Advanced radiation and remote sensing

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Contents

1   Introduction

This course is a continuation of the course *radiation and remote sensing* in the bachelor program. Its goal is to recapitulate the most important material of the previous course and to give an extended knowledge on the physical processes involved like spectroscopy, thermal radiation etc., in order to be able to work with our radiative transfer model ARTS. After the course, you should have a deeper understanding of radiation and remote sensing, and you should be able to use ARTS and the tools around it for your own projects.

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Modus operandi

The course consists of a mixture of short lecture and a lot of practical exercises. Don't expect any polish. Don't even expect everything to work properly.

Examination

As an exam, you are expected to investigate a small remote sensing or radiation problem of your own choice. (Hopefully, you will find some inspiration for a project during the course.) You have to present your results in the last week of the course in a 10 minute presentation. Presentations will be graded, and the grade will be based on the criteria ambition level, originality, figure quality, and presentation quality.

Contributions

Many have contributed to this course: Theresa Mieslinger and Theresa Lang prepared the initial exercises, based on my old exercises from a course given at the University of Bremen, together with Björn-Martin Sinnhuber. I have used some ideas from Björn-Martin's old course

notes, particularly in the area of rotational spectra.

The script is based on my handwritten notes from the first pass of the course. Lukas Kluft created the basic LaTeX structure and the initial draft of Section 4. Theresa Lang created the initial draft of Section 7. Christoph Sauter, Jakob Doerr, and Laura Dietrich created initial drafts of other sections from my notes.

Recommended reading

Fundamentals of molecular spectroscopy by C. N. Banwell and E. M. McCash (Mc Graw Hill Verlag).

2 Practical information

This section can be also be found online on our webpage at https://www.mi.uni-hamburg.de/en/arbeitsgruppen/strahlung-und-fernerkundung/intern/howtos/arts-lecture.html.

Getting started

The material needed for the course is distributed via a subversion repository. Subversion is a version control system and can be used via the command line client svn.

These steps have to be done only once:

```
cd ~
svn co https://arts.mi.uni-hamburg.de/svn/rt/arts-lectures/trunk arts-lectures
```

Setting up the environment (do this once in every new terminal)

Every time you open a new terminal, you need to source the course environment. If you know that your default shell (echo $SHELL) is bash and not tcsh, you can skip the first command:

```
bash --login
source ~/arts-lectures/bin/arts-init.bash
```

You can check if the ARTS model is found by running:

```
arts --version
```

Updating the lecture package

Use the `svn update` command to ensure that you have the latest version of the lecture files:

```
cd ~/arts-lectures
svn update
```

Getting the lecture notes

Change to the directory `script/` and run make:

```
cd ~/arts-lectures/script
make
```

This will generate two PDF files, one optimised for viewing on the screen, one optimised for printing.

Running the exercises

Don't forget to run the `source` command from the subsection 'Setting up the environment'
above. You need to do this every time you open a new terminal.

Change to the directory of the exercise and run arts for the exercise controlfile. This example
runs the first exercise:

```
cd ~/arts-lectures/exercises/01-rotational_spectra
arts absorption.arts
```

This will run the ARTS program on the exercise controlfile. ARTS writes several output files
that can be found in the `results/` directory.

To plot the results you can use the Python script in the exercise directory, which you can run
by typing:

```
python plot_xsec.py
```

This script will write the plots as PDF files in the `plots/` subdirectory. You can use Evince
to display the plots:

```
evince plots/plot_xsec_N2O_800hPa_300K.pdf
```

3 Absorption coefficients and absorption cross-sections

The law of Lambert, Beer, and Bouguer describes how radiation is absorbed by a gas in a transmission experiment:

$$\mathrm{dI}(\nu)/\mathrm{ds} = \alpha(\nu)\mathrm{I}(\nu) \qquad \mathrm{I}_1(\nu) = \mathrm{I}_0(\nu)\exp\left(\int \alpha(\nu)\mathrm{ds}\right) \tag{1}$$

where I is radiation intensity (in $\mathrm{W/m^2/sr/Hz}$), ds is distance in the direction in which the radiation travels, $\alpha(\nu)$ is the *absorption coefficient* (in $1/\mathrm{m}$), and ν is frequency (in Hz). We can take the above equations as the definition of α.

For a gas, $\alpha(\nu)$ is richly structured; it contains *spectral lines* at certain frequencies where absorption is strongly enhanced, and regions of little (or in any case less) absorption in-between.

These lines come from quantum mechanics, to understand them we need to understand the

physical properties of single gas molecules. The absorption coefficient $\alpha(\nu)$ can in good approximation be decomposed as

$$\alpha(\nu) = n\sigma(\nu) \tag{2}$$

where n is the number density (in $1/\text{m}^3$) of the absorbing molecule and $\sigma(\nu)$ is the *absorption cross-section* (in m^2). Cross-section on one hand refers to the unit, on the other hand it allows also a simple geometrical interpretation of the molecules as radiation-intercepting objects of a given cross-sectional area. The linearity in the equation implies that the concentration of the molecules is so low, that they do not 'shadow' each other; twice as many molecules means twice as much radiation absorbed. Earth's atmosphere is so tenuous that this approximation is always valid.

We can now turn to the physics underlying the absorption cross-section $\sigma(\nu)$.

4   Energy states and photons

Absorption and emission of a photon can happen if the internal energy of a molecule changes. The difference in two energy states E and the frequency of the photon ν are connected through the Planck constant h.

$$E_f - E_i = \Delta E = h\nu \tag{3}$$

Figure 1 is a graphical illustration of the above equation.

The transitions between different energy levels can be divided into three types, corresponding to different states of the molecule, as show in Figure 2. Each transition type is characteristic for a specific region of the electro-magnetic spectrum. One can distinguish changes in a molecules rotation (microwave), vibration (infrared) and electronic transitions (UV/visible).

Molecules consist of different atoms. There are diatomic molecules with two atoms (O_2, N_2, NO, HCl, CO) and polyatomic molecules with three or more atoms (O_3, NO_2, CO_2). We will mainly discuss diatomic molecules, because they are easier to understand.

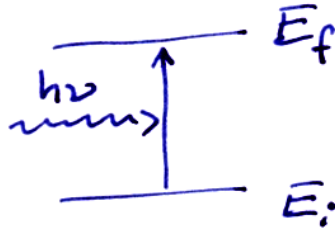As shown in Figure 3, one can distinguish between three types of interaction between a photon

Figure 1: Schematic drawing of a molecular energy transition.

and a molecule: absorption, spontaneous emission and stimulated emission.

