Radiative Transfer

7. Line radiative transfer

Aurore Bacmann / IPAG / Université Grenoble Alpes

Introduction

- Contrary to the case of dust, the opacities in the gas are generally dominated by spectral lines (and not by a continuous emission)
- These lines can be in absorption or in emission, in the whole wavelength spectra, coming from a large variety of objects: stellar spectra or ionised nebulae spectra in the UV/visible, in the (sub)mm and radio domain for cold interstellar clouds, or in the X-ray domain for very hot regions like the solar corona or galaxy clusters
- These lines correspond to transitions between quantified energy levels in atoms or molecules (bound-bound transitions) and are described by quantum mechanics
- Continuous radiation on which lines can superpose can be thermal (eg dust emission) or non thermal (eg synchrotron emission)
- Transitions between bound levels can be due to collisions (collisional transitions), or to absorbing or emitting a photon (radiative transitions)
- In this chapter we will describe the basics of line radiative transfer, discuss systems which we frequently encounter and their energy diagrams, and solve the radiative transfer

1. Emission and absorption

1.1 Levels, statistical weights, partition function

- We will first mention again the essential information to describe quantum states in atoms and molecules

- Let us consider an atom or a molecule with N_{lev} energy levels
  - E_i is the energy of level i (convention $E_i < E_{i+1}$)
  - g_i is the level degeneracy (statistical weight)
  - N_i is the number of atoms per unit volume in the state of energy E_i (level occupation number)
  - N is the total number of atoms or molecules per unit volume: $N = \sum_i N_i$
  - We can also define the occupation fraction $n_i = \dfrac{N_i}{N}$ with $\sum_i n_i = 1$

1.1 Levels, statistical weights, partition function

- When we solve radiative transfer, we try to determine n_i
- The equation that describes the level occupation at LTE is the Boltzmann distribution:

$\frac{n_j}{n_i} = \frac{N_j}{N_i} = \frac{g_j}{g_i} \mathrm{e}^{-\frac{E_j - E_i}{kT}}$, with T the temperature and k the Boltzmann constant

- At LTE, we can define the partition function: $Z(T) = \sum_i g_i \, \mathrm{e}^{-\frac{E_i}{kT}}$ (sum over all states)
- It allows us to calculate the occupation fraction n_i directly instead of n_j/n_i

$$n_i = \frac{1}{Z(T)} g_i \, \mathrm{e}^{-\frac{E_i}{kT}}$$

1.2 Einstein coefficients

- This is probably not new, but just in case…
- The Einstein coefficients / probabilities are defined
  - A_{ji} : Einstein coefficient for spontaneous emission. The number of spontaneous radiative transitions per unit volume and per unit time between state j and state i and that correspond to the emission of a photon of frequency ν_{ij} such as $h\nu_{ij} = E_j - E_i$ is $A_{ji}\,N_j$

    A_{ji} is in s^{-1}

    $\dfrac{1}{A_{ji}}$ is the time, in s, that the atom can spend in state j before its de-excitation towards state i, assuming no collisional de-excitation. It is the level lifetime.

