Simple Radiative Transport

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1. Introduction

Climate change, its causes, and possible remedies are in public focus. There is a consensus on the human made climate change amoung a vast majority of climate scientist. Yet there are still people who promote the idea that there is no climate change or if there is climate change that the causes are natural and not made und thus also not influencable by humeans.

As a small contribution to the ongoing discussions in the public realm the objective of this report is to define and implement a very basic model of the earth's athmosphere and determine the amount of infrared radiation that is absorbed in the $15\mu m$ absorption band of CO_2. This results of this little model are only meant to show the effect of CO_2 under quite simplifying assumptions are by no means a replacement for the many excellent research made in this field.

The model is described below and the source code is made available so that everbody interested can check the results. If the author has made a mistake, be it inde model definiion or the computationla code, he would be very appreciative for any hint.

2. Model Description

The key assumptios of the simple athmospehre model are:

- The athmosphere consists mostly of molecules that don't interact with infrared radiation in the $15\mu m$ range
- Only CO_2 is absorbing and emitting infrared radiation
- The temperature and pressure of the athmosphere is assumed to be fixed, thus there is no self consistency between absorbtion and temperature
- Only upward travelling radiation is considered
- The main result is the difference in infrared radiation at the top of the athmosphere (TOA) at $70km$ escaping to free space
- Scatterng will be neglected
- The athmospheric gas is in local thermodynamic equalibrium so that all enery levels are occupied according to the Boltzmann factor
- All spectroscopic data of CO_2 ar etaken fro the HITRAn data base.

2.1. Radiation Transport Equation

The radiation transport equation reads:

$$\frac{dI_\lambda}{ds} = -\kappa_\lambda I_\lambda + \epsilon_\lambda \tag{1}$$

with:

$$I_\lambda : \left[\frac{W}{m^2\ sr\ m}\right]$$
$$\epsilon_\lambda : \left[\frac{W}{m^3\ sr\ m}\right]$$
$$\kappa_\lambda : \left[\frac{1}{m}\right]$$

The spantaneous emission ϵ_λ is given by:

$$\epsilon_\lambda = \frac{1}{4\pi}\frac{hc}{\lambda}N_u A_{ul} f(\lambda)\frac{\lambda^2}{c} \tag{2}$$

A_{ul} ist the Einstein coefficient of spontaneous emission from upper to lower energy state, N_u the density of the upper state and is the $f(\lambda)$ line shape. The absorption coefficient κ_λ is given by:

$$\kappa_\lambda = \frac{h}{\lambda}\left(B_{lu}N_l - B_{ul}N_u\right) f(\lambda)\frac{\lambda^2}{c} \tag{3}$$

with the Einstein coefficients of absorption and stimulated emission:

$$B_{ul} = \frac{1}{8\pi}\frac{\lambda^3}{h}A_{ul} \quad , \quad \left[\frac{m^3}{Js^2}\right] \tag{4}$$
$$B_{lu} = \frac{g_u}{g_l}B_{ul} \tag{5}$$

The ensities of the upper and lower states are given by the Boltmann distribution at local temperature T:

$$N_u = N\frac{g_u}{Q(T)}\exp\left(-\frac{E_u}{k_B T}\right) \tag{6}$$
$$N_l = N\frac{g_l}{Q(T)}\exp\left(-\frac{E_l}{k_B T}\right) \tag{7}$$

g_u and g_l are the degenercies of the upper and lower level respectively and Q(T) is the partition function.

2.2. Line Shapes

The main line broadening mechanisms is gases are natural line broadening, Doppler broadening and pressure broadening. Natural line broadening can be neglected. Pressure broadening is dominant in lower denser parts of the athmosphere whereas Doppler broadening becomes the dominat broadening mechanism in higher diluted regions of the athmosphere.

2.2.1. Doppler Broadeing

Doppler broadened line shapes are given by a Gaussian function:

$$f_G(\lambda) = \sqrt{\frac{\ln 2}{\pi \Delta\lambda^2}} \exp\left(-\frac{ln2}{\Delta\lambda^2}(\lambda - \lambda_0)^2\right) \tag{8}$$

$$\int_{-\infty}^{\infty} f_G(\lambda) d\lambda = 1 \tag{9}$$

with the half width at half maximum (HWHM) line width:

$$\frac{\Delta\lambda}{\lambda} = \frac{v}{c} = \frac{1}{c}\sqrt{\frac{2k_B T}{m}} \tag{10}$$

Doppler bradening is determined by the temperature and the mass of the particles.