There are three conditions to be fulfilled for a molecule to absorb a photon:

1. The frequency of the photon has to match one of the molecule's energy transitions.
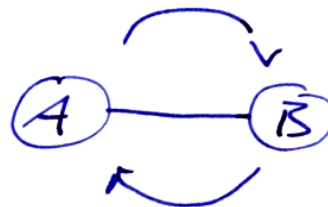
$$\Delta E = h\nu \tag{4}$$

2. The net absorption has to be proportional to the difference of occupation probabilities of states i and f: $p_i - p_f$. Where p_i is given by the Boltzmann distribution (in local

Transition types
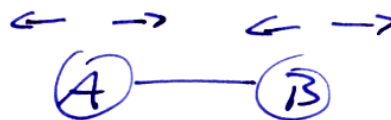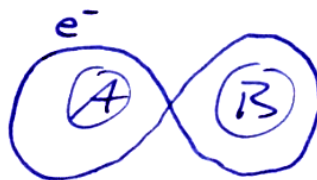
Energy levels of a molecule are due to:

- rotation

micro-wave

- vibration

infra-red

- electronic transitions

uv/visible

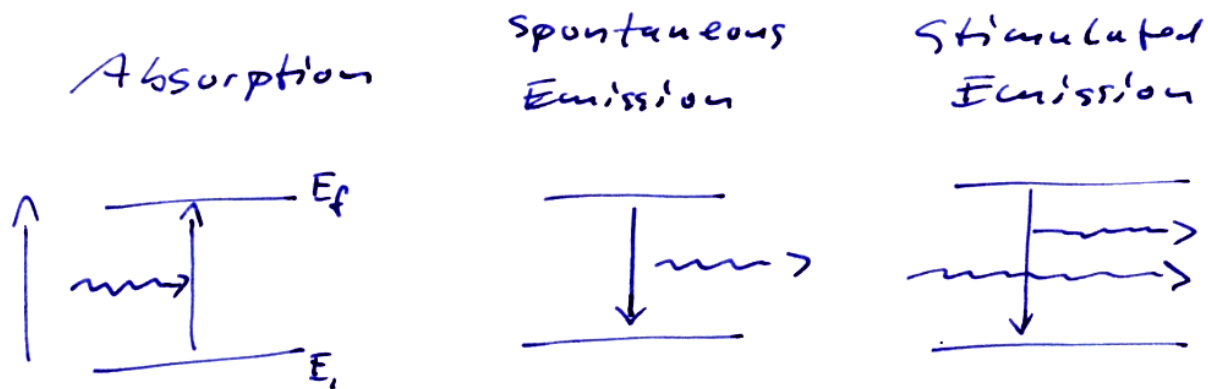Figure 2: Types of molecular energy transitions.

Figure 3: Ways for a molecule to interact with radiation.

thermodynamic equilibrium).

$$p_i = \frac{q_i e^{-E_i/(kT)}}{\sum_{j=1}^{\infty} q_j e^{-E_j/(kT)}} \tag{5}$$

The denominator is often referred to as $Q(T)$. It has various names like total internal partition sum, partition function, or Zustandssumme. The variable q_i (or q_j) is called degeneracy factor. It is needed in order to take into account that an energy level can exist more than once.

3. Absorption is proportional to the electric dipole matrix element μ_{if} between states i and f.

$$\mu_{if} = \mu \iiint \psi_f^*(x, y, z) \psi(x, y, z) \, dx \, dy \, dz \tag{6}$$

Where μ is the magnitude of the dipole operator, μ_{if} is a constant for each transition and ψ is the wave function from quantum mechanics.

Combining all conditions, one can define the absorption coefficient α.

$$\alpha(\nu) = n \sum_{f,i} S_{fi}(T)\delta(\nu_{fi} - \nu) \tag{7}$$

With number density n, line strength S_{fi}, difference of state energies $h\nu_{fi}$ and Dirac's delta function δ (physically not true, will be replaced later by a so called "line shape" function.

The line strength is different for each transition and defined as follows.

$$S_{fi} = \frac{8\pi^3 \nu_{fi} |\mu_{fi}|^2 q_i}{3hcQ(T)} \left(e^{E_i/(kT)} - e^{E_f/(kT)} \right) \tag{8}$$

Although this equation looks complicated, there is only one truly independent variable, the temperature T. All other variables are constants of the transition, or fundamental constants.

Spectral line catalogues are collections of these transition parameters. There is one line in the catalogue for each spectral line (thousands for each molecule). The most well-known is the HITRAN catalogue.

5   Rotational spectra

5.1   Moment of inertia and classical rotational energy

The kinetic energy E of a mass m moving linearly at a speed v is

$$E = \frac{1}{2}mv^2 \quad .$$
(9)

Using the definition of the momentum p (*German: Impuls*)

$$p = mv \quad ,$$
(10)

this can also be written as

$$E = \frac{p^2}{2m} \quad .$$
(11)

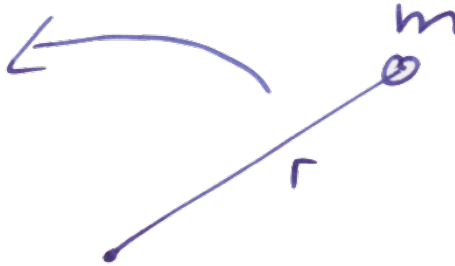Now imagine a mass that is not moving linearly, but **rotating**, as sketched in Figure 4. The

Figure 4: Sketch of a rotating mass.

formula for the kinetic energy of a rotation looks very similar to the linear case:

$$E_r = \frac{1}{2}I\omega^2 = \frac{J^2}{2I} \quad , \tag{12}$$

only velocity v is replaced by the **angular velocity** ω (*German: Winkelgeschwindigkeit*), the mass m is replace by the **moment of inertia** I (*German: Trägheitsmoment*), and the momentum p is replace by the **angular momentum** J (German: Drehimpuls).

These are defined as:

$$\omega = \frac{d\phi}{dt} \quad , \tag{13}$$

where ϕ is the angle of rotation,

$$I = mr^2 \quad , \tag{14}$$

where r is the distance from the axis of rotation, and

$$J = I\omega \quad . \tag{15}$$

The moment of inertia I is a measure of how 'massive' an object appears with respect to rotation.

5.2 Using moments of inertia to classify molecules

Any real object can not only rotate around a single axis, but could rotate around any axis, and the moment of inertia I depends on the axis of rotation. We can describe any object by its three main axes of rotation (the symmetry axes) and the associated three moments of inertia I_A, I_B, I_C. (More exactly speaking, the inertia in the general case is a 3x3 tensor, which becomes diagonal if the coordinate system is aligned properly; the moments of inertia are the eigenvalues of this tensor.)

We can use the moments of inertia to classify the molecules and divide them into groups, as shown in Figure 5.

5.3 Rotational energy for the special case of a diatomic molecule

It is a good idea to first focus on the simplest type of molecule, consisting of only two atoms. It can rotate around two axes, but has the same moment of inertia for both.

Generalising Equation 14, the total moment of inertia for a collection of masses can be calcu-
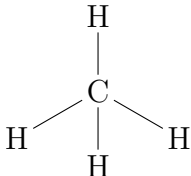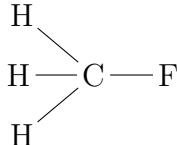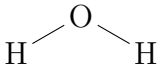
Linear	Spherical top	Symmetric top	Asymmetric top
H—Cl	(CH$_4$ structure)	(CH$_2$F structure)	(H$_2$O structure)
$I_A \approx 0$, $I_B = I_C$	$I_A = I_B = I_C$	$I_A \neq 0$, $I_B = I_C \neq I_A$	$I_A \neq I_B \neq I_C$

Figure 5: Using moments of inertia to classify molecules with different symmetry.

lated as the sum of the moment of inertia for each individual mass:

$$I = \sum_i m_i r_i^2 \quad . \tag{16}$$

We have to know the axis of rotation, so that we can calculate all the r_i.

