

Chapter 6

Infra-red and Microwave Remote Sensing

6.1 Spectroscopy of rotational and vibrational transitions

Absorption (and emission) of a photon can take place, if a change in internal energy of the molecule ($E_f - E_i = \nabla \cdot \mathbf{E} = h \cdot \nu$), with ν as the frequency of the molecule.

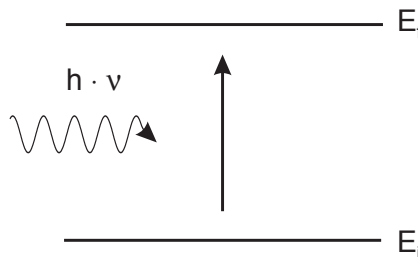


Figure 6.1: Changing the energy level by absorbing a photon.

Energy levels of a molecule due to:

- rotation:
transitions in the microwave region ($\nu \approx 10 - 1000\text{GHz}$)

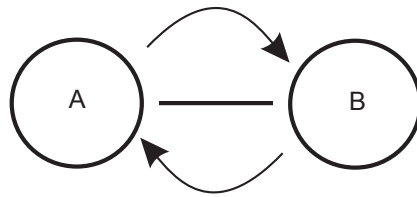


Figure 6.2: Rotating molecule.

- vibration:

transitions in the infra-red ($\lambda \approx 10\mu\text{m}$)

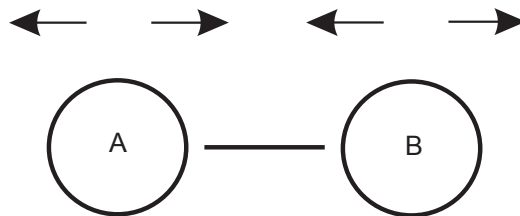


Figure 6.3: Vibrating molecule.

- electronic transitions:

transition in the ultra-violet and visible ($\lambda \approx 100\text{nm} - 1000\text{nm}$)

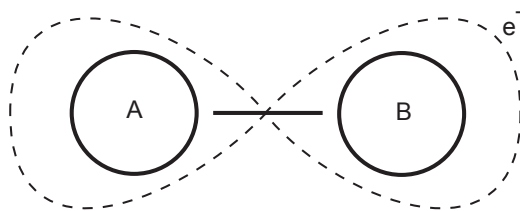


Figure 6.4: Electric transitions.

Remark: We will mainly discuss diatomic molecules, because they are much easier to handle than the polyatomic molecules. Many gases in the

atmosphere are diatomic (e.g.: O₂, NO, HCl, CO, ...), but some important gases are not (e.g.: O₃, H₂O, CO₂, ...).

6.1.1 Line Strength

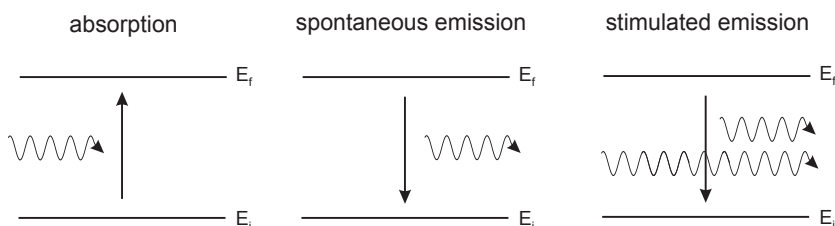


Figure 6.5: The three kinds of energy transition.

There are three conditions of emission:

1. $\Delta E = h\nu_{fi} = E_f - E_i$
2. Net absorption is proportional to the difference occupation probabilities of states i and f : $\sigma_i - \sigma_f$ where σ_i is given by the Boltzmann distribution (if in thermodynamic equilibrium):

$$\sigma_i = \frac{g_i \exp(-E_i/kT)}{\underbrace{\sum_j g_j \exp(-E_j/kT)}_{Q(T)}}$$

With $Q(T)$ as partition function (in German called "Zustandssumme" - sum of states) and g the statistical weight.