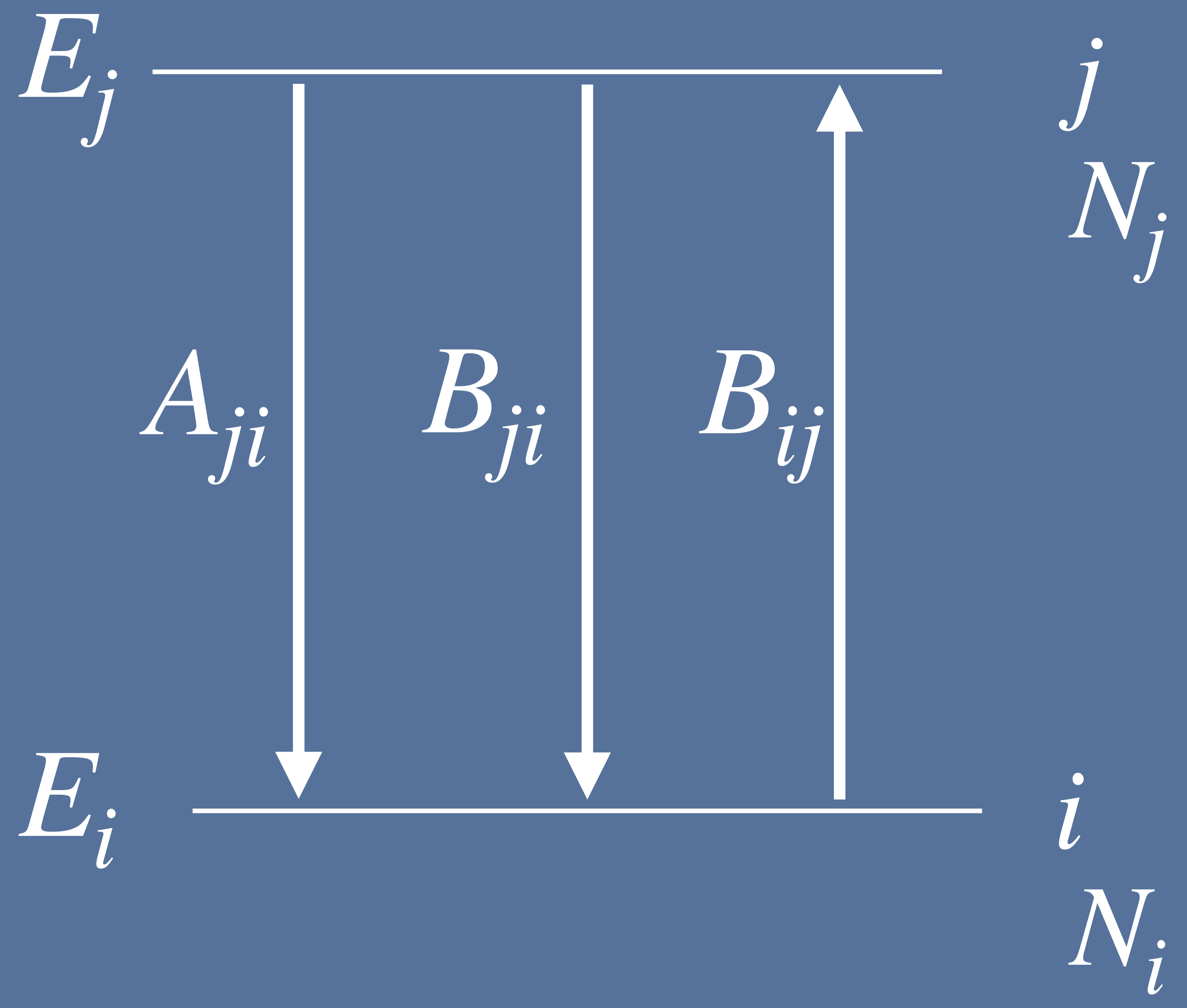
1.2 Einstein coefficients

- B_{ij} : Absorption coefficient. The number of radiative transitions per unit volume and per unit time induced by a photon of energy $h\nu_{ij} = E_j - E_i$ corresponding to the absorption of this photon is $B_{ij}\, N_i\, J_{\nu_{ij}}$ with $J_{\nu_{ij}}$ the intensity of the radiation field at frequency ν_{ij}

- B_{ji} : stimulated emission coefficient. The number of radiative transitions per unit volume and per unit time between level j and level i induced by a photon of energy $h\nu_{ij} = E_j - E_i$ corresponding to the emission of a second photon with the same energy is $B_{ji}\, N_j\, J_{\nu_{ij}}$. It is Einstein who discovered the existence of this process. It is also called “induced emission”.

- Unit of B_{ij} and B_{ji} ?

1.2 Einstein coefficients



1.2 Einstein coefficients

- Using microreversibility of these processes, which is verified at TE, we obtain the relation: $N_j\,(A_{ji} + B_{ji}\, J_{\nu_{ij}}) = N_i\, B_{ij}\, J_{\nu_{ij}}$

- The number of radiative transitions leading to a change from level i to level j in the atom (or molecule) per second is equal to the number of radiative transitions leading to a change from level j to level i.

