Parameterization of continua caused by gaseous constituents

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Abstract: The calculation of broadband continua caused by atmospheric trace gases like O_2, N_2, H_2O, CO_2 is described. The collision induced bands of O_2 and N_2, due to interaction of molecule pairs, are simulated by empirical models from literature. For H_2O the well know CKD continuum is used where a special treatment of the line wing calculation is necessary. For CO_2 an own continuum was determined, taking into account contributions more than $25 cm^{-1}$ apart from the line-center.

1 Introduction

The emission of the terrestrial atmosphere in the infrared spectral region is dominated by vibrational-rotational bands of a large number of atmospheric trace species such as H_2O, CO_2, O_3, CH_4, N_2O. In the case of measuring their emission with high spectral resolution the individual vibrational-rotational lines of most trace species can be resolved. In addition to the molecular lines, absorption features extending over wide spectral regions and varying slowly with frequency are present in atmospheric infrared emission spectra. This so-called *continuum* radiance has its origin in different physical mechanisms:

- collision-induced absorption bands due to the interaction of molecule pairs like N_2-N_2, N_2-O_2, O_2-O_2,
- superposition of line wings from strongly absorbing bands such as the 6.3 μm ν_2 band of H_2O and the 4.3 μm ν_3 band of CO_2

The different gaseous continua are calculated in the module **gascon_m** which include calls of the individual subroutines for the different continua.

2 O_2 Continuum

The O_2 Continuum is calculated by the subroutine **calc_o2cont@gascon_m**. The implementation is based on the empirical model by [1]. They combined laboratory measurements of normalized binary absorption coefficients $B_{O_2-O_2}$ and $B_{N_2-O_2}$ to the normalized absorption coefficient B_{O_2-air} assuming a composition of 21% O_2 and 79% N_2. The temperature and wavenumber dependence of the normalized absorption coefficient for O_2-air is modeled using a simple empirical law:

$$B_{O_2-air}(\nu,T) = B^0_{O_2-air}(\nu) \exp\left[\beta^0_{O_2-air}(\nu)\left(\frac{1}{T_0}-\frac{1}{T}\right)\right] \tag{1}$$

with the reference temperature T_0 = 296 K and the normalized absorption coefficient $B^0_{O_2-air}$ and an empirically determined exponent for the temperature dependence $\beta^0_{O_2-air}$ at reference temperature, both tabulated as a function of wavenumber in the wavenumber region 1365 cm^{-1} to 1800 cm^{-1} in steps of 5 cm^{-1}. The normalized absorption coefficient $B^0_{O_2-air}$ and the exponent for the temperature dependence $\beta^0_{O_2-air}$ are given in units of [cm^{-1} Am^{-2}] and [K], respectively. For calculation of the O_2 continuum at arbitrary wavenumbers these coefficients are linearly interpolated. The absorption cross-section σ_{O_2} of the O_2 continuum in units of [cm^2/molec] can then be calculated by:

$$\sigma_{O_2}(\nu,\rho_{O_2},T) = \frac{\rho_{O_2} \times B^0_{O_2-air}(\nu)}{(0.21\ Am)^2} \times \exp\left[\beta^0_{O_2-air}(\nu)\left(\frac{1}{T_0}-\frac{1}{T}\right)\right] \tag{2}$$

where ρ_{O_2} is the density of O_2 in units of [molec/cm^3].
The subroutine **calc_o2cont@gascon_m** also supports the calculation of the derivative of the O_2 absorption cross section with respect to temperature given by:

$$\begin{aligned}\frac{d\sigma_{O_2}}{dT}(\nu,\rho_{O_2},T) &= \frac{\rho_{O_2} \times B^0_{O_2-air}(\nu)}{(0.21\ Am)^2} \times \frac{\beta^0_{O_2-air}(\nu)/T-1}{T} \\ &\quad \times \exp\left[\beta^0_{O_2-air}(\nu)\left(\frac{1}{T_0}-\frac{1}{T}\right)\right]\end{aligned} \tag{3}$$

3 N_2 Continuum

The N_2 Continuum is calculated by the subroutine **calc_n2cont@gascon_m**. The implementation is based on the empirical model by [2] The temperature and wavenumber dependence of the normalized absorption coefficient $B_{N_2-N_2}$ for pure N_2 is modeled using a simple empirical law:

$$B_{N_2-N_2}(\nu,T) = B^0_{N_2-N_2}(\nu) \exp\left[\beta^0_{N_2-N_2}(\nu)\left(\frac{1}{T_0}-\frac{1}{T}\right)\right] \tag{4}$$