3. Absorption is proportional to the electric dipole matrix element μ between states i and f :

$$\mu_{if} = \mu \iiint \psi_f^*(\Theta, \phi, \chi) \psi_i(\Theta, \phi, \chi) d \cos \Theta d\phi d\chi$$

With μ as magnitude of dipole element.

Taking point 1 to 3 together leads to:

$$\alpha(\nu) = n \cdot \sum_{f,i} S_{fi}(T) \delta(\nu_{fi} - \nu) \quad (6.1)$$

with:

n: number density

S_{fi} : line strength of frequency of transition

$h\nu_{fi} = E_f - E_i$

δ : Dirac's function is actually not really true will be replaced later by "line shape" function.

$$S_{fi} = \frac{8\pi^3 \nu_{fi} |\mu_{fi}|^2 g_i}{3hcQ(T)} (e^{-E_i/kT} - e^{-E_f/kT}) \quad (6.2)$$

Thus practice in order to calculate S_{fi} (and α) we need to know:

- frequency of the transition: ν_{fi}
- dipole matrix element: $|\mu_{fi}|^2$ (+ statistical weight g_i)
- Energies of the states: E_i and E_f
(Note that lower state energy E_i is sufficient, since $E_f = E_i + h\nu_{fi}$)
- partition function: $Q(T)$

In practice these quantities are often collected in (large) data bases. Often used in the so called HITRAN database.

6.1.2 Line Shape Function

Natural Line Width

The condition that absorption occurs only for frequency ν with exactly $h\nu = E_f - E_i$ is not really true, because due to Heisenberg's Uncertainty Principle the energies have some uncertainty, so that some absorption is also possible for frequencies a bit smaller and a bit larger than ν_{fi} . So called "natural line width".

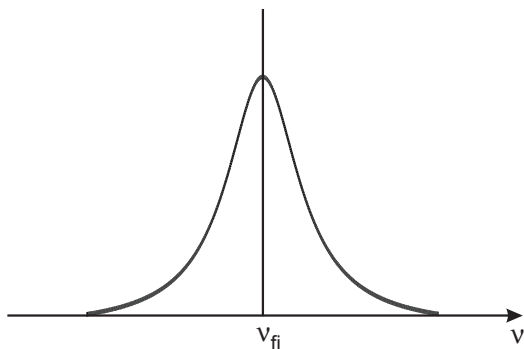


Figure 6.6: ν_{fi} or the "natural line width".

Pressure Broadening

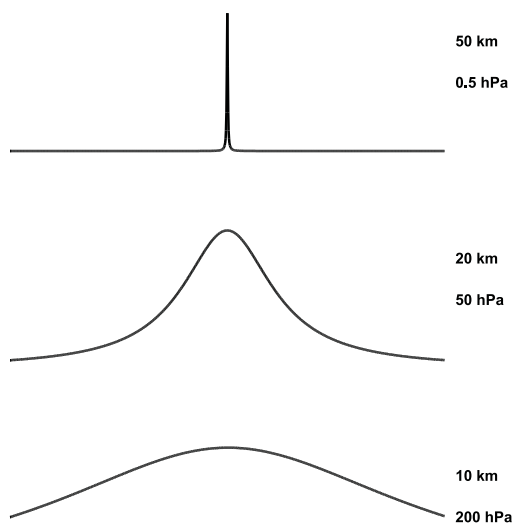


Figure 6.7: The pressure broadening of spectral lines

If the lifetime of the states are reduced (e.g. by collisions between molecules) the finite lifetime will correspond to a finite energy uncertainty ΔE by Heisenberg's principle.

Assume that number of molecules in states i decays exponentially: $n = n_0 e^{-\alpha t}$. Electromagnetic radiation emitted (or absorbed) will have a give frequency, decaying exponentially.