- Using Boltzmann's law: $\dfrac{N_j}{N_i} = \dfrac{g_j}{g_i} \exp\left(-\dfrac{h\nu_{ij}}{kT}\right)$

- And Planck's law: $J_{\nu_{ij}} = B_{\nu_{ij}} = \dfrac{2h{\nu_{ij}}^3}{c^2}\,\dfrac{1}{\exp\left(\dfrac{h\nu_{ij}}{kT}\right) - 1}$ (at LTE, we have $J_{\nu_{ij}} = B_{\nu_{ij}}$)

1.2 Einstein coefficients

- We obtain $J_{\nu_{ij}} = \dfrac{A_{ji}/B_{ji}}{\dfrac{N_i B_{ij}}{N_j B_{ji}} - 1} = \dfrac{A_{ji}/B_{ji}}{\dfrac{g_i B_{ij}}{g_j B_{ji}} \exp \dfrac{h\nu_{ij}}{kT} - 1}$
- This relation is verified for all temperatures, so we can identify the terms using Planck's law:
- $\dfrac{A_{ji}}{B_{ji}} = \dfrac{2h\nu^3}{c^2}$ and $g_i B_{ij} = g_j B_{ji}$
- Knowing A_{ji}, we can calculate the others.

1.3 Relation with the absorption coefficient and emissivity

- Spectral lines are not infinitely narrow but are broadened by different processes which give them an absorption profile $\phi(\nu)$ and an emission profile $\psi(\nu)$
- These profiles describe the transition probability for photons of frequency ν
- The profile functions are normalised: $\int \phi(\nu) d\nu = 1$ and $\int \psi(\nu) d\nu = 1$
- Their maximum occurs for $\nu = \nu_{ij}$ (such as $h\nu_{ij} = E_j - E_i$) and they decrease rapidly for $\nu < \nu_{ij}$ and $\nu > \nu_{ij}$
- We should replace $B_{ij} J_{\nu_{ij}}$ by $B_{ij} J_{\nu_{ij}} \phi(\nu)\, d\nu$ and A_{ji} by $A_{ji} \psi(\nu)\, d\nu$

1.3 Relation with the absorption coefficient and emissivity

- The emissivity is linked to the radiative decay rate A_{ji} by
  - $j_{ij,\nu} = \dfrac{h\nu_{ij}}{4\pi} N_j A_{ji} \psi(\nu)$
  - unit: $\mathrm{erg\,s^{-1}\,cm^{-2}\,cm^{-1}\,Hz^{-1}\,sr^{-1}}$
- The extinction coefficient is written
  - $\alpha_{ij,\nu} = \dfrac{h\nu_{ij}}{4\pi} (N_i B_{ij} - N_j B_{ji})\, \phi(\nu)$
  - unit: $\mathrm{cm^{-1}}$
- The absorption and emission profiles are identical if between both processes, no change in frequency occurs, or if on the contrary there is a complete frequency redistribution

1.3 Relation with the absorption coefficient and emissivity

Source function

- If we assume that the emission profile $\psi(\nu)$ and absorption profile $\phi(\nu)$ are identical, the source function S_ν for the line can be written:

$$S_\nu = \frac{j_\nu}{\alpha_\nu} = \frac{N_j A_{ji}}{N_i B_{ij} - N_j B_{ji}} = \frac{N_j A_{ji}}{N_j B_{ji}} \frac{1}{\frac{N_i B_{ij}}{N_j B_{ji}} - 1} = \frac{2h\nu^3}{c^2} \frac{1}{\frac{g_i B_{ij}}{g_j B_{ji}} \exp \frac{h\nu}{kT} - 1}$$

- $S_\nu = \dfrac{2h\nu^3}{c^2} \dfrac{1}{\exp \frac{h\nu}{kT} - 1}$

1.3 Relation with the absorption coefficient and emissivity

Excitation temperature

- In Chapter 4, we had defined the excitation temperature such as $S_\nu = B_\nu(T_\mathrm{ex})$:

$$S_\nu = \frac{2h\nu^3}{c^2}\frac{1}{\exp\frac{h\nu_{ij}}{kT} - 1} \quad \Rightarrow \quad \frac{N_j}{N_i} = \frac{g_j}{g_i}\exp\frac{h\nu_{ij}}{kT_\mathrm{ex}}$$

- The excitation temperature is the temperature that gives the relative populations of two levels (whether or not there is a transition between them)

- In the general case, the excitation temperature is different for each pair of levels.