Per definition, the molecule will rotate around its **center of gravity**. (If the center of gravity would move, there would be a translational motion of the entire molecule, but here we want to focus on rotation as a internal degree of freedom of the molecule.) The center of gravity has the property that

$$m_1 r_1 = m_2 r_2 \tag{17}$$

The geometry is as shown in Figure 6. It can be shown, that this two-body problem can be reduced to an equivalent one-body problem, the rotation of a single mass μ around an axis at a distance r_0, which simply is given by

$$r_0 = r_1 + r_2 \quad . \tag{18}$$
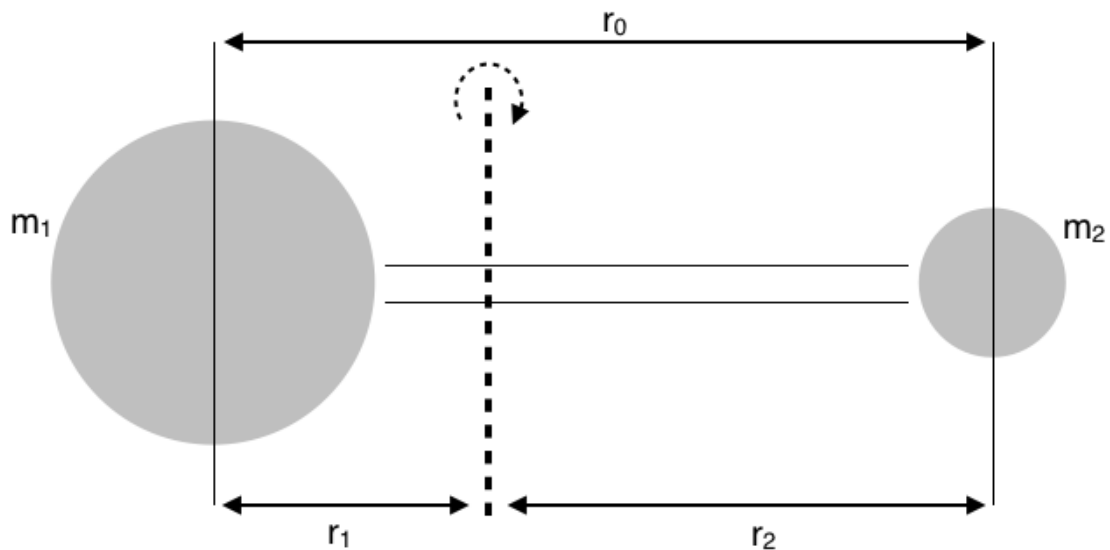
Figure 6: Sketch of a diatomic and asymmetric molecule of atomic masses m_1 and m_2 at a distance of r_0.

5.3 Rotational energy for the special case of a diatomic molecule

The **reduced mass** μ is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad , \tag{19}$$

or equivalently

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad . \tag{20}$$

The reduced mass is very useful, because the moment of inertia follows directly from it and the interatomic distance r_0:

$$I = \mu r_0^2 \quad , \tag{21}$$

and then the rotational energy can be calculated from Equation 12.

It is instructional to look at two extreme cases for the reduced mass:

$$(m_1 >> m_2) \quad \Rightarrow \quad \mu = \frac{m_2}{(m_1 + m_2)/m_1} \approx m_2 \tag{22}$$

$$(m_1 = m_2) \quad \Rightarrow \quad \mu = \frac{m_1^2}{2m_1} = \frac{1}{2}m_1 = \frac{1}{2}m_2 \tag{23}$$

5.4   Quantum mechanics: discrete energy levels

In quantum mechanics, only discrete energy levels for rotation are allowed, and these turn out to be:

$$E_{\mathcal{J}} = \frac{\hbar^2}{2I} \mathcal{J}(\mathcal{J} + 1), \qquad \text{with} \quad \mathcal{J} = 0, 1, 2, \dots \quad , \tag{24}$$

where $\hbar = h/2\pi$ is the reduced Planck constant and $\mathcal{J}$ the rotational quantum number. Note the similarity to the classical expression for the total energy ($E_r = J^2/(2I)$) which we have worked out above. The moment of inertia plays exactly the same role in both expressions. The classical J^2 is replaced by the $\hbar^2 \mathcal{J}(\mathcal{J} + 1)$ expression, so the rotational quantum number $\mathcal{J}$ roughly corresponds to the classical angular momentum.

The fraction in the above equation is called the **rotational constant**

$$B = \frac{\hbar^2}{2I} \quad , \tag{25}$$

so that

$$E_{\mathcal{J}} = B\mathcal{J}(\mathcal{J}+1), \qquad \text{with} \quad \mathcal{J} = 0, 1, 2, \ldots \tag{26}$$

Note that B is inversely proportional to the moment of inertia I.

The connection beween rotational quantum number $\mathcal{J}$ and energy (expressed in units of B) is shown in Figure 7. Red arrows in the figure indicate energy transitions. From Quantum mechanics, it turns out that the only transitions that are allowed are those where $\Delta\mathcal{J} = \pm 1$.

This is an example of a **selection rule**. A closer look at the red arrows in Figure 7 reveals that the allowed transition energy differences are equidistant. They can be described by the simple formula

$$\Delta E_{\mathcal{J}} = 2B(\mathcal{J}+1), \qquad \mathcal{J} = 0, 1, 2, \ldots . \tag{27}$$
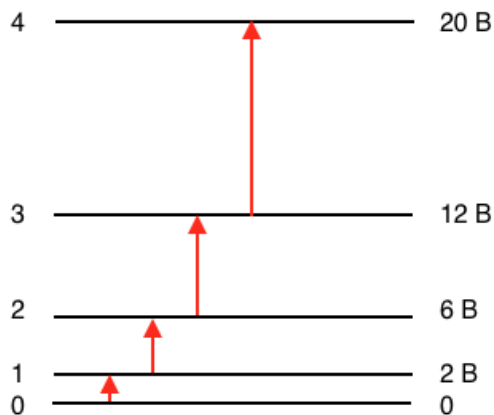
Figure 7: Rotational energy levels. Values for $\mathcal{J}$ are given on the left and corresponding energy levels (in units of the rotational constant B) are given on the right.

Besides their native unit of Joule, energy(diferences) can be conveniently expressed in **wavenumbers** (Kaysers)

$$\tilde{\nu} = \frac{\Delta E}{hc} \qquad \left[\frac{1}{cm}\right] \tag{28}$$

or in frequency (Hz)

$$\nu = \frac{\Delta E}{h} \qquad [Hz] \quad , \tag{29}$$

so energy differences translate directly to the observed spectrum.

In the literature, molecular energy differences and the rotational constant B are most often given in units of Kaysers.

Note that we have assumed in all the above that there is only one axis around which the molecule can rotate. If there are more axis of rotation, the spectrum will be more complex.

In the exercise, we will look at some of these rotational spectra.

6 Vibrational spectra

Now we will turn to vibration, another mode of molecular internal energy. Just like rotational energy, vibrational energy is quantified, hence can lead to spectroscopic transitions (= absorption lines). I will use the terms *vibration* and *oscillation* as synonyms here.

6.1 Classical harmonic oscillator

We start off by looking at a harmonic oscillator in classical mechanics (see Figure 8). We can picture a diatomic molecule as two atoms (point masses), connected by a spring. The simplest possible assumption on the restoring force f, if the molecule is stretched or compressed, is

$$f = -k(r - r_{eq}) \qquad \text{(Hooke's law)} \tag{30}$$

at the point r from the equilibrium point r_{eq} with a spring constant k.