This corresponds to a superposition of waves with different wavelength or frequencies. In fact the Fourier transform of $e^{-\alpha t}$ is:

$$F(\nu) = \sqrt{\frac{2}{\pi}} \frac{a}{\alpha^2 + \nu^2} \quad (6.3)$$

This is the so called Lorentz-line shape. This effect is very important for pressure broadening where a is proportional to pressure p . Empirically write:

$$a = w \cdot p \cdot \left(\frac{T_0}{T}\right)^x \quad (6.4)$$

Where w and x are constants.

Thermal or Doppler Broadening

If an emitting or absorbing molecule moves relative to an observer, the frequency of the emitted (absorbed) radiation will be shifted by the (relativistic) Doppler Effect. Molecular speed are Gaussian distributed. In effect this leads to a line broadening. The Fourier transform of the Doppler line shape is:

$$F_{Doppler} = \frac{I}{\Delta\nu} \sqrt{\frac{\ln 2}{\pi}} \exp\left(-\ln 2 \left(\frac{\nu - \nu_0}{\Delta\nu}\right)^2\right) \quad (6.5)$$

With the line width:

$$\Delta\nu = \frac{\nu_0}{c} \sqrt{\frac{2kT}{m} \ln 2} \quad (6.6)$$

(m as molecular mass)

In reality, both pressure broadening and Doppler broadening are important so that the overall line-shape is a convolution of both.

$$F(\nu) = \int F_{Lorentz}(\nu - \nu') \cdot F_{Doppler}(\nu) d\nu' \quad (6.7)$$

This function is called the Voigt-line shape.

6.1.3 Rotational Transitions

Classically, the rotational energy is given by:

$$T = \frac{1}{2}I\omega^2 = \frac{J^2}{2I} \quad (6.8)$$

with

ω : rotational frequency

I : moment of inertia

J : angular momentum $J = I \cdot \omega$

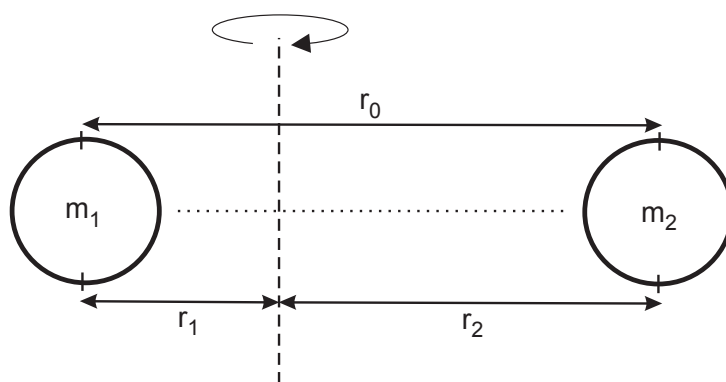


Figure 6.8: Rotational transitions of a molecule.

$$\begin{aligned} r_0 &= r_1 + r_2 \\ m_1 r_1 &= m_2 r_2 \\ I &= \sum_i m_i r_i^2 \\ I &= \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2 \end{aligned}$$

with:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \Rightarrow \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

μ as "reduced mass"

Angular momentum quantized:

$$E_J = \frac{\hbar^2}{2I} J(J+1) \quad ; J = 0, 1, 2, \dots \quad (6.9)$$

with J as the rotational quantum number

or energy expressed in wave numbers (remember $\tilde{\nu} = E/hc$):

$$F(J) = \frac{\hbar}{4\pi I c} J(J+1) = B \cdot J(J+1) \quad (6.10)$$

with rotational constant B :

$$B = \frac{\hbar}{4\pi I c} = \frac{\hbar}{4\pi c \mu r^2} \quad (6.11)$$

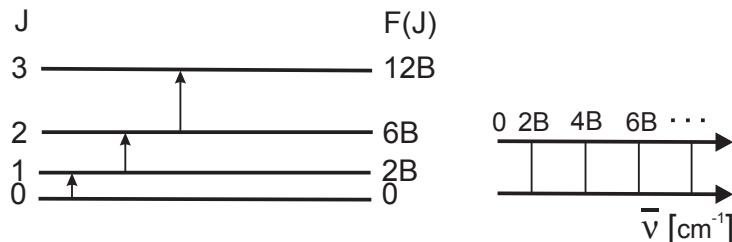


Figure 6.9: Frequency for several energy levels.

