitation and the angular momentum exchange of the involved states. The values of β were determined empirically by Strow et al. [4]. The nondiagonal elements of W are given by $\mathbf{W}_{j,k} = -\epsilon\mathbf{K}_{j,k}$. $\epsilon = \beta(v_i,j,k)\beta(v_f,j,k)$ depends on the β-factors of both initial and final vibrational level.

2.2 Calculation of the absorption coefficients within the DND approach

The exact calculation of the volume absorption coefficients $\sigma_a^{Vol}(\nu)$ can be performed using a numerical diagonalization procedure [6] (DND) which leads to the following expression for $\sigma_a^{Vol}(\nu)$:

$$\sigma_a^{Vol}(\nu) = \frac{N_g}{\pi}\sum_n \frac{A_n}{\rho_n d_n^2}\,\frac{Re\Lambda_{nn}}{\nu_n}\,\frac{1-\exp\frac{-h\Lambda_{nn}}{kT}}{1-\exp\frac{-h\nu}{kT}}\,\frac{Im\Lambda_{nn}Re\Omega_{nn}+Im\Omega_{nn}(\nu-Re\Lambda_{nn})}{(\nu-Re\Lambda_{nn})^2+(Im\Lambda_{nn})^2} \tag{3}$$

$$\Omega_{nn} = \sum_j d_j\mathbf{T}_{jn}\sum_k \mathbf{T}^{-1}_{nk}\rho_k d_k \tag{4}$$

Here ν_n is the center wavenumber of line n, ν is the wavenumber, N_g the number density of the absorbing gas g, A_n the HITRAN line intensity corrected for temperature T, ρ_k the density of the initial state of the transition k and d_n, d_j the dipole matrix elements of the transitions n and j, respectively. The transformation matrix $\mathbf{T}$ and the diagonal matrix of eigenvalues Λ are determined by the relation

$$\Lambda = \mathbf{T}^{-1}(\vec{\nu_0} - iP\mathbf{W})\mathbf{T} \tag{5}$$

with the vector of line center wavenumbers $\vec{\nu_0}$ and the total pressure P. Since $\mathbf{T}$ and Λ 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 Λ is necessary for each atmospheric layer. A polynomal 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 α_i, β_i, γ_i and δ_i:

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

with $T_0 = 200K$. These parameters are read from the file 'linemix.dat' ($1.4 in the main kopra input file).

2.3 Calculation of the absorption coefficients within the Rosenkranz approximation

The Rosenkranz approximation [7] (RK) which only considers first order line mixing errors requires less computational effort. Within this approximation $\sigma_a^{Vol}(\nu)$ can be written as

$$\sigma_a^{Vol}(\nu) = \frac{N_g}{\pi} \sum_n A_n \left(\frac{\alpha_{L_n} + (\nu - \nu_n) p Y_n}{(\nu - \nu_n)^2 + (\alpha_{L_n})^2} \right) \tag{7}$$

Here ν_n is the center wavenumber of line n, α_{L_n} are the Lorentzian half widths and A_n the line strengths. The first-order line mixing coefficients Y_n are given by

$$Y_n = 2 \sum_{j \neq n} \frac{d_j}{d_n} \frac{\mathbf{W}_{j,n}}{\nu_n - \nu_j} \tag{8}$$

with the dipole matrix elements d_n and d_j. The temperature dependences of Y_n are parameterized similar to Eq. 6 using the precalculated parameters a_n,b_n,c_n and d_n provided by the file 'linemix.dat':

$$Y_n(T) = \left(\frac{200K}{T} \right)^{0.75} \left[a_n + b_n(T - 200K) + c_n(T - 200K)^2 + d_n(T - 200K)^3 \right] \tag{9}$$

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 centers for pressures of 100 hPa and increase up to 12 % at 500 hPa. For this reason KOPRA calculates line-mixing within the Rosenkranz approximation only at atmospheric layers with a pressure below 100 hPa while at layers with a pressure above 100 hPa the exact DND approach is used by default.