Classically, if the molecule is stretched or squeezed a bit, it will start to oscillate, due to the restoring force. The motion with this particular restoring force is called *harmonic oscillation* an is described by sinusoidal functions. The angular frequency $\tilde{\omega}$ of the oscillation is given by
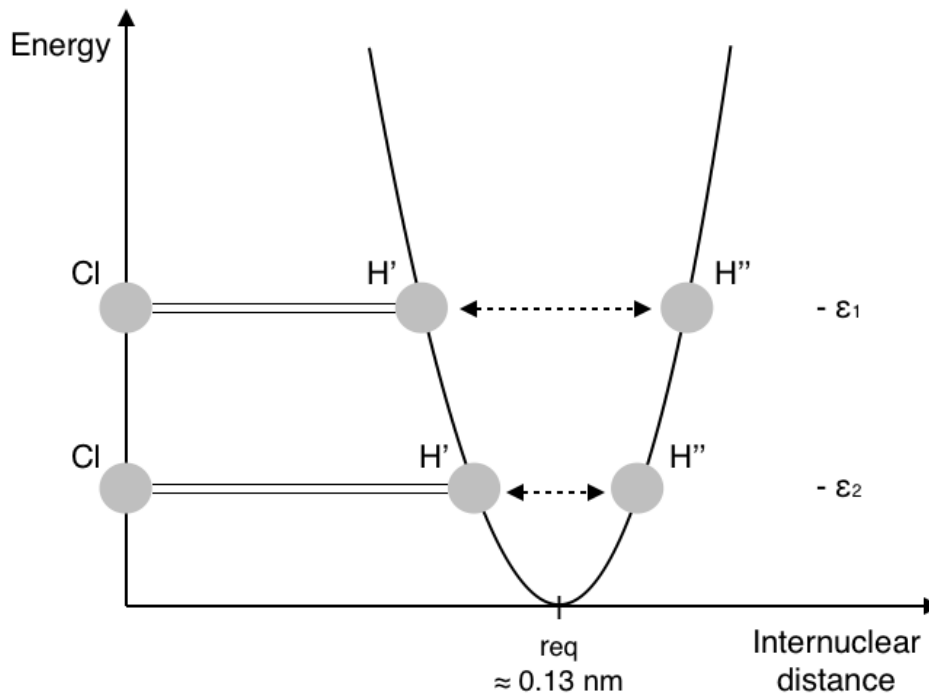
Figure 8: Energy curve for HCl molecules for extension or compression. After Banwell and McCash.

$$\tilde{\omega} = \sqrt{\frac{k}{\mu}} \quad , \tag{31}$$

where k is the spring constant from Equation 30 and μ is the reduced mass, as defined in Equation 19. (For a single 'mass on a spring' pendulum, μ would simply be the mass, but for the system of two oscillating masses we have to use the reduced mass.)

The essence of the equation above is that a stiffer spring leads to a faster oscillation, whereas a larger (reduced) mass leads to a slower oscillation. Both agrees well with intuition.

The energy that is contained in the vibration will depend on the oscillation amplitude $\Delta r_{\max} = \max(r - r_{eq})$. At the turning points (most stretched or compressed positions), there is only potential (=spring) energy, and no kinetic energy. Because of energy conservation, the total energy of the vibration stays on this same value, only for example then the oscillation goes through $r = r_{eq}$, all is in the form of kinetic energy. So, we can calculate the energy contained in the vibration as

$$E = \frac{1}{2}k(r - r_{eq})^2 = \frac{1}{2}k\Delta r^2 \quad . \tag{32}$$

6.2   Quantum mechanical harmonic oscillator

For a real molecule, vibrational energy is quantised, so only certain vibrational energy levels are allowed. The quantum mechanically possible energy levels turn out to be

$$E_v = (v + \frac{1}{2})\hbar\tilde{\omega} \qquad (v = 0, 1, 2, ...) \quad , \tag{33}$$

where $\tilde{\omega} = 2\pi\tilde{v}$ is the angular frequency of vibration ($\tilde{v}$ being the plain frequency), and $\hbar = h/(2\pi)$ is the reduced Planck constant (also called Dirac constant).

Transformed into spectroscopic units of Kayser we get

$$\varepsilon_v = \frac{E_v}{hc} = (v + \frac{1}{2})\tilde{v} \qquad (v = 0, 1, 2, ...) \quad . \tag{34}$$

The lowest vibrational level is at

$$E_0 = \frac{1}{2}\hbar\tilde{\omega} \quad . \tag{35}$$

Therefore a molecule can never have **zero** vibrational energy! This is different from rotation,

where the lowest state had zero energy. Figure 9 illustrates the vibrational energy levels. Compare it to Figure 7 of the rotational energy levels to see the fundamental difference: The vibrational levels are equidistant.

The frequency of the observed spectral line corresponds to the energy difference $\tilde{\nu}$ between adjacent levels. Since all the levels are equidistant, all the possible 'pure' vibrational transitions would map to a single spectral line at frequency $\tilde{\nu}$. Put typically such 'pure' transitions are not allowed, only transitions that also involve changes in the rotational state.

If molecules rotate, the energy separation is 1 - $10\,\mathrm{cm}^{-1}$ whereas if they vibrate, the energy separation is 100 - $10\,000\,\mathrm{cm}^{-1}$. This is a large difference in characteristic energy. We can therefore assume that the two motions occur independently. (This is a case of the Born-Oppenheimer approximation, which strictly also includes optical transitions). We write

$$E_{total} = E_{rot} + E_{vib} \qquad [\mathrm{J}] \tag{36}$$

$$\varepsilon_{total} = \varepsilon_{rot} + \varepsilon_{vib} \qquad \left[\mathrm{cm}^{-1}\right]. \tag{37}$$
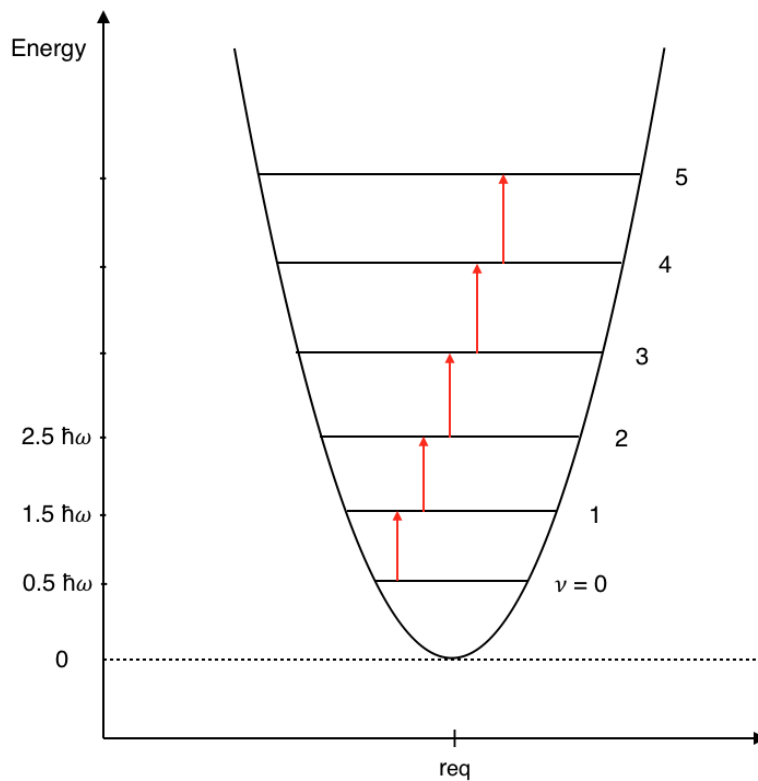
Figure 9: Allowed vibrational energy levels and transitions between them. After Banwell and McCash.