Frequencies for transitions:

$$\tilde{\nu}_{(J+1) \leftarrow J} = F(J+1) - F(J) \quad (6.12a)$$

$$= B(J+1)(J+2) - BJ(J+1) \quad (6.12b)$$

$$= 2B(J+1) \quad (6.12c)$$

So the allowed transitions are $\Delta J = \pm 1$. (e.g. argue with conservation of angular momentum: photon carries spin ± 1)

6.1.4 Vibrational Transitions

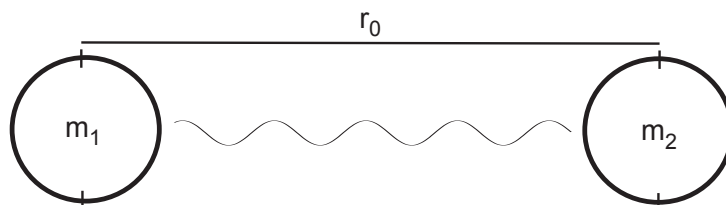


Figure 6.10: Vibrational transitions of a molecule.

Vibration of molecule around equilibrium bond length (i.e. bond length) r_0 can be approximated by harmonic oscillator. The restoring force F from r to r_0 is given by the Hooke's Law with k as the restoring force constant:

$$F = -k(r - r_0) \quad (6.13)$$

The energy levels of a harmonic oscillator are defined as:

$$E_v = \left(v + \frac{1}{2}\right) h\omega \quad v = 0, 1, 2, \dots \quad (6.14)$$

$\omega = \frac{1}{2\pi} \left(\frac{k}{\mu}\right)^{\frac{1}{2}}$ as vibrational frequency and v as vibrational quantum number
The observed transitions for $\Delta v = \pm 1$ are:

$$h\nu_{v+1 \leftarrow v} = E_{v+1} - E_v \quad (6.15a)$$

$$= \left(v + 1 + \frac{1}{2}\right) h\omega - \left(v + \frac{1}{2}\right) h\omega \quad (6.15b)$$

$$= h\omega \quad (6.15c)$$

So the energy-difference is independent of the vibrational quantum number v , all at the same frequency!

$$G(v) = \frac{E_v}{hc} \quad (6.16)$$

$$\tilde{\nu} = G(v + 1) - G(v) \quad (6.17a)$$

$$= \frac{E(v + 1) - E(v)}{hc} \quad (6.17b)$$

$$= \frac{1}{2\pi c} \left(\frac{k}{\mu}\right)^{\frac{1}{2}} = \frac{\omega}{c} \quad (6.17c)$$

Real molecules do not exactly obey laws of simple harmonic motion because real bonds although elastic are not so homogeneous as to obey Hooke's law.

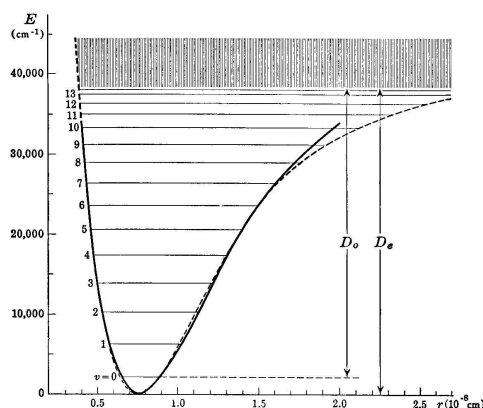


Figure 6.11: The energy levels of an anharmonic oscillator

A purely empirical expression which fits this curve to a good approximation is the Morse's Potential:

$$V(r) = D_e(1 - \exp(-a(r - r_0)))^2 \quad (6.18)$$

with r the bond length, D_e as dissociation energy and a as the constant for a particular molecule. a is defined as:

$$a = \left(\frac{k}{2hcD}\right)^{\frac{1}{2}} \quad (6.19a)$$

the vibrational levels for the anharmonic oscillator are defined by the extension of the Schroedinger equation:

$$G(v) = \left(v + \frac{1}{2}\right)\tilde{\omega} - \left(v + \frac{1}{2}\right)^2\tilde{\omega}X_e \quad v = 0, 1, 2, \dots \quad (6.20)$$

with X_e the anharmonicity constant which, for bond stretching vibrations, is always small and positive (around +0.01), so that the vibrational levels crowd more closely together with increasing v .

6.1.5 Combined Rotational and Vibrational Transitions

Write energy levels in wave numbers:

rotational levels:

$$F(J) = BJ(J + 1) \quad (6.21)$$

vibrational levels:

$$G(v) = \left(v + \frac{1}{2}\right) \tilde{\nu}_0 \quad (6.22)$$

overall levels:

$$S(v, J) = G(v) + F(J) \quad (6.23)$$

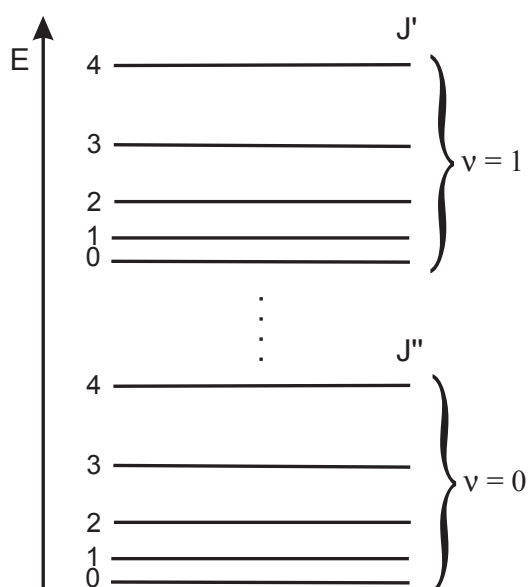


Figure 6.12: The overall levels, when combining the transitions.

$$\tilde{\nu}(J) = S(v + 1, J') - S(v, J'') \quad (6.24)$$

with: $J' = J'' \pm 1$ while $(\Delta J = \pm 1)$

$$S(v, J) = \left(v + \frac{1}{2}\right) \tilde{\nu}_0 + BJ(J + 1) \quad (6.25)$$

Now there are three possibilities for $v + 1 \leftarrow v$:

1.

$$\Delta J = -1 \quad (6.26a)$$

$$\rightarrow \tilde{\nu}(J) = S(v + 1, J - 1) - S(v, J) \quad (6.26b)$$

$$= \tilde{\nu}_0 - 2BJ \quad \rightarrow \text{"P-branch"} \quad (6.26c)$$

2.

$$\Delta J = +1 \quad (6.27a)$$

$$\rightarrow \tilde{\nu}(J) = S(v + 1, J + 1) - S(v, J) \quad (6.27b)$$

$$= \tilde{\nu}_0 + 2B(J + 1) \quad \rightarrow \text{"R-branch"} \quad (6.27c)$$

3.

$$\Delta J = 0 \quad (6.28a)$$

$$\rightarrow \tilde{\nu}(J) = \tilde{\nu}_0 \quad \rightarrow \text{"Q-branch"} \quad (6.28b)$$