- At LTE, the populations are given by Boltzmann's law and $\dfrac{N_j}{N_i} = \dfrac{g_j}{g_i}\exp\left(-\dfrac{h\nu_{ij}}{kT}\right)$ for all levels, with T the gas kinetic temperature. In this case, all excitation temperatures are equal to the gas kinetic temperature: $T_\mathrm{ex} = T$

1.3 Relation with the absorption coefficient and emissivity

Excitation temperature

- The absorption coefficent can be written

$$\alpha_{ij,\nu} = \frac{h\nu_{ij}}{4\pi} N_i B_{ij} \phi(\nu) \left[1 - \exp\left(-\frac{h\nu_{ij}}{kT_{\rm ex}}\right)\right]$$

- It therefore contains a negative term of induced emission, which we must take into account in the radio domain, especially when $\exp\left(-\frac{h\nu_{ij}}{kT_{\rm ex}}\right)$ is close to unity.
- On the other hand, in the visible/UV domain, if $T_{\rm ex} \sim 10^4\,\mathrm{K}$ (eg in stellar atmospheres), the exponential term is $\ll 1$ and induced emission can be neglected

1.3 Relation with the absorption coefficient and emissivity

Excitation temperature

- If the induced emission term is $\gg 1$, the absorption coefficient becomes negative and the medium behaves like a possible amplifier. In the radio domain, this is the maser effect (“Microwave amplification”) analogous to lasers in the optical .
- In order to have a maser, we need $\frac{N_j}{N_i} > \frac{g_j}{g_i}$, which is frequent, in particular for non linear molecules.
- The population inversion is possible if processes (radiative or not) can populate the upper level of the transition

1.4 Oscillator strength

- In classical radiation theory, the absorption coefficient of a harmonic oscillator is equal to $\dfrac{\pi e^2}{mc}$ where m is the electron mass, and e its charge.
- This quantity is equal to 0.0265 cm^2
- In quantum theory, this quantity has to be multiplied by a parameter called the oscillator strength f_{ij}, smaller than unity, and that represents the number of classical oscillators equivalent to the transition.
- The absorption coefficient can be written $\alpha_{ij,\nu} = N_i \dfrac{\pi e^2}{mc} f_{ij}\, \phi(\nu) \left[1 - \exp\left(-\dfrac{h\nu_{ij}}{kT_{\rm ex}}\right)\right]$
- And the Einstein coefficients: $B_{ji} = \dfrac{\pi e^2}{mc} f_{ij} \dfrac{4\pi}{h\nu}$ and $A_{ji} = \dfrac{8\,\pi^2 e^2 \nu^2}{mc^3} \dfrac{g_i}{g_j} f_{ij}$

1.5 Example of atomic and molecular species

1.5.1 Atomic species

Hydrogen and hydrogenoid atoms

- The energy of the ground state for H is

$$E_1 = -R_y = -\frac{m_e e^4}{2\hbar^2} = -\frac{m_e c^2 \alpha^2}{2} = -13.6\,\text{eV}$$

- R_y is the Rydberg constant
- α is the fine structure constant: $\alpha = \dfrac{e^2}{\hbar c} \simeq \dfrac{1}{137}$
- m_e is the electron mass. Rigorously speaking, we should use the reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p} \sim m_e$$

1.5.1 Atomic species

Hydrogen and hydrogenoid atoms

- For a hydrogenoid atom of charge Z, we have: $E_1 = -Z^2 \frac{m_e e^4}{2\hbar^2} = -Z^2 R_y$

- The energies of other electronic levels are expressed with n, principal quantum number: $E_n = \frac{E_1}{n^2} = E_{nlms}$,
  - l is the orbital angular momentum of the electron: $l = 0, 1, 2, \ldots, n-1$
  - m is the projection of the angular momentum: $-l \leq m \leq +l$ in steps of 1
  - $s = \pm 1/2$ is the electronic spin
- The excited electronic states of the H atom have energies much higher than that of the ground state, which means they are hardly populated at low temperatures