2.2.2. Pressure Broadening

Pressure broadening is caused by the collisions between molecules, in the present model between N_2 and O_2 with CO_2. The main determining factors are the concentration of the collision partners and the collison frequency. The line shapes are given by a Lorentz function:

$$f_L(\lambda) = \frac{1}{\pi}\frac{\Delta\lambda}{(\lambda - \lambda_0)^2 + \Delta\lambda^2} \tag{11}$$

$$\int_{-\infty}^{\infty} f_L(\lambda) d\lambda = 1 \tag{12}$$

Contrary to the Gaussian line shapes of Doppler broadeing Lorentz functions have a much wider extend. In oder to keep computation times low the Lorentz functions have to be cut at a point. To estimate the introduced error the normlized Lorentz function is integrated from $-x_p$ to x_p:

$$F(x_p) = \frac{1}{\pi}\int_{-x_p}^{x_p} \frac{1}{1+x^2} dx = \frac{1}{\pi}(\arctan(x_p) - \arctan(-x_p)) \tag{13}$$

$F(x_p) = 0.9$ at $x_p \approx 6.3$, 0.97 at $x_p = 20$ and 0.99 at $x_p = 40$. In the absorption computations limit is set at $20\Delta\lambda$ so that approximatly 3% of the radiation power is missing. To compensate for this a backround of 3% of a moving average will be added.

2.3. Integration of the Radiation Transfer Equation

The intensity in Equation 1 is integrated along a path from the earth surface to the TOA (top of athmosphere) which is assumed to be at a heigth of $70km$. Assuming constant κ and ϵ in Equation 1 the solution is given by:

$$I(s) = I(s_0)\exp(-\kappa(s - s_0)) + \frac{\epsilon}{\kappa}(1 - \exp(-\kappa(s - s_0))) \tag{14}$$

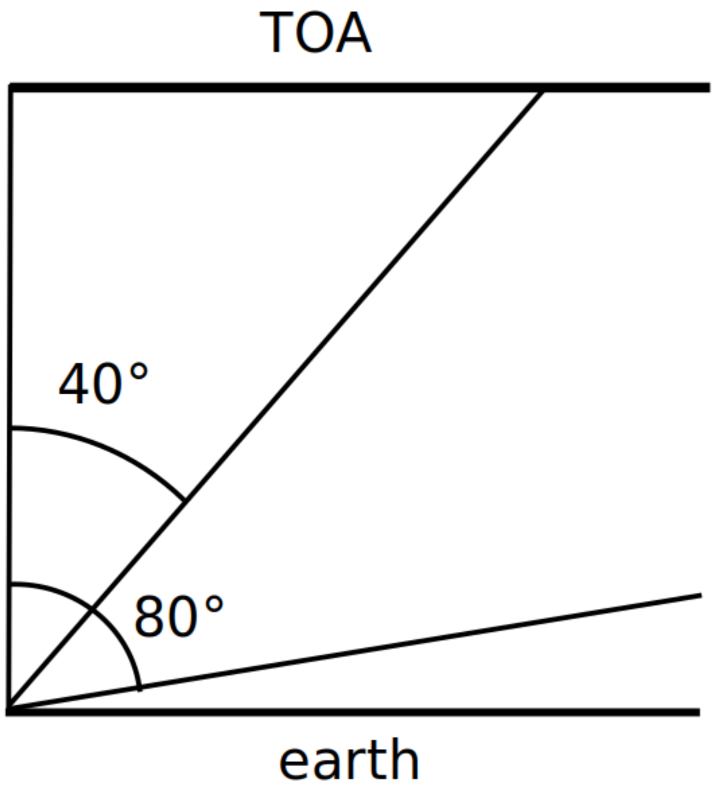

Figure 1: "Geometry of the athmosphere"

Because κ and ϵ are not constant along the path from earths surface to TOA the integration is subdivided into many steps. At each step κ and ϵ are aclculated using local values of temperature and density.

In order to compute the total irradiance emenating from an area element of the surface to TOA the integration has to be done over the half sphere:

$$F(\theta) = \int_0^{2\pi} \int_0^{\pi/2} I(\theta) \sin(\theta) \cos(\theta) d\theta d\phi \tag{15}$$

$$= 2\pi \int_0^{\theta} I(\theta) \sin(\theta) \cos(\theta) d\theta \tag{16}$$

The intensity $I(\theta)$ is computed at 0^o and two further angles (in the computations 40^o and 80^o are chosen), the intermedite values are interpolated by a cubic polnomial (Chapter

B). After determining the polynomial cofficients:

$$a_2 = \frac{(F_1 - F_0)\theta_2^3 - (F_2 - F_0)\theta_1^3}{\theta_1^2\theta_2^3 - \theta_1^3\theta_2^2} \tag{17}$$

$$a_3 = \frac{(F_2 - F_0)\theta_1^2 - (F_1 - F_0)\theta_2^2}{\theta_1^2\theta_2^3 - \theta_1^3\theta_2^2} \tag{18}$$

the integral is given by:

$$F(\theta) = 2\pi \int_0^\theta \left(a_0 + a_2\theta^2 + a_3\theta^3\right) \sin(\theta)\cos(\theta)d\theta d\phi \tag{19}$$