35

Combining the discrete energy levels results in

$$\varepsilon_{\mathcal{J},\nu} = \varepsilon_{\mathcal{J}} + \varepsilon_\nu = B\mathcal{J}(\mathcal{J}+1) + (\nu + \frac{1}{2})\tilde{\nu} \quad . \tag{38}$$

Note: There are higher order therms in both rotation (zentrifugal stretching) and vibration (non-constant restoring force) that I am ignoring here.

The selection rule states, that

$$\Delta\nu = 0, \pm 1 \quad \text{and} \quad \Delta\mathcal{J} = \pm 1 \quad \text{(see Figure 10)} \quad . \tag{39}$$

This means, we normally cannot observe the vibrational fundamental directly. Rotational levels will be filled to varying degrees in a population of molecules. This results in different line intensities.
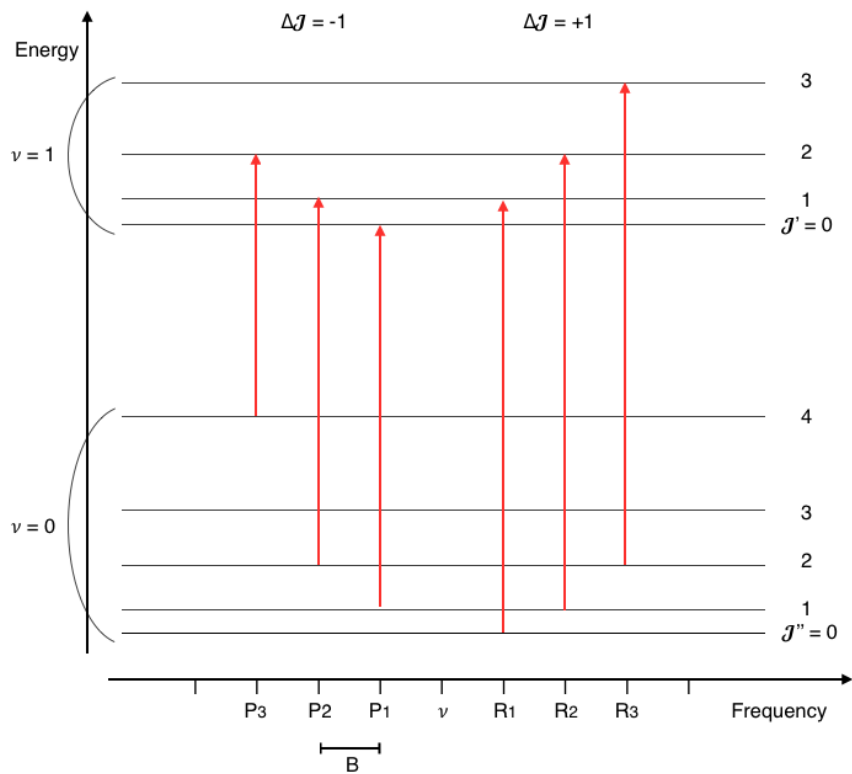
Figure 10: Transitons between vibrational - rotational energy levels. After Banwell and Mc-Cash.

The transition frequencies are divided into two branches:

$$\Delta \mathcal{J} = +1 \quad \text{(R-Branch)}$$
$$\Delta \varepsilon_{\mathcal{J},v} = \tilde{v} + 2B(\mathcal{J}'' + 1), \qquad \mathcal{J}'' = 0, 1, 2$$
$$\Delta \mathcal{J} = -1 \quad \text{(P-Branch)}$$
$$\Delta \varepsilon_{\mathcal{J},v} = \tilde{v} - 2B(\mathcal{J}' + 1), \qquad \mathcal{J}' = 0, 1, 2$$

They can be combined into:

$$\Delta \varepsilon_{\mathcal{J},v} = \tilde{v} + 2Bm, \qquad m = \pm 1, \pm 2, \pm 3, \dots \tag{40}$$

These are the frequencies of the observed lines.

So why are the branches called 'P' and 'R'? For more complicated molecules, $\Delta \mathcal{J} = 0$ and ± 2 may also be allowed. All possible branches are:

$\Delta \mathcal{J} =$	-2	-1	0	+1	+2
Name	O	P	Q	R	S

The number of vibrational modes (different types of vibrations) in a molecule is 3N-5 for linear molecules and 3N-6 for nonlinear molecules, where N is the number of atoms (see for example http://www.wag.caltech.edu/home/jang/genchem/infrared.htm). So, for a diatomic molecule, there is only one possible mode of vibration, just like there is only one mode of rotation.

More interesting are molecules with three or more atoms. The most important molecules for Earth's greenhouse effect, H_2O and CO_2, are tri-atomic. Their vibrational modes are summarised in Figure 11. H_2O is nonlinear, therefore it has

$$n_{vib,H2O} = 3*3 - 6 = 9 - 6 = 3 \tag{41}$$

vibrational modes. CO_2 is linear, therefore it has

$$n_{vib,CO2} = 3*3 - 5 = 9 - 5 = 4 \tag{42}$$

vibrational modes. However, two of these 4 modes (symmetric bending) have the same fundamental frequency. One corresponds to motion in the paper plain, as shown in Figure 11, the other to motion perpendicular to the paper plain. Furthermore, the symmetric stretch mode of CO_2 at 1330 cm^{-1} is not associated with a change in the dipole moment, and therefore is not infrared active, so that CO_2 has only two active infrared vibration modes.

7 Line shape

There are three mechanisms that lead to a broadening of absorption lines:

- Natural line width

- Pressure broadening

- Doppler broadening
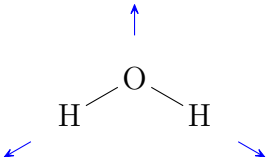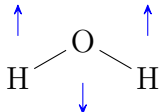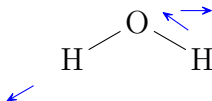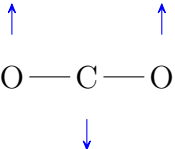
Symmetric stretch	Symmetric bend	Asymmetric stretch
$\tilde{\nu}_1 = 3651.7\,\mathrm{cm}^{-1}$	$\tilde{\nu}_2 = 1595.0\,\mathrm{cm}^{-1}$	$\tilde{\nu}_3 = 3755.8\,\mathrm{cm}^{-1}$
$\tilde{\nu}_1 = 1330.0\,\mathrm{cm}^{-1}$	$\tilde{\nu}_2 = 667.3\,\mathrm{cm}^{-1}$	$\tilde{\nu}_3 = 2349.3\,\mathrm{cm}^{-1}$

Figure 11: Vibrational modes of H_2O and CO_2.