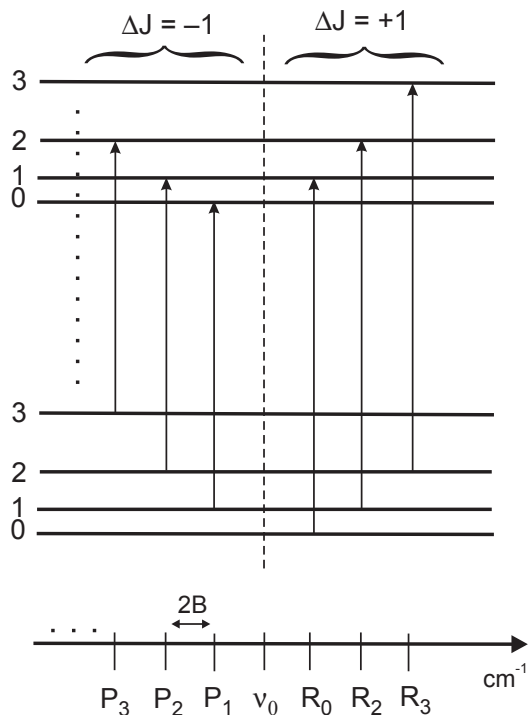


Figure 6.13: The three possibilities P-, Q-, R-branch.

6.2 Microwave Remote Sensing: Heterodyn Principle

Signals in the microwave and in particular sub-millimeter wave region can not be amplified and further analysed directly due to technological constraints. Instead, the atmospheric microwave signal is first down converted to a lower frequency (say, from 100 GHz down to 1 GHz) and this downconverted signal is then further processed. This is done by the so called heterodyn principle. In the heterodyn principle the atmospheric signal is mixed with a second reference signal of a similar frequency (the so called local oscillator, LO) in a non-linear element, typically a diode. The output of the mixing is a signal at the difference frequency between the atmospheric signal and the LO. This can be understood as follows:

Suppose that the atmospheric signal (electric field) is given by

$$E_{\text{sig}} \cos(\omega_{\text{sig}}t + \phi)$$

and the LO is given by

$$E_{\text{LO}} \cos(\omega_{\text{LO}}t).$$

Because the detector is a non-linear element, the output will not only be the sum of the two input signals, but there will also be higher order contributions. E.g., for the second order the output will be quadratic in the two electric input fields:

$$\begin{aligned} & (E_{\text{sig}} \cos(\omega_{\text{sig}}t + \phi) + E_{\text{LO}} \cos(\omega_{\text{LO}}t))^2 \\ &= \frac{1}{2} E_{\text{sig}}^2 (1 + \cos(2\omega_{\text{sig}}t + \phi)) \\ & \quad + \frac{1}{2} E_{\text{LO}}^2 (1 + \cos(2\omega_{\text{LO}}t)) \\ & \quad + E_{\text{sig}} E_{\text{LO}} (\cos(\omega_{\text{sig}} + \omega_{\text{LO}})t + \phi) + \cos(\omega_{\text{sig}} - \omega_{\text{LO}})t + \phi) \end{aligned}$$

Thus the result will contain very high frequency contributions ($2\omega_{\text{sig}}$ and $2\omega_{\text{LO}}$) which are typically filtered out, and also the difference frequency ($\omega_{\text{sig}} - \omega_{\text{LO}}$) which is of particular importance here. Note that the amplitude of the difference signal is linearly proportional to the amplitude of the atmospheric signal.

The difference frequency is called the intermediate frequency IF:

$$\omega_{\text{IF}} = \omega_{\text{sig}} - \omega_{\text{LO}}.$$

Note that for a given IF and LO frequency, the signal from two atmospheric frequency ranges will be mixed into the IF:

$$\omega_{\text{sig}} = \omega_{\text{LO}} \pm \omega_{\text{IF}}.$$

These two frequency regions are called the upper and lower side bands.

Receivers can be operated in a double sideband mode, i.e. receiving both side band simultaneously. Or they can be operated as single sideband (SSB) receivers, where one of the side bands is filtered out.

6.2.1 Quasi Optics

In order to couple the atmospheric signal into the receiver (mixer), a set up of optical elements may be necessary, known as the quasi optics. However, because of the long wavelength compared to the size of the (quasi-) optical elements, instead of geometric optics, the principle of Gaussian optics needs to be applied.