The contributions of the different polynomial orders assuming constant $I(\theta)$ are:

$$\int_0^\theta \sin(\theta)\cos(\theta)d\theta = 0.5$$
$$\int_0^\theta \theta^2\sin(\theta)\cos(\theta)d\theta = 0.37$$
$$\int_0^\theta \theta^3\sin(\theta)\cos(\theta)d\theta = 0.38$$

2.4. The HITRAN Data

The spectroscopic CO_2 data where taken from the HIRAN database ([2]). The standard HITRAN data files use a fixed size format and information that are not used in the present report. HITRAN allows to define ones own format and data output. For easier handling the entries are seperated by commas. The data rows are composed of:

1. Molecule ID, for CO_2 this is 2
2. Isotopologue ID, for CO_2 $1-9$
3. the transition wavenumber ν $[cm^{-1}]$
4. the line strength multiplied by isotopologue abunadance S, $[cm^{-1}/(molec\ cm^{-2}]$
5. Einstein coefficient of spontaneous emission A $[s^{-1}]$
6. pressure line broadeing coefficient by collisions with air molecules γ_{air} $[cm^{-1}atm^{-1}]$
7. pressure line broadeing coefficient by collisions with CO_2 molecules γ_{self} $[cm^{-1}atm^{-1}]$
8. energy of the lower state E" $[cm^{-1}]$
9. temperature exponent n_{air} for the air broadened HWHM
10. pressure shift induced by air δ_{air}, referred to $p = 1atm$ $[cm^{-1}atm^{-1}]$
11. upper state degeneracy g'

12. upper state degeneracy g"

In the present report wavelenght λ $[m]$ and energy $[J]$ is used, whereas HITRAN uses wavenumber $[cm^{-1}]$. The transition from wavelenth to wavenumber has to be done carefully.

$$
\begin{aligned}
\lambda_{ul} &\leftarrow \frac{10^{-2}}{\nu} && [m] \\
\Delta E_{ul} &\leftarrow \frac{hc}{\lambda_{ul}} && [J] \\
E_l &\leftarrow hc\frac{E''}{10^{-2}} && [J] \\
E_u &\leftarrow E_l + \Delta E_u l && [J] \\
\gamma_a &\leftarrow \frac{\gamma_{air}}{10^{-2}} 10^{-5} && \left[\frac{1}{m\ Pa}\right] \\
\gamma_s &\leftarrow \frac{\gamma_{self}}{10^{-2}} 10^{-5} && \left[\frac{1}{m\ Pa}\right] \\
\delta_a &\leftarrow \frac{\delta_{air}}{10^{-2}} 10^{-5}
\end{aligned}
$$

The HWHM Doppler line broadening is given by:

$$\alpha_D(T) = \frac{\nu_{ij}}{c}\sqrt{\frac{2N_A kT \ln 2}{M}}$$

The temperatue and pressure dependence of pressure broadened line width and pressure shift are defined by HITRAN as follows [1]:

$$
\begin{aligned}
\gamma(p,T) &= \left(\frac{T_{ref}}{T}\right)^{n_{air}} (\gamma_{air}(p_{ref}, T_{ref})(p - p_{self}) + \gamma_{self}(p_{ref}, T_{ref})p_{self}) \\
\nu_{ij}^* &= \nu_{ij}\delta(p_{ref})p
\end{aligned}
$$

Temperature dependent partition functions can be found at [3].

3. Results

4. Bibliography

[1] HITRAN. *Definitions and Units*. URL: https://hitran.org/docs/definitions-and-units/.

[2] HITRAN. *Main Page*. URL: https://hitran.org/.

[3] HITRAN. *Partition Functions*. URL: https://hitran.org/docs/iso-meta/.

A. Integration of the Radiation Transfer Equation

The radiation transfer equation Equation 1 is of the form:

$$\frac{dy}{dx} = -ay + b \tag{20}$$

If a and b are contant the solution can be written as:

$$y(x) = c(x)\exp(-ax) \tag{21}$$

Inserting into Equation 20 yields:

$$\frac{dy}{dx} = \frac{dc(x)}{dx}\exp(-ax) - ac(x)\exp(-ax) = -ac(x)\exp(-ax) + b \tag{22}$$

and further:

$$\frac{dc(x)}{dx} = b\exp(ax) \tag{23}$$

This can be integrated:

$$dc(x) = b\exp(ax)dx \tag{24}$$

$$\int_{c_0}^{c} dc(x) = b\int_0^x \exp(ax)dx \tag{25}$$

$$c - c_0 = \frac{b}{a}\left(\exp(ax) - 1\right) \tag{26}$$

And finally:

$$y(x) = y(0)\exp(-ax) + \frac{b}{a}\left(1 - \exp(-ax)\right) \tag{27}$$

B. Cubic Polynomial Interpolation

$$y(x) = a_0 + a_1x + a_2x^2 + a_3x^3 \tag{28}$$

With $a_0 = y(0)$ and $\frac{dy(0)}{dx} = 0$ it follows that $a_1 = 0$. The coefficients a_2 and a_3 are determined by the linear system:

$$y(x_1) = y(0) + a_2x_1^2 + a_3x_1^3 \tag{29}$$
$$y(x_2) = y(0) + a_2x_2^2 + a_3x_2^3 \tag{30}$$

which can be written as matrix equation:

$$x \begin{pmatrix} x_1^2 & x_1^3 \\ x_2^2 & x_2^3 \end{pmatrix} \begin{pmatrix} a_2 \\ a_3 \end{pmatrix} = \begin{pmatrix} y(x_1) - y(0) \\ y(x_2) - y(0) \end{pmatrix} \tag{31}$$