with the reference temperature T_0 = 296 K and the normalized absorption coefficient $B^0_{N_2-N_2}$ and an empirically determined exponent for the temperature dependence $\beta^0_{N_2-N_2}$ at reference temperature, both tabulated as a function of wavenumber in the wavenumber region 2125 cm^{-1} to 2600 cm^{-1} in steps of 5 cm^{-1}. The normalized absorption coefficient $B^0_{N_2-N_2}$ and the exponent for the temperature dependence $\beta^0_{N_2-N_2}$ are given in units of [cm^{-1} Am^{-2}] and [K], respectively. For calculation of the N_2 continuum at arbitrary wavenumbers these coefficients are linearly interpolated. The relative efficiency $E^{N_2}_{O_2/N_2}$ of collisions of N_2 with O_2 and N_2 molecules can be modeled by the following wavenumber-independent expression:

$$E^{N_2}_{O_2/N_2}(T) = 1.294 - 0.4545(T/T_0) \tag{5}$$

The N_2-air collision-induced spectra in the Earth's atmosphere from the pure N_2 data can then be calculated by:

$$B_{N_2-air}(\nu,T) = [0.79 + 0.21 \times E^{N_2}_{O_2/N_2}(T)] \times B_{N_2-N_2}(\nu,T) \tag{6}$$

The absorption cross-section σ_{N_2} of the N_2 continuum in units of [cm^2/molec] considering the composition of air by 79% N_2 and 21% O_2 can then be calculated by:

$$\begin{aligned} \sigma_{N_2}(\nu,\rho_{N_2},T) &= \frac{\rho_{N_2} \times B^0_{N_2-N_2}(\nu)}{(0.79\ Am)^2} \times [0.8387 - 0.0754\frac{T}{T_0}] \\ &\quad \times \exp\left[\beta^0_{N_2-N_2}(\nu)\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \end{aligned} \tag{7}$$

where ρ_{N_2} is the density of N_2 in units of [molec/cm^3].
The subroutine **calc_n2cont@gascon_m** also supports the calculation of the derivative of the N_2 absorption cross section with respect to temperature given by:

$$\begin{aligned} \frac{d\sigma_{N_2}}{dT}(\nu,\rho_{N_2},T) &= \frac{\rho_{N_2} \times B^0_{N_2-N_2}(\nu)}{0.79\ Am^2} \times \exp\left[\beta^0_{N_2-N_2}(\nu)\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \\ &\quad \times \left[\frac{0.8387 - 0.0754\frac{T}{T_0}}{T}\left(\frac{\beta^0_{N_2-N_2}(\nu)}{T} - 1\right) - \frac{0.0754}{T_0}\right] \end{aligned} \tag{8}$$

4 H_2O Continuum

The H_2O Continuum is calculated by the subroutine **calc_h2ocont@gascon_m**. The implementation is based on the CKDv2.2 model by [3] This model introduces an empirical lineshape correction factor (χ-factor) which accounts for the non-Lorentzian behaviour of H_2O lines. The specific realization of Clough's continuum parameterization is coupled with the definition of the continuum: The absorption of all water vapor transitions is separated into the *local absorption* and the *continuum absorption*. The local absorption is defined as a Lorentzian lineshape out to ± 25 cm^{-1} apart form the line center, minus the Lorentz value at 25 cm^{-1}. The continuum is then simply defined by any observed absorption not attributable to the local absorption.
Application of this definition of the H_2O continuum to KOPRA calculations requires the subtraction of the so-called *basement*, which is the Lorentz value at 25 cm^{-1}, from the absorption coefficient of each individual H_2O line out to ± 25 cm^{-1} apart form the line center. Furthermore, calculation of absorption coefficient of H_2O lines is restricted to the region inside of ± 25 cm^{-1} apart form the line center. Therefore, a switch is introduced into the subroutine **add_lines_chilm@addlin_m** to perform this restriction and subtraction for H_2O lines in the case the H_2O continuum is included.
The original CKD model was developed by fitting the parameters in analytical χ-factors to reach agreement between the calculated continuum and laboratory measurements. For pragmatic reasons these χ-factors were used to calculate continuum coefficients $C^0_s(\nu,T)$ for the self-broadening component and $C^0_f(\nu)$ for the foreign-broadening component at reference pressure p_{ref} such that the continuum absorption cross section in units of [cm^2/molec] is given by:

$$\begin{aligned} \sigma_c(\nu,T,vmr_{H_2O}) &= \nu \tanh\left(\frac{hc\nu}{2kT}\right)\left(\frac{p}{p_{ref}}\right)\left(\frac{T_{ref}}{T}\right) \\ &\quad \times \left[vmr_{H_2O}\ C^0_s(\nu,T) + (1 - vmr_{H_2O})\ C^0_f(\nu)\right] \end{aligned} \tag{9}$$

Values of C_s^0 are tabulated for temperatures of 296 K and 260 K and C_f^0 for a temperature of 296 K in the wavenumber range from -20 cm^{-1} up to 20000 cm^{-1} in steps of 10 cm^{-1}. For calculation of the water vapor continuum at arbitrary wavenumbers these coefficients are interpolated linearly in wavenumbers. In the case of C_s^0 an exponential interpolation to arbitrary temperatures is performed.