7.1   Natural line width

So far we know that the difference between two energy states E_f and E_i equals the frequency ν times the Planck constant h:

$$h\nu = E_f - E_i \quad . \tag{43}$$

So absorption (and emission) would happen at exactly one frequency and the line shape would be a delta-function. There is a fundamental quantum mechanical principle that prevents this from being true: Heisenbergs's uncertainty principle sais that one cannot know position and momentum of a particle simultaneously:

$$\Delta x \Delta p \approx \hbar \quad , \tag{44}$$

where $\hbar$ is the reduced Planck constant. Another manifestation of this principle is:

$$\Delta E \Delta t \approx \hbar = 10^{-34} \text{ Js} \quad . \tag{45}$$

Thus, the shorter the lifetime of a state, the more uncertain is its energy. The groundstate has an infinite lifetime, so its energy is exactly known:

$$\Delta t = \infty \rightarrow \Delta E = 0 \quad .$$ (46)

The first excited electronic state, however, has a finite lifetime

$$\Delta t = 10^{-8} \text{ s} \rightarrow \Delta E = \frac{\hbar}{\Delta t} = \frac{10^{-34}}{10^{-8}} = 10^{-26} \text{ J} \quad ,$$ (47)

and the associated frequency uncertainty is

$$\Delta\nu = \frac{\Delta E}{h} = \frac{10^{-26} \text{ J}}{10^{-34} \text{ Js}} = 10^8 \text{ Hz} \quad .$$ (48)

This seems a large number at first sight, but electronic transitions typically have frequencies of 10^{14}-10^{16} Hz (visible spectral range). Therefore natural line width can be considered as small. However, the actual shape of the line is important.

The finite lifetime of the upper state means that it decays with time:

$$\frac{dn(t)}{dt} = -An(t) \quad , \tag{49}$$

where n is the number of molecules in the excited state and A is the Einstein A coefficient for spontaneous emission. The solution of this equation is

$$n(t) = n(0)e^{-At} = n(0)e^{-\frac{t}{\tau}} \quad , \tag{50}$$

where τ is the lifetime.

The derivative $\frac{dn(t)}{dt}$ is the rate at which the excited state decays, but at the same time it is also the rate of spontaneously emitted photons (whenever a state decays, a photon is emitted). Thus, for the radiation flux L we can write:

$$L(t) = L(0)e^{-At} \quad . \tag{51}$$

So L also decays exponentially in time. If a signal amplitude is not constant in time, it cannot

be monochromatic. The frequency spectrum is given by the Fourier transform of Equation 51:

$$F_L(\nu) = \frac{1}{\pi} \frac{A/4\pi}{(\nu - \nu_0)^2 + (A/4\pi)^2} = \frac{1}{\pi} \frac{\gamma_N}{(\nu - \nu_0)^2 + \gamma_N^2} \quad . \tag{52}$$

F_L is called a Lorentz-Function (also Cauchy distribution or Breit Wigner distribution), and γ_N is the natural line width parameter.

7.2   Doppler Broadening

Doppler Broadening is conceptually simpler than natural broadening. It is due to the thermal motion of the molecules, which Doppler-shifts the frequency (at any point in time one part of the molecules is moving towards me and one part is moving away). The Maxwell-distribution for velocity (valid for LTE) is:

$$p(u) = \sqrt{\frac{m}{2\pi kT}} \ \exp\left(\frac{-mu^2}{2kT}\right) \quad , \tag{53}$$

where u is the velocity and m is the mass of the molecule. Non-relativistic Doppler-shift is given by

$$\nu - \nu_0 = \frac{\nu_0 u}{c} \quad .$$
(54)

The faster the molecule, the larger the Doppler-shift. Combining this with the Maxwell velocity distribution gives

$$F_D(\nu) = \frac{1}{\gamma_D \sqrt{\pi}} \exp\left[-\left(\frac{\nu - \nu_0}{\gamma_D} \right)^2 \right] \quad ,$$
(55)

with the 'Doppler width'

$$\gamma_D = \frac{\nu}{c} \sqrt{\frac{2kT}{m}} \quad .$$
(56)

Note that F_D is a Gaussian.

7.3   Pressure Broadening

Collisions between molecules also limit the lifetime of energy states ("collisional broadening"). If one assumes that collisions themselves take no time, that there is no interaction between collisions and that collisions completely "reset" the state, then the resulting shape is again Lorentzian:

$$F_L(\nu) = \frac{1}{\pi} \frac{\gamma_C}{(\nu - \nu_0)^2 + \gamma_C^2} \quad . \tag{57}$$

The rate of collision is proportional to pressure. Empirically γ_C is calculated as follows:

$$\gamma_C = p \cdot \mathrm{AGAM} \left(\frac{T_{ref}}{T} \right)^{\mathrm{NAIR}} \quad , \tag{58}$$

where AGAM and NAIR are in the spectral line catalogue. (In reality there are some more parameters.)

So which of the broadening mechanisms do we use in reality? We neglect natural broadening, but have to use thermal and collisional broadening (γ_D and γ_C). The shape then is a con-

volution of Lorentz and Gauss shape, called "Voigt-Function". There is no analytical form of this function, only numerical approximations.

In the exercise you will find out which effect of broadening dominates when.

8   Thermal radiation

We now want to look at the balance between Radiation and Temperature. If an object receives more radiation, its temperature rises. And a higher temperature results in a higher emission of radiation. We first look at a black body that absorbs all incoming radiation without any reflection. This is the case e.g. in a hollow space. If the Temperature is kept constant, there will be a radiative equilibrium between the walls and the radiation on the inside of the hollow space. This radiative equilibrium is *only* dependent on the temperature, every other dependancy would be contradicting the laws of Thermodynamics.

The relationship between temperature and radiation is described in what now is known as

Planck's law:

$$I_\nu = B_\nu(T) = \frac{2h\nu^3}{c^2(e^{\frac{h\nu}{kT}} - 1)}, \qquad B_\lambda(T) = \frac{2hc^2}{\lambda^5(e^{\frac{hc}{\lambda kT}} - 1)} \quad , \qquad (59)$$

where I_ν is the spectral radiance [$\mathrm{W\,m^{-2}\,sr^{-1}\,Hz^{-1}}$], B the Planck function, T the temperature, h the Plack constant, ν the frequency, c the speed of light, k the Boltzmann constant and λ the wave length. The low frequency approximation of Planck's law is the Rayleigh-Jeans law, which was already known before Planck's law:

$$I_\nu = B_{\nu,RJ}(T) = \frac{2kT}{c^2}\nu^2 \quad . \qquad (60)$$

Wien's displacement law states that the black body radiation curve for different temperatures peaks at a frequency proportional to the temperature

$$\nu_{max} \propto T \quad . \qquad (61)$$

When radiation meets a surface, it is either absorbed or reflected. The absorption coefficient α therefore has values between 0 and 1. A body that emits thermal radiation has an emissivity

coefficient ε between 0 and 1. An emissivity coefficient $\varepsilon = 0$ means no radiation is emitted, a body with $\varepsilon = 1$ emits the same amount of radiation that a blackbody of the same temperature would emit:

$$I_\nu = \varepsilon(\nu)B_\nu(T) \quad . \tag{62}$$

Absorption and Emission have to balanced, otherwise this would be contradicting the second law of Thermodynamics. *Kirchhoff's law of thermal radiation* states that for all frequencies and angles

$$\varepsilon(\vartheta, \varphi, \nu) = \alpha(\vartheta, \varphi, \nu) \quad . \tag{63}$$

We now apply these rules to our climate system. The earth itself emits radiation at the temperature of its surface. Due to the natural greenhouse effect, the temperature at earth's surface is increased by 34 K. This can be seen in Figure 12 which shows the spectra of longwave radiation of the earth as seen from space.