Using Cramer's rule the solution is given by:

$$a_2 = \frac{(y(x_1) - y(0))x_2^3 - (y(x_2) - y(0))x_1^3}{x_1^2 x_2^3 - x_1^3 x_2^2} \tag{32}$$

$$a_3 = \frac{(y(x_2) - y(0))x_1^2 - (y(x_1) - y(0))x_2^2}{x_1^2 x_2^3 - x_1^3 x_2^2} \tag{33}$$

C. Line Shapes

C.1. Gaussian Lineshape

$$\frac{\Delta\lambda}{\lambda} = \frac{v}{c} = \frac{1}{c}\sqrt{\frac{2k_B T}{m}} \tag{34}$$

$$\exp(-a x_h^2) = \frac{1}{2} \tag{35}$$

$$-a x_h^2 = \ln\frac{1}{2} \tag{36}$$

$$a = \frac{\ln 2}{x_h^2} \tag{37}$$

$$x_h = x_{hwhm} = \Delta\lambda \tag{38}$$

$$a = \frac{\ln 2}{\Delta\lambda^2} \tag{39}$$

$$\int \exp\left(-\frac{\ln 2}{\Delta\lambda^2}x^2\right) dx = \sqrt{\frac{\pi}{a}} \tag{40}$$

$$\sqrt{\frac{a}{\pi}} \int \exp\left(-\frac{\ln 2}{\Delta\lambda^2}x^2\right) dx = 1 \tag{41}$$

$$\sqrt{\frac{\frac{\ln 2}{\Delta\lambda^2}}{\pi}} \int \exp\left(-\frac{\ln 2}{\Delta\lambda^2}x^2\right) dx = 1 \tag{42}$$

$$\Delta\lambda = \frac{1}{c}\sqrt{\frac{2k_BT}{m}}\lambda \tag{43}$$

$$\sqrt{\frac{\ln 2}{\pi\Delta\lambda^2}}\int \exp\left(-\frac{\ln 2}{\Delta\lambda^2}(\lambda-\lambda_0)^2\right)dx = 1 \tag{44}$$

C.2. Lorentz Lineshape

$$L(\nu) = \frac{a^2}{(\nu-\nu_0)^2 + a^2} \tag{45}$$

$$L(\nu_0) = 1 \tag{46}$$

$$L(\nu_h) = 1/2 = \frac{a^2}{(\nu_h-\nu_0)^2 + a^2} \tag{47}$$

$$(\nu_h-\nu_0)^2 + a^2 = 2a^2 \tag{48}$$

$$(\nu_h-\nu_0) = \Delta\nu = a \tag{49}$$

$$L(\nu) = \frac{\Delta\nu^2}{(\nu-\nu_0)^2 + \Delta\nu^2} \tag{50}$$

$$L(\lambda) = \frac{b^2}{c^2(1/\lambda - 1/\lambda_0)^2 + b^2} \tag{51}$$

$$L(\lambda) = \frac{b^2}{c^2\left(\frac{\lambda-\lambda_0}{\lambda\lambda_0}\right)^2 + b^2} \tag{52}$$

$$L(\lambda) = \frac{b^2\lambda^2\lambda_0^2}{c^2}\frac{1}{(\lambda-\lambda_0)^2 + \lambda^2\lambda_0^2 b^2/c^2} \tag{53}$$

$$L(\lambda_0) = 1 \tag{54}$$

$$L(\lambda_h) = \frac{1}{2} = \frac{b^2\lambda_h^2\lambda_0^2}{c^2} \frac{1}{(\lambda_h - \lambda_0)^2 + \lambda_h^2\lambda_0^2 b^2/c^2} \tag{55}$$

$$2\frac{b^2\lambda_h^2\lambda_0^2}{c^2} = (\lambda_h - \lambda_0)^2 + \lambda_h^2\lambda_0^2 b^2/c^2 \tag{56}$$

$$\frac{b^2\lambda_h^2\lambda_0^2}{c^2} = (\lambda_h - \lambda_0)^2 \tag{57}$$

$$\frac{b^2}{c^2} = (\lambda_h - \lambda_0)^2 \frac{1}{\lambda_h^2\lambda_0^2} \tag{58}$$

$$L = (\lambda_h - \lambda_0)^2 \frac{1}{(\lambda - \lambda_0)^2 + (\lambda_h - \lambda_0)^2} \tag{59}$$