2.4 Convolution of line mixing line shape with a Doppler line profile

For atmospheric radiative transfer applications both line shapes must be convolved with a Doppler shape to obtain

$$\sigma_a^{Vol}(\nu) = \frac{N_g}{\pi} \sum_n \frac{\tilde{A}_n}{\alpha_{D_n}} \left[ReW(x_n, y_n) + \tilde{Y}_n ImW(x_n, y_n) \right] \tag{10}$$

$$\tilde{A}_n = A_n, \quad x_n = \frac{\nu - \nu_n}{\alpha_{D_n}}, \quad y_n = \frac{\alpha_{L_n}}{\alpha_{D_n}}, \quad \tilde{Y}_n = pY_n \quad \text{for RK} \tag{11}$$

$$\begin{gathered} \tilde{A}_n = \frac{A_n}{\rho_n d_n^2} \frac{Re\Lambda_{nn}}{\nu_n} \frac{1 - \exp \frac{-h\Lambda_{nn}}{kT}}{1 - \exp \frac{-h\nu}{kT}} Re\Omega_{nn}, \\ x_n = \frac{\nu - Re\Lambda_{nn}}{\alpha_{D_n}}, \quad y_n = \frac{Im\Lambda_{nn}}{\alpha_{D_n}}, \quad \tilde{Y}_n = \frac{Im\Omega_{nn}}{Re\Omega_{nn}} \quad \text{for DND} \end{gathered} \tag{12}$$

where α_{D_n} is the Doppler half width and $W(x_n, y_n)$ is the complex probability function which is resolved numerically by means of an accelerated Humlicek algorithm [8].

3 Detailed balance requirements

It can be shown that detailed balance requirements on **W** forces

$$\sum_n \tilde{A}_n \tilde{Y}_n = 0 \tag{13}$$

Any violation of this sum rule – produced by numerical errors in line strength calculation or neglection of lines – may result in large errors of the absorption coefficient in the far wing region of the band. For this reason all lines of a given branch for which relaxation matrix elements have been calculated are considered in the forward calculation even if some of them are located outside the spectral interval under consideration. However, an additional correction routine is implemented in the code which calculates $\sum_n \tilde{A}_n \tilde{Y}_n = \Delta$ and recalculates $\tilde{Y}_n^{corr} = \tilde{Y}_n - \Delta$ in order to guarantee Eq. 13.

4 Combined treatment of line mixing and far wing effects

In the case of Q-branch coupling, line mixing is disregarded for microwindows with boundaries farther away than 10 cm^{-1} from all lines of the branch under consideration because of far wing effects caused by the finite duration of collisions. An empirical χ-factor as introduced by Cousin et al. [9][10][11] (see also Part II: 'Analytical expressions') is used instead for all CO_2 lines in order to consider the sub-Lorentzian behavior of the line wings. For P- and R- line mixing, a different approach is chosen since those branches cover spectral intervals much bigger than the region where the impact approximation is valid and hence, both, line mixing and far wing effects have to be considered. In this case, far wing effects are considered by applying a branch correction factor calculated within the code (see also section 1.5 of Part V: 'Absorption coefficients, line collection and frequency grid') to the Rosenkranz or DND line mixing absorption coefficient in the whole spectral region under consideration.