Comparing the radiational intensities to the Planck curves shows at which temperature the
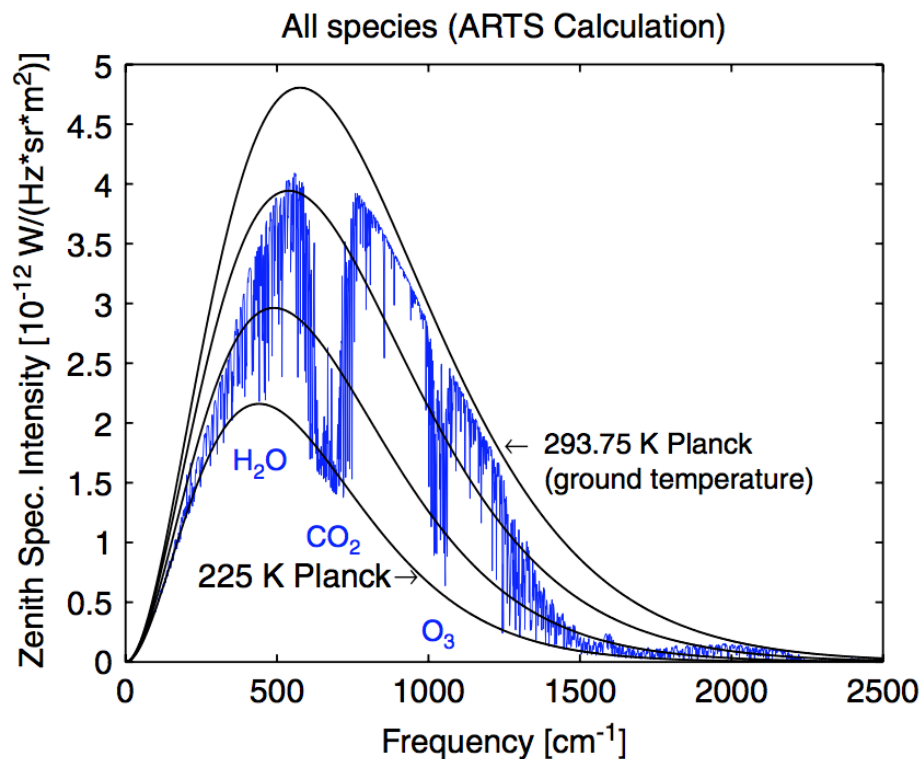
Figure 12: Clear-sky OLR spectra of the earth as seen from space. The area between the top curve and the blue curve is caused by the natural greenhouse effect. From Buehler et al., 2006.

radiation was emitted

$$T_b = B_\nu^{-1}(I_\nu) \quad , \tag{64}$$

where T_b is called the brightness temperature. Using the brightness temperature in remote sensing is very common since it is an intuitive unit for the intensity. E.g., one would interpret $T_b = 300\,\mathrm{K}$ as a high value since there are not much higher temperatures in the atmosphere. $T_b = 200\,\mathrm{K}$ on the other hand, would not be very much.

9 Radiative transfer equation

First we need to define some important radiation quantities:

Spectral Radiance = monochromatic pencil beam radiance = Intensity (I) The radiation power per square meter that is traveling in a particular direction, per frequency interval, per solid angle interval. Unit:

$$\frac{\mathrm{W}}{\mathrm{m^2\,Hz\,sr}}$$

Radiance (L) is obtained by integrating I over frequency. Unit:

$$\frac{\mathrm{W}}{\mathrm{m}^2\,\mathrm{sr}}$$

Irradiance = Radiative Flux (F) is obtained by integrating L over solid angle (one hemisphere), taking the projection onto the nominal direction of the flux. Unit:

$$\frac{\mathrm{W}}{\mathrm{m}^2}$$

The radiative transfer equation (RTE) describes the change of radiation along a path, for example from the ground to a sensor above the surface. The RTE is expressed in terms of the Intensity I. It can be written as

$$\frac{\mathrm{d}I}{\mathrm{d}s} = -(\alpha + \sigma)I + \alpha B(T) + \sigma \int_\Omega PI \, , \frac{\mathrm{d}\Omega}{4\pi} \tag{65}$$

where $\mathrm{d}s$ is a path element. The first term on the right hand side is the radiation loss due to extinction by absorption (absorption coefficient α) and scattering (scattering coefficient σ). The second term is a source term due to thermal emission $B(T)$. The third term is a source

term due to radiation that is scattered into the path. It is calculated using the phase matrix P of the scattering particles. The calculation involves an integration of the intensity over the whole solid angle Ω. Note, that normally every variable depends on the frequency and the viewing direction.

We see that if we include scattering in the RTE, it is very difficult to solve, because in order to compute the intensity in one direction, we need to know the intensity in every other direction.

One of the most used simplifications of the RTE is to neglect scattering. If we look at thermal radiation, this is mostly true for a clear sky atmosphere. If we neglect scattering, the last term as well as the σ in the first term vanish and the (clear sky) RTE looks like this:

$$\frac{\mathrm{d}I}{\mathrm{d}s} = -\alpha I + \alpha B(T) = \alpha(B(T) - I) \quad . \tag{66}$$

This equation is also known as Schwarzschild's equation because if was formulated by K. Schwarzschild in 1906.

Using this equation, let's look at what happens in a homogeneous medium (α and T constant). If the radiation passes through the medium long enough ($s \rightarrow \infty$) the difference between B and I has to get smaller and smaller. This means that eventually, I will converge to B. This

makes sense because if we look through a thick enough medium, we hardly see which radiation came into the medium, we only see the emission of the medium.

Schwarzschild's equation can be integrated along a path through a layer (a complete derivation can be found in Petty, Eq. 8.5 - 8.13):

$$I(s) = I(0)e^{-\tau(0,s)} + \int_0^s \alpha(s')B(s') \quad, e^{-\tau(s',s)}ds' \tag{67}$$

where $\tau(0, s)$ is the opacity between the points, defined as

$$\tau(0, s) = \int_0^s \alpha(s')ds' \quad. \tag{68}$$

We see that the layer emits radiation, while the incoming radiation $I(0)$ is attenuated exponentially.

In radiative transfer models such as ARTS, the atmosphere is usually divided into homogeneous layers and the RTE is calculated through these layers. So to understand the calculations in the model, it is useful to look at the solution of Schwarzschild's equation in a homogeneous

layer. The only difference is the opacity, which in a homogeneous layer, we can write as

$$\tau(0, s) = \int_0^s \alpha(s')\,ds' = \alpha s \quad . \tag{69}$$

To get the solution, we just plug a homogeneous layer from 0 to s into the integral form of the equation:

$$I(s) = I(0)e^{-\alpha s} + \alpha B(T) \int_0^s e^{-\alpha(s-s')}\,ds' \quad , \tag{70}$$

which, after some algebra, gives

$$I(s) = I(0)e^{-\alpha s} + B(T)\left(1 - e^{-\alpha s}\right) \quad . \tag{71}$$

With the definition of the transmission $t = e^{-\alpha s}$, we can rewrite the solution as

$$I(s) = tI(0) + (1 - t)B(T) \quad . \tag{72}$$

It is instructional to look at two extreme cases of the solution:

Optically thick What happens if the opacity of the layer is very high, so $t \to 0$? Then we just see the Planck emission of the layer. The incoming radiation does not reach us.

Optically thin What happens if the opacity of the layer is 0, to $t \to 1$? Then we just see the incoming radiation $I(0)$. The layer doesn't do anything.

A more interesting special case is when the opacity is small, but not zero. For small opacities, we can use a linear approximation of the transmission, which comes from the Taylor expansion of the exponential function:

$$t = e^{-\tau} \approx 1 - \tau \quad . \tag{73}$$

If we plug this into the solution of a homogeneous layer, we get

$$I(s) = tI(0) + (1 - t)\,B(T) \approx I(0) + \tau\,(B - I(0)) \quad , \tag{74}$$

which has exactly the same form as Schwarzschild's equation itself.