$$\Delta\lambda_{hwhm} = \lambda - \lambda_0 \tag{60}$$

$$L = \frac{\Delta\lambda^2}{(\lambda - \lambda_0)^2 + \Delta\lambda^2} \tag{61}$$

$$\int_{-\infty}^{-\infty} \frac{1}{1 + x^2} dx = \arctan(\infty) - \arctan(-\infty) = \pi \tag{62}$$

$$x = \frac{(\lambda - \lambda_0)}{\Delta\lambda} \tag{63}$$

$$dx = \frac{1}{\Delta\lambda} d\lambda \tag{64}$$

$$L = \frac{\frac{1}{\pi}\Delta\lambda}{(\lambda - \lambda_0)^2 + \Delta\lambda^2} \tag{65}$$

$$L = \frac{1}{\pi} \frac{\Delta\lambda}{\left(\lambda - \lambda_0\right)^2 + \Delta\lambda^2} \tag{66}$$

$$\int \frac{1}{\pi} \frac{\Delta\lambda}{\left(\lambda - \lambda_0\right)^2 + \Delta\lambda^2} d\lambda = 1 \tag{67}$$

$$\int \frac{1}{\pi} \frac{\Delta\lambda}{\left(\lambda - \lambda_0\right)^2 + \Delta\lambda^2} d\lambda = 1 \tag{68}$$

D. Supplementary Material

E. Line Strength

$$(S/d)_n = \frac{1}{\Delta\nu} \sum_j S_j(T_n) \tag{69}$$

$$S_j(T_n) = \frac{Q_r(T_s)Q_v(T_s)}{Q_r(T_n)Q_v(T_n)} \frac{1 - \exp(-h\nu_j/k_B/T_s)}{1 - \exp(-h\nu_j/k_B/T_n)} \exp\left(\frac{E_j T_n T_s}{k_B T_0 T_s}\right) S_j(T_s) \tag{70}$$

$$\gamma(T, p) = \gamma(T_0, p_0) \frac{p}{p_0} \left(\frac{T_0}{T}\right)^{x_m} \tag{71}$$

$$T_0 = 273.15K \tag{72}$$

$$p_0 = 1013.25mbar \tag{73}$$

$$x_m = 3/4 \tag{74}$$

E.1. Radiation Transfer Equation in Frequency Space

$$\frac{dI_\nu}{ds} = -\kappa_\nu I_\nu + \epsilon_\nu \tag{75}$$

$$I_\nu : \left[\frac{W}{m^2\ sr\ Hz}\right] \tag{76}$$

$$\epsilon_\nu : \left[\frac{W}{m^3\ sr\ Hz}\right] \tag{77}$$

$$\kappa_\nu : \left[\frac{1}{m}\right] \tag{78}$$

$$\epsilon_\nu = \frac{1}{4\pi} h\nu N_u A_{ul} f(\nu) \quad , \quad \left[\frac{W}{m^3 sr Hz}\right] \tag{79}$$

$$\int f(\nu) d\nu = 1 \tag{80}$$

E.1.1. Equilibrium

$$\frac{dI_\nu}{ds} = -\kappa_\nu I_\nu + \epsilon_\nu = 0 \tag{81}$$

E.1.2. Planck

$$u_\nu = \frac{4\pi}{c^3}\frac{2h\nu^3}{} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \quad , \quad \left[\frac{J}{m^3 Hz}\right] \tag{82}$$

with:

$$I_\nu = \frac{u_\nu}{4\pi} c \tag{83}$$

$$I_\nu = \frac{2h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \quad , \quad \left[\frac{W}{m^2 sr Hz}\right] \tag{84}$$

$$\kappa_\nu = \frac{1}{4\pi} h\nu N_u A_{ul} f(\nu) \quad \left(\exp\left(\frac{h\nu}{k_B T}\right) - 1\right) \frac{c^2}{2h\nu^3} \quad , \quad \left[\frac{1}{m}\right] \tag{85}$$

$$\kappa_\nu = \frac{1}{8\pi} \frac{c^2}{\nu^2} N_u A_{ul} \left(\exp\left(\frac{h\nu}{k_B T}\right) - 1\right) f(\nu) \quad , \quad \left[\frac{1}{m}\right] \tag{86}$$

$$\kappa_\nu = \frac{h\nu}{c} \left(N_l B_{lu} - N_u B_{ul}\right) f(\nu) \tag{87}$$

$$\kappa_\nu = \frac{h\nu}{c} N \left(g_l \exp\left(-\frac{E_l}{k_B T}\right) B_{lu} - g_u \exp\left(-\frac{E_u}{k_B T}\right) B_{ul}\right) f(\nu) \tag{88}$$

$$\kappa_\nu = \frac{h\nu}{c} N \exp\left(-\frac{E_u}{k_B T}\right) \left(\exp\left(-\frac{(E_u - E_l)}{k_B T}\right) g_l B_{lu} - g_u B_{ul}\right) f(\nu) \tag{89}$$