The present CKDv2.2 model includes modifications of the original CKDv0 model to maintain better agreement with laboratory ansd atmospheric continuum measurements. These modifications are performed by correction factors to the continuum coefficients to reduce deviations with measurements in specific spectral regions.

Derivatives of the water vapor continuum with respect to temperatures are implemented by calculating the differential quotient for a temperature increment of dT = 0.1 K.

5 CO_2 Continuum

The CO_2 continuum absorption arises from the superposition of the extreme wings of many distant lines. To account for this CO_2 continuum in accurate line-by-line calculations it would be required to include CO_2 lines over a very large spectral region. This method would increase the required computation time dramatically. Therefore, CO_2 continuum coefficients are precalculated for different temperatures as a function of wavenumber.

The generation of CO_2 continuum coefficients is performed by a stand-alone program **create_co2coe.f90**. This program calculates the CO_2 absorption cross section at user-defined spectral positions and user-defined temperatures by superimposing all spectral lines out of a spectral region which also can be specified by the user. The spectral line shape used for the calculation of the continuum coefficients is the Lorentzian line shape modified by so-called χ-factors which account for the non-Lorentzian behavior of CO_2 lines. We used the asymmetric χ-factors of Menoux et al. (1987, 1991). As the temperature dependence of the asymmetric χ-factors for the O_2 broadening has not been investigated and, on the other hand, the temperature dependence of of the symmetric χ-factors indicate significant differences for N_2- and O_2 broadening we applied for O_2 broadening at low temperatures symmetric χ-factors.[4]These χ-factors are interpolated and extrapolated linearly in temperature. In cases where extrapolation leads to negative χ-factors they are set to zero.

The continuum cross-section includes all contributions of linewings out of ± 25 cm^{-1} apart from the line center plus the χ-modified Lorentz value at 25 cm^{-1} of each CO_2 line. Application of these continuum cross-section to KOPRA line-by-line calculations requires the subtraction of the χ-modified Lorentz value at 25 cm^{-1} from the absorption coefficient of each individual CO_2 line out to ± 25 cm^{-1}. Furthermore, calculation of absorption coefficient of CO_2 lines is restricted to the region inside of ± 25 cm^{-1} apart form the line center. Therefore, a switch is introduced into the subroutine **add_lines@addlin_m** to perform this restriction and subtraction for CO_2 lines in the case the CO_2 continuum is included.

The CO_2 continuum coefficients to be used by KOPRA are stored in the module **co2coe_m**. They were calculated for 6 different temperatures covering the range from 150 K to 350 K and for wavenumbers from 0 to 10000 cm^{-1} with 5 cm^{-1} spacing. The continuum coefficients can be assumed to be linear in pressure because the Lorentz line shape is only applied to regions more than 25 cm^{-1} apart from the line center where the air broadening half width is negligible to the distance from the line center. Therefore, the continuum coefficients stored in **co2coe_m** have units of $[\frac{cm^2}{molec\ hPa}]$.

In the subroutine **calc_co2cont@gascon_m** these continuum coefficients are interpolated linearly to the actual wavenumber and interpolated by the Steffen Interpolation scheme (subroutine **intp_steffen@varsub_m**) to the actual temperature. In order to obtain the continuum absorption cross-sections in units of $[\frac{cm^2}{molec}]$ the interpolated coefficients are multiplied by the actual pressure.
Derivatives of the CO_2 continuum with respect to temperatures are implemented by calculating the differential quotient for a temperature increment of $dT = 0.1$ K.

Bibliography

[1] F. Thibault, V. Menoux, R. Le Doucen, L. Rosenmann, J.-M. Hartmann, and C. Boulet, "Infrared collision–induced absorption by O_2 near 6.4 μm for atmospheric applications: measurements and empirical modeling," *Appl. Opt.* **36**(3), pp. 563–567, 1997.

[2] W. J. Lafferty, A. M. Solodov, A. Weber, W. B. Olson, and J.-M. Hartmann, "Infrared collision–induced absorption by N_2 near 4.3 μm for atmospheric applications: measurements and empirical modeling," *Appl. Opt.* **35**(30), pp. 5911–5917, 1996.

[3] S. A. Clough, "The water vapor continuum and its role in remote sensing," in *Optical Remote Sensing of the Atmosphere*, vol. 2 of *OSA Tech. Dig. Ser.*, pp. 76–78, Optical Society of America, Washington, D.C., 1995.

[4] C. Cousin, R. Le Doucen, C. Boulet, and A. Henry, "Temperature dependence of the absorption in the region beyond the 4.3–μm band head of CO_2. 2: N_2 and O_2 broadening," *Appl. Opt.* **24**(22), pp. 3899–3907, 1985.