Typical elements used are (focussing and non-focussing) mirrors. Wire grids can be used as polarization dependent elements, reflecting the signal in one polarization direction and transmitting the signal in the perpendicular direction. Wire grids are also used as beam splitters, that can be used to construct interferometers, used as band pass frequency filters in the quasi optical set up.

6.2.2 Calibration

The received power P is under the Rayleigh-Jeans approximation proportional to the equivalent blackbody temperature T and the frequency bandwidth $\Delta\nu$:

$$P = k_B T \Delta\nu,$$

with k_B the Boltzmann constant. However, the detected power P will be both due to contributions from the (atmospheric) signal, and from the receiver itself. Thus, a system like this is called a Total Power Receiver.

To extract the weak atmospheric signal from the total power received a calibration is needed. This is typically done by a periodic hot-cold calibration: the instrument observes alternately a hot and a cold blackbody of known temperatures and then the (unknown) atmospheric signal. Assuming that the response of the receiver is linear to the input signal, the atmospheric brightness temperature can then be calibrated by the known hot and cold blackbody temperatures:

$$T_{\text{atm}} = T_{\text{cold}} + (T_{\text{hot}} - T_{\text{cold}}) \frac{P_{\text{atm}} - P_{\text{cold}}}{P_{\text{hot}} - P_{\text{cold}}}.$$

The total power P is proportional to the sum of the atmospheric brightness temperature T_{atm} and the system noise temperature T_{sys} . The system noise temperature can also be determined through a hot/cold calibration:

$$T_{\text{sys}} = \frac{T_{\text{hot}} - Y T_{\text{cold}}}{Y - 1},$$

with

$$Y = P_{\text{hot}}/P_{\text{cold}}.$$

The lower the system noise temperature, the better the signal to noise ratio of the receiver. The sensitivity of a receiver is proportional to

$$T_{\text{sys}} (\Delta\nu\Delta t)^{-1/2}.$$

The sensitivity can thus be improved by reducing the system noise temperature, by increasing the measurement time Δt or by increasing the spectral band width $\Delta\nu$.

6.2.3 Spectrometer

Spectrometer types used in microwave radiometers:

- Filter bank
- Acousto Optical Spectrometer (AOS)
- Chirp Transform Spectrometer (CTS)

The typical band width of an AOS is about 1 GHz and less for a CTS, with a typical spectral resolution of about 1 MHz (and again less for a CTS). This means that in practice only one or at best very few individual rotational lines can be measured simultaneously. This is one of the disadvantages of current microwave or submillimeter wave receivers.

Below is a schematic of the Radiometer from Atmospheric Measurements (RAM), operated by the University of Bremen since 1994 in Spitsbergen.

Scheme of a RAM Module

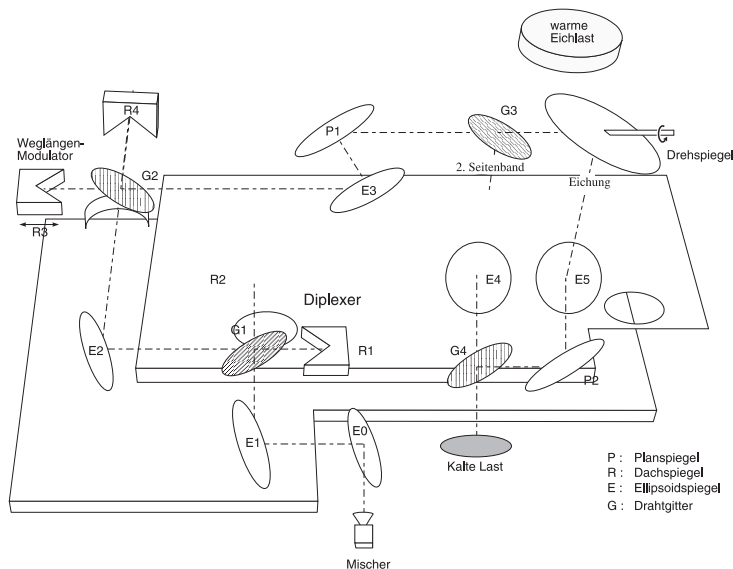


Figure 6.14: Scheme of the RAM quasi-optics.