$$g_l B_{lu} = g_u B_{ul} \tag{90}$$

$$\kappa_\nu = \frac{h\nu}{c} N g_u B_{ul} \exp\left(-\frac{E_u}{k_B T}\right) \left(\exp\left(-\frac{h\nu}{k_B T}\right) - 1\right) f(\nu) \tag{91}$$

$$\kappa_\nu = \frac{h\nu}{c} B_{ul} N_u \left(\exp\left(-\frac{h\nu}{k_B T}\right) - 1\right) f(\nu) \quad , \quad \left[\frac{1}{m}\right] \tag{92}$$

$$\frac{h\nu}{c} B_{ul} N_u = \frac{1}{8\pi} \frac{c^2}{\nu^2} N_u A_{ul} \tag{93}$$

$$B_{ul} = \frac{1}{8\pi} \frac{c^3}{h\nu^3} A_{ul} \quad , \quad \left[\frac{m^3}{J s^2}\right] \tag{94}$$

E.2. Radiation Transfer Equation in Wavelength Space

$$I_\lambda = \frac{2\pi h c^2}{\lambda^5} \frac{1}{\exp\left(\dfrac{hc}{\lambda k_B T}\right) - 1} \tag{95}$$

$$I = \int I_\lambda d\lambda \tag{96}$$

$$I_\nu d\nu = I_\lambda d\lambda \tag{97}$$

$$\nu = \frac{c}{\lambda} \tag{98}$$

$$d\nu = -\frac{c}{\lambda^2} d\lambda \tag{99}$$

$$I_\nu \frac{c}{\lambda^2} d\lambda = I_\lambda d\lambda \tag{100}$$

$$I_\nu \frac{c}{\lambda^2} = I_\lambda \tag{101}$$

$$I_\nu = I_\lambda \frac{\lambda^2}{c} \tag{102}$$

$$\frac{dI_\lambda}{ds} = -\kappa_\lambda I_\lambda + \epsilon_\lambda \tag{103}$$

$$\kappa_\lambda = \frac{h}{\lambda_0} \left(N_l B_{lu} - N_u B_{ul}\right) f(\lambda) \frac{\lambda^2}{c} \tag{104}$$

$$\kappa_\lambda = \frac{h\lambda}{c} \left(N_l B_{lu} - N_u B_{ul}\right) f(\lambda) \quad , \quad \left[\frac{1}{m}\right] \tag{105}$$

$$\epsilon_\nu f(\nu) d\nu = \epsilon_\lambda f(\lambda) d\lambda \tag{106}$$

$$f(\nu) d\nu = f(\lambda) d\lambda \tag{107}$$

$$\epsilon_\nu = \epsilon_\lambda \tag{108}$$

$$\epsilon_\lambda = \frac{1}{4\pi} \frac{hc}{\lambda} N_u A_{ul} f(\lambda) \quad , \quad \left[\frac{W}{m^3 sr\ m}\right] \tag{109}$$

$$\int f_\lambda d\lambda = 1 \tag{110}$$

$$B_{ul} = A_{ul}\frac{\lambda^3}{8\pi h} \quad , \quad \left[\frac{m^3}{Js^2}\right] \tag{111}$$

$$B_{lu} = \frac{g_u}{g_l}B_{ul} \tag{112}$$

$$< \epsilon >= \int \epsilon_\lambda(\lambda)d\lambda \tag{113}$$

$$< \kappa >= \frac{\int \kappa_\lambda(\lambda)I_\lambda(\lambda)d\lambda}{\int I_\lambda(\lambda)d\lambda} \tag{114}$$

In thermal equilibrium the intensity is constant:

$$\frac{dI_\lambda}{ds} = -\kappa_\lambda I_\lambda + \epsilon_\lambda = 0 \tag{115}$$

$$\kappa_\lambda = \frac{\epsilon_\lambda}{I_\lambda} \tag{116}$$

and the intensity is given by Planck's formula:

$$I_\lambda = \frac{2hc^2}{\lambda^5}\frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \tag{117}$$

With this the net absorption coefficient κ_λ is:

$$\kappa_\lambda = \frac{\frac{1}{4\pi}\frac{hc}{\lambda}N_u A_{ul} f(\lambda)}{\frac{2hc^2}{\lambda^5}\frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1}} = \frac{\lambda^4}{8\pi c}A_{ul}N_u\left(\exp\left(\frac{hc}{\lambda k_B T}\right) - 1\right) f(\lambda) \tag{118}$$

The densities of upper and lower state are given by:

$$N_u = N\frac{g_u}{Q(T)}\exp\left(-\frac{E_u}{k_B T}\right) \tag{119}$$

$$N_l = N\frac{g_l}{Q(T)}\exp\left(-\frac{E_l}{k_B T}\right) \tag{120}$$

which yields:

$$\kappa_\lambda = \frac{\lambda^4}{8\pi c}A_{ul}N\frac{g_u}{Q(T)}\left(\exp\left(-\frac{E_l}{\lambda k_B T}\right) - \exp\left(-\frac{E_u}{\lambda k_B T}\right)\right) f(\lambda) \tag{121}$$