5 The input data file 'linemix.dat'

The input file 'linemix.dat provides line mixing data which is needed for both DND and RK line mixing calculation. The format of the data is specified within the file header. For each branch the following data is repeated:

branch specific data:

Record nb.	Data items
1	IG,VU,VL,BRAN,LI,B0,VMIN,VMAX, BETALF,BETAUF,BETALS,BETAUS
2	AS1A,AS1B,AS1C,AS1D
3	AS2A,AS2B,AS2C,AS2D
4	AS3A,AS3B,AS3C,AS3D
5	AS4A,AS4B,AS4C,AS4D
6	AF1A,AF1B,AF1C,AF1D
7	AF2A,AF2B,AF2C,AF2D
8	AF3A,AF3B,AF3C,AF3D
9	AF4A,AF4B,AF4C,AF4D

IG	HITRAN Molecule-/Isotope number
VU	HITRAN upper global quanta index
VL	HITRAN lower global quanta index
BRAN	branch specifier (P,Q,R)
LI	number of considered lines
B0	rotational constant of isotope
VMIN	wavenumber of first line in branch
VMAX	wavenumber of last line in branch
BETA-L,U-F,S	β-values of lower state(L) and upper state (U) for foreign- (F) and self- (S) broadening
A-S,F-1,2,3,4-A,B,C,D	parameter for **W**-matrix calculation as defined in Eq. 6. S,F = self-/foreign broadening; A,B,C,D = $\alpha, \beta, \gamma, \delta$

line specific data (repeated for each line of the branch):

Record nb.	Data items
1	J,S,YSA,YSB,YSC,YSD,YFA,YFB,YFC,YFD
2	full HITRAN record of this line

J	rotational quantum number of ground state
S	symmetry of lower and upper state, respectively
Y-S,F-1,2,3	parameter for Y-coefficient calculation as defined in Eq. 9. S,F = self-/foreign broadening

Bibliography

[1] L. L. Strow and D. Reuter, “Effect of line mixing on atmospheric brightness temperatures near 15 μm,” *Appl. Opt.* **27**(5), pp. 872–878, 1988.

[2] B. Funke, “Modellierung des line–mixing Effekts in Q–Zweigen von CO_2–Banden für die Berechnung von atmosphärischen Infrarotspektren,” Master’s thesis, Institut für Meteorologie und Klimaforschung, Universität Karlsruhe, Forschungszentrum Karlsruhe, 1995.

[3] A. Ben-Reuven, “Impact broadening of microwave spectra,” *Phys. Rev.* **145**(1), pp. 7–22, 1966.

[4] L. L. Strow, D. C. Tobin, and S. E. Hannon, “A compilation of first–order line–mixing coefficients for CO_2 Q–branches,” *J. Quant. Spectrosc. Radiat. Transfer* **52**(3/4), pp. 281–294, 1994.

[5] D. C. Tobin, “Carbon dioxide lineshapes in $\Pi \leftarrow \Sigma$ and $\Pi \leftarrow \Delta$ vibrational transitions,” Master’s thesis, University of Maryland Baltimore County, 1993.

[6] R. Gordon and R. P. McGinnis, “Line shapes in molecular spectra,” *J. Chem. Phys.* **49**, p. 2455ff, 1968.

[7] P. W. Rosenkranz, “Shape of the 5 mm oxygen band in the atmosphere,” *IEEE Transactions on Antennas and Propagation* **AP–23**(4), pp. 498–506, 1975.

[8] M. Kuntz, “A new implementation of the Humlicek algorithm for the calculation of the Voigt profile function,” *J. Quant. Spectrosc. Radiat. Transfer* **57**(6), pp. 819–824, 1997.

[9] R. Le Doucen, C. Cousin, C. Boulet, and A. Henry, “Temperature dependence of the absorption in the region beyond the 4.3–μm band head of CO_2. 1: Pure CO_2 case,” *Appl. Opt.* **24**(6), pp. 897–906, 1985.

[10] V. Menoux, R. Le Doucen, and C. Boulet, “Line shape in the low–frequency wing of self–broadened CO_2 lines,” *Appl. Opt.* **26**(3), pp. 554–562, 1987.

[11] V. Menoux, R. Le Doucen, J. Boissoles, and C. Boulet, “Line shape in the low frequency wing of self– and N_2–broadened ν_3 CO_2 lines: temperature dependence of the asymmetry,” *Appl. Opt.* **30**(3), pp. 281–286, 1991.