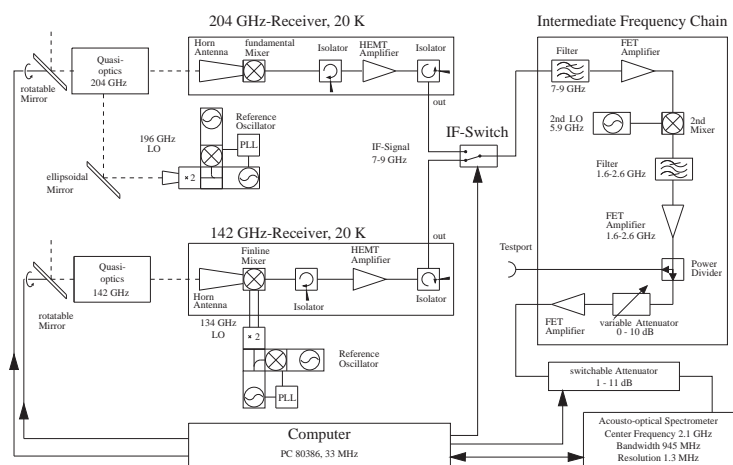


Figure 6.15: Schematic Overview of the RAM (technical).

Here is an example of the spectrum measured by the RAM. The dominant feature is an ozone rotational line at about 142 GHz, measured at high

spectral resolution. This high spectral resolution enables one to separate the contributions from different altitudes through their different pressure broadening.

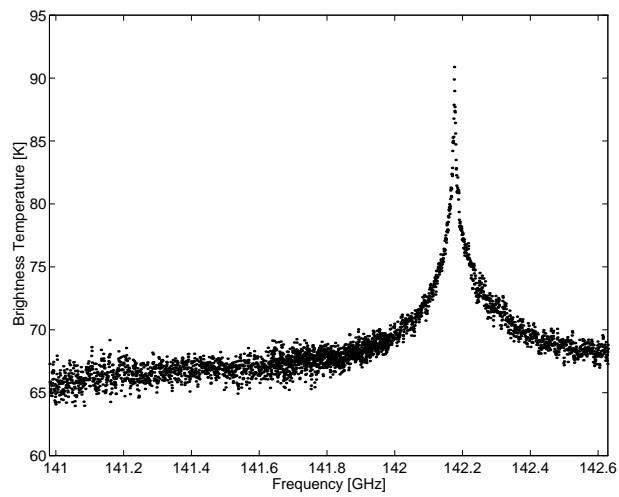


Figure 6.16: RAM spectrum.

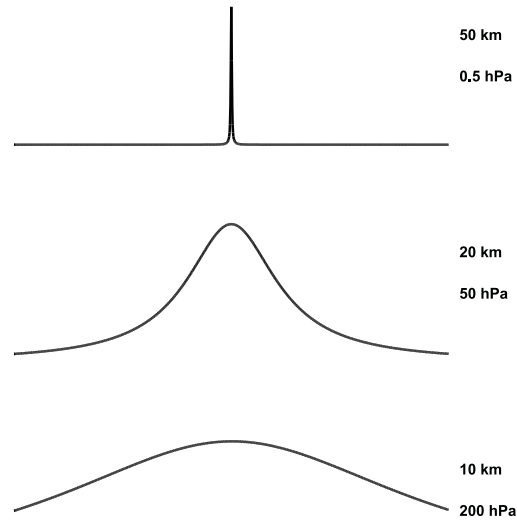


Figure 6.17: The pressure broadening of spectral lines