With:

$$B_{ul} = \frac{1}{8\pi}\frac{\lambda^3}{h}A_{ul} \quad , \quad \left[\frac{m^3}{Js^2}\right] \tag{122}$$

$$B_{lu} = \frac{g_u}{g_l}B_{ul} \tag{123}$$

this becomes

$$\kappa_\lambda = \frac{h\lambda}{c}\left(B_{ul}N\frac{g_u}{Q(T)}\exp\left(-\frac{E_l}{\lambda k_B T}\right) - B_{lu}N\frac{g_l}{Q(T)}\exp\left(-\frac{E_u}{\lambda k_B T}\right)\right)f(\lambda) \tag{124}$$

and:

$$\kappa_\lambda = \frac{h\lambda}{c}\left(B_{lu}N_l - B_{ul}N_u\right)f(\lambda) \tag{125}$$

F. Random

$$g_1 B_{12} = g_2 B_{21} \tag{126}$$

$$A_{21} = 8\pi h\nu^3 B_{21} \tag{127}$$

$$\kappa(\nu - \nu_0) = (N_1 B_{12} - N_2 B_{21})\frac{h\nu_0}{c}f(\nu - \nu_0) \tag{128}$$

$$S = \frac{1}{N}(N_1 B_{12} - N_2 B_{21})\frac{h\nu_0}{c} \tag{129}$$

$$S = \frac{g_2}{Q_{tot}(T)}\frac{A_{21}}{8\pi c\nu_0^2}\exp(-E_1/k_B T)(1 - \exp(-h\nu_0/k_B T)) \tag{130}$$

Power per unit area

$$B(\nu, T) = \frac{2\pi h\nu^3}{c^2}\frac{1}{\exp(h\nu/k_B T) - 1} \tag{131}$$

$$\frac{dI_\nu}{dz} = -\alpha_\nu(I_\nu - B(\nu, T)) \tag{132}$$

$$\alpha_\nu = N\sigma_\nu \tag{133}$$

$$\sigma_\nu = \sum_i \frac{S_i}{\pi} \frac{\gamma_i}{\gamma_i^2 + (\nu - \nu_i)^2} \tag{134}$$

$$B_{ul} = A_{ul} \frac{8\pi h \nu_0^3}{c^3} \tag{135}$$

$$\epsilon_\nu = \frac{h\nu}{4\pi} N_u A_{ul} f(\nu) \tag{136}$$

$$\kappa_\nu = \frac{h\nu_0}{c} (N_l B_{lu} - N_u B_{ul}) f(\nu) \tag{137}$$

$$\frac{dI_\nu}{ds} = -\kappa_\nu I_\nu + \epsilon_\nu \tag{138}$$

Equlibrium

$$\frac{dI_\nu}{ds} = -\kappa_\nu I_\nu + \epsilon_\nu = 0 \tag{139}$$

$$I_\nu = \frac{2h\nu^3}{c^2} \frac{1}{\exp(h\nu/k_B T) - 1} \tag{140}$$

$$u_\nu = \frac{4\pi 2h\nu^3}{c^3} \frac{1}{\exp(h\nu/k_B T) - 1} \tag{141}$$

$$I_\nu = \frac{u_\nu}{4\pi} c \tag{142}$$

$$\kappa_\nu I_\nu = \epsilon_\nu = \frac{h\nu}{4\pi} N_u A_{ul} \tag{143}$$

$$\kappa_\nu = \frac{h\nu}{4\pi} N_u A_{ul} (\exp(h\nu/k_B T) - 1) \frac{c^2}{2h\nu^3} \tag{144}$$

$$I_\nu = \frac{2\pi h\nu^3}{c^2} \frac{1}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \tag{145}$$

$$I = \int I_\nu d\nu \tag{146}$$

$$\frac{dI_\nu}{ds} = -\kappa_\nu I_\nu + \epsilon_\nu \tag{147}$$

$$\kappa_\nu = \frac{h\nu_0}{c} \left(N_l B_{lu} - N_u B_{ul}\right) f(\nu) \tag{148}$$

$$\epsilon_\nu = \frac{1}{4\pi} h\nu_0 N_u A_{ul} f(\nu) \tag{149}$$

$$\int f_\nu d\nu = 1 \tag{150}$$

$$B_{ul} = A_{ul} \frac{c^3}{8\pi h\nu^3} \tag{151}$$

$$B_{lu} = \frac{g_u}{g_l} B_{ul} \tag{152}$$

F.1. Wavlengths Average Absorption

$$\frac{dI(\lambda)}{ds} = -I(\lambda)\kappa(\lambda) \tag{153}$$

The absorption is a sum of line absorptions:

$$\kappa(\lambda) = \sum_i \kappa_i(\lambda_i) f_i(\lambda) \tag{154}$$

Integrating over wavelengths:

$$\frac{d}{ds} \int_{\Delta\lambda} I(\lambda) d\lambda = -\sum_i \int_{\Delta\lambda} I(\lambda)\kappa_i(\lambda_i) f_i(\lambda) d\lambda \tag{155}$$