10 Jacobians

Inverse modeling is needed for estimating an atmospheric state variable $\vec{x}$ by measuring an affected variable $\vec{y}$

$$\vec{y} = F(\vec{x}) \rightarrow \vec{x} = ?$$

The physical relationship between $\vec{x}$ and $\vec{y}$ is described by F, the so called forward model:

$$\vec{y} = F(\vec{x}) + \vec{\varepsilon} \quad ,$$

where $\vec{y}$ is the variable which should be measured, F is the forward model dependent on the variable of the atmospheric state $\vec{x}$ (e.g. temperature profile, altitude) and $\vec{\varepsilon}$ is the noise.

Definition

Jacobian: The Jacobian is defined as the partial derivative of the forward model at the ith element of the vector $\vec{y}$ (e.g. i^{th} frequency) to a variation of the jth element of the atmospheric state vector (e.g. altitude).

$$J_{i,j} = \frac{\partial F_i}{\partial x_j}$$

For example if the temperature is retrieved, then the Jacobian describes how the brightness temperature ($\vec{y}$) at a certain frequency changes when the temperature ($\vec{x}$) at the jth level changes. Hence a Jacobian could be understood as the sensibility of $\vec{y}$ at the ith element if the jth element of $\vec{x}$ varies. There are two possible methods of calculating a Jacobian.

Pertubation Method

This method is a 'naive' but always working method. It is quite straightforward to implement and can be used where other methods fail. The Jacobian is calculated by perturbing the state variable $\vec{x}$ by a small disturbance $\vec{\Delta x}$. The Jacobian corresponding to the state variable $\vec{x}$ can

thus be calculated as

$$J(i,j) = \frac{\partial y_i}{\partial x_j} \approx \frac{\Delta y_i}{\Delta x_j} = \frac{F(\vec{x} + \vec{\Delta x_j}) - F(\vec{x})}{\Delta x} \quad , \tag{75}$$

where Δx is the jth element of $\vec{\Delta x}$, as in:

$$\vec{\Delta x_j} = \begin{bmatrix} 0 \\ \vdots \\ 0 \\ \Delta x \\ 0 \\ \vdots \\ 0 \end{bmatrix}$$

This method is relatively inefficient because one has to run the full forward model F for every element of $\vec{x}$, only perturbing them once at a time.

Analytical Method

For the analytical method, we use the integral form of the clear-sky radiative transfer equation (RTE) for a given frequency

$$y = I = I_0 \cdot e^{-\int_0^\infty \alpha(s')ds'} + \int_0^\infty \alpha(s)B(T(s))) \cdot e^{-\int_0^s \alpha(s')ds'}ds \quad ,$$

where α is the absorption coefficient and B is the thermal emission. Or in a discrete form

$$I = I_0 \cdot \underbrace{e^{-\sum_{j=0}^N \alpha_j \Delta s_j'}}_{Transmission} + \sum_{i=0}^N \underbrace{\alpha_i \Delta s_i B(T_i)}_{Emission} \cdot \underbrace{e^{-\overbrace{\sum_{j=0}^i \alpha_j \Delta s_j}^{\substack{Opacity}}}}_{Transmission} \quad ,$$

with the layerthickness Δs and the incoming Radiation I_0.

As is shown in figure 13, if the atmosphere is perturbed at one layer, this will affect the emission at this layer and the transmission of everything behind.
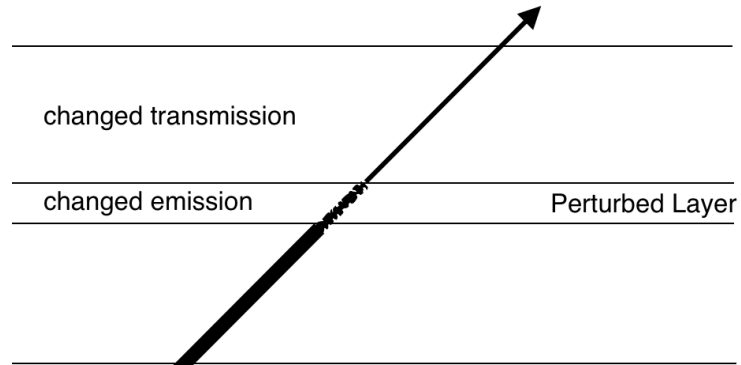
changed transmission

changed emission

Perturbed Layer

Figure 13

Emission:

$$\frac{\partial}{\partial x_k}(\alpha_k \Delta s_k B(T_k)) = \Delta s_k B(T_k)\frac{\partial \alpha_k}{\partial x_k}$$

If x is the number density of some gas(n):

$$\alpha = n \cdot \sigma \to \frac{\partial \alpha}{\partial n} = \sigma \quad , \tag{76}$$

where n is the density and σ is the absorption cross-section.

Transmission:

$$\tau = \sum_{i=0}^{N} \alpha_i \Delta s_i = \alpha_1 \Delta s_1 + \alpha_2 \Delta s_2 + \cdots + \alpha_N \Delta s_N \quad , \tag{77}$$

The change of the transmission can be written as

$$\frac{\partial \tau}{\partial x_k} = \Delta s_k \frac{\partial \alpha_k}{\partial x_k} \quad .$$

Pro and Cons of the different calculations of Jacobians

Numerical Perturbation Method This method is very easy to implement and it works for any parameter in a "black-box" kind of way which makes the method very "foolproof". Therefore it takes a lot of time to calculate the Jacobian.

Analytical Method This method needs a lot of "housekeeping" and is not always feasible. But it is also more accurate and faster than the Numerical Perturbation Method.
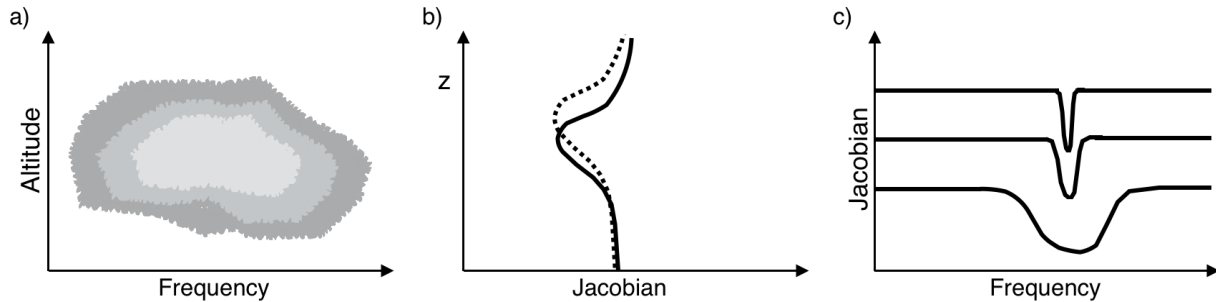
Figure 14

Displaying Jacobians

Since the Jacobian is a matrix, there are three basic ways to display it:

1. **Contour plot:** Frequency dependence for all altitudes, figure 14a)
2. **Row plot:** Altitude dependence for selected frequencies, figure 14b)
3. **Column plot:** Frequency dependence for selected altitudes, figure 14c)

Opacity rule

Jacobians tell us where the information comes from or rather where changes in the atmosphere affect the radiation most.

The opacity rule tells us something about the origin of the radiation. The origin of the thermal radiation is the distance where the opacity, as calculated from the observer, reaches 1.