Assuming that the intensity is constant within the integration intervall:

$$\frac{dI}{ds} = -\frac{I}{\Delta\lambda}\sum_i \kappa_i(\lambda_i)\int_{\Delta\lambda} f_i(\lambda)d\lambda \tag{156}$$

$$= -\frac{I}{\Delta\lambda}\sum_i \kappa_i(\lambda_i) \tag{157}$$

Integrating along the path:

$$\frac{dI}{I} = -\frac{1}{\Delta\lambda}\sum_i \kappa_i(\lambda_i)ds \tag{158}$$

yields:

$$\ln\frac{I(z)}{I(z_0)} = -\frac{1}{\Delta\lambda}\int_{z_0}^{z}\sum_i \kappa_i(\lambda_i)ds \tag{159}$$

and finally:

$$I(z) = I(z_0)\exp\left(-\frac{1}{\Delta\lambda}\int_{z_0}^{z}\sum_i \kappa_i(\lambda_i)ds\right) \tag{160}$$

With $\int_{z_0}^{z}\sum_i \kappa_i(\lambda_i)ds \approx 210^{-3}$ the intensity at TOA is near zero, that means all the intensity is absorbed. This of course is wrong. The false assumption is that the intensity along the path in the atmosphere is independent of wavelength.

F.2. Reinhart

Equation (8) and (9):

$$dI_a(u_j) = S_0 f(u_j)\Delta u_j\left(1 - \exp\left(-\int \alpha(\rho, u_j)d\rho\right)\right)2\pi\cos\theta\sin\theta d\theta \tag{161}$$

In Reinhart the expression for $\alpha(\rho, u_j)$ is not explicitely given, so the value of κ_i as defined above is taken.

$$f(u) = \frac{15}{\pi^4}\frac{u^3}{\exp(u) - 1} \tag{162}$$

$$u = \frac{h\nu}{k_B T} \tag{163}$$

$$S_0 = \sigma T^4 \tag{164}$$

If $\exp\left(-\int \alpha(\rho, u_j)d\rho\right)$ only depends slightly on the angle θ the integral over *theta* is:

$$\int_0^{\pi/2} 2\pi\cos\theta\sin\theta d\theta = \pi \tag{165}$$

Sum over all lines:

$$F = \sum_j I_a(u_j) = \sum_j S_0 f(u_j)\Delta u_j \left(1 - \exp\left(-\int \alpha(\rho, u_j)d\rho\right)\right) \tag{166}$$

The sum $F = \pi S_0 \sum_j f(u_j)\Delta u_j$ has to equal the intensity emitted from the earth surface. Assuming $f(u_j)\Delta u_j$ approximately constant:

$$\sum_j \left(1 - \exp\left(-\int \alpha(\rho, u_j)d\rho\right)\right) \tag{167}$$

is the relative absorption. The value in the line intervall $[12 - 18\mu m]$ is 1.810^{-3} at 400 ppm CO_2 and 3.610^{-3} at 800 ppm CO_2. If instead of κ_i $\kappa_i/\Delta\lambda$ is taken for α the values are 2.410^4 and 2.810^4 respectively. The integral

If the angle between surface normal and the path direction is θ the path lngth as function of the height z measured from the surface is given by:

$$s = \frac{z}{\cos\theta} \tag{168}$$

Assuming constant κ and ϵ in Equation 1 the solution is given by:

$$I = c(s)\exp(-\kappa s) \tag{169}$$

Inserting into Equation 1 yields:

$$\frac{dI}{ds} = \frac{dc(s)}{ds}\exp(-\kappa s) - \kappa c(s)\exp(-\kappa s) = -\kappa c(s)\exp(-\kappa s) + \epsilon \tag{170}$$

and:

$$\frac{dc(s)}{ds} = \epsilon \exp(\kappa s) \tag{171}$$

Transforming

$$\frac{dc(s)}{\epsilon} = \exp(\kappa s)ds \tag{172}$$

$$\int_{c_0}^{c} \frac{dc(s)}{\epsilon} = \int_0^z \exp(\kappa s)ds \tag{173}$$

$$\frac{c - c_0}{\epsilon} = \frac{1}{\kappa}\left(\exp(\kappa z) - 1\right) \tag{174}$$

$$c = c_0 + \epsilon\frac{1}{\kappa}\left(\exp(\kappa z) - 1\right) \tag{175}$$

$$I = c_0\exp(-\kappa z) + \epsilon\frac{1}{\kappa}\left(1 - \exp(-\kappa z)\right) \tag{176}$$

$$I = I(0)\exp(-\kappa z) + \frac{\epsilon}{\kappa}\left(1 - \exp(-\kappa z)\right) \tag{177}$$