1.5.1 Atomic species

Hydrogen and hydrogenoid atoms

- The transitions between levels have an energy

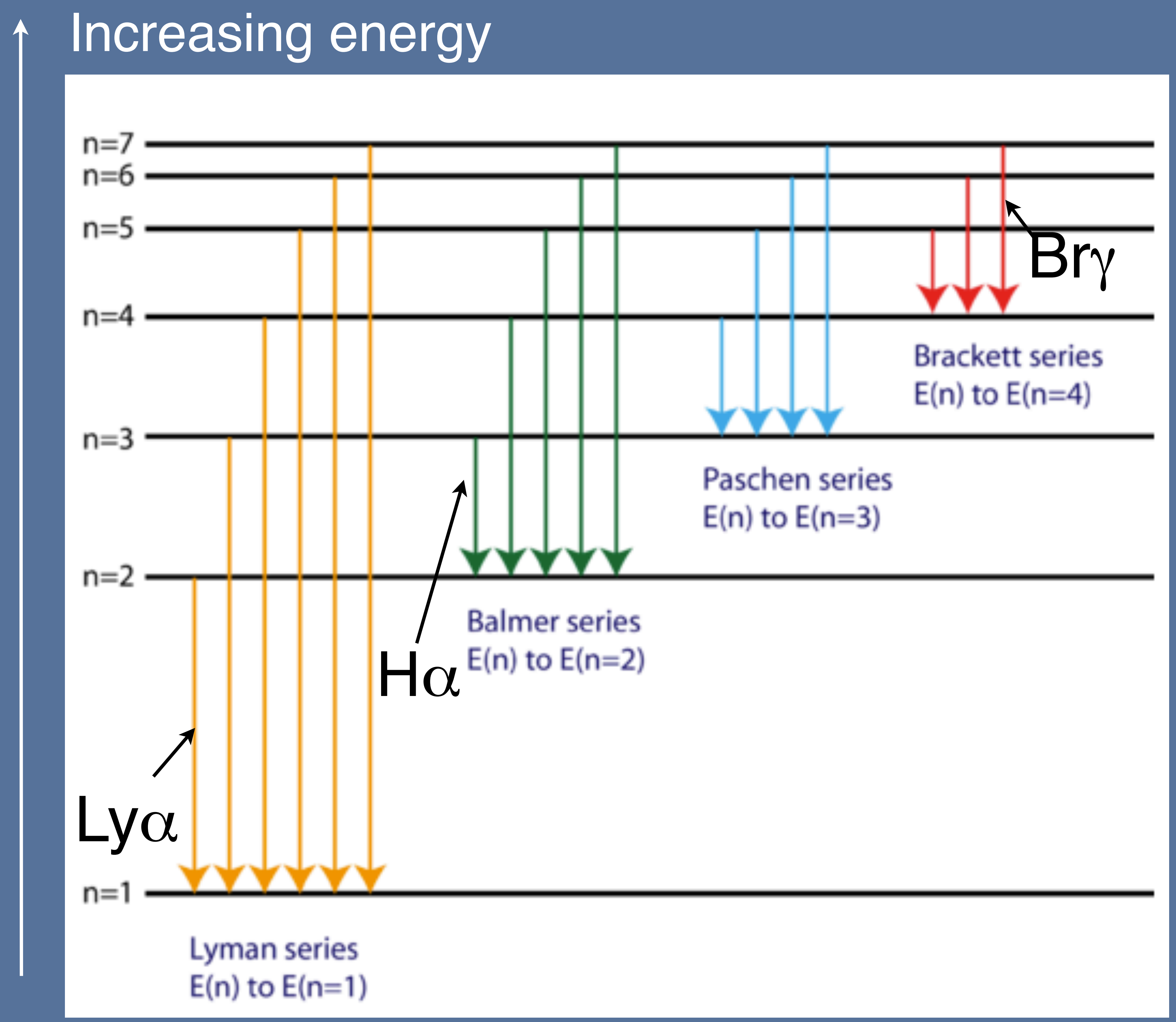
$$E_{ji} = E_j - E_i = -E_1\left(\frac{1}{j^2} - \frac{1}{i^2}\right)$$

- The oscillator strength is $f_{ji} = \frac{2^6}{3\sqrt{3}\pi}\frac{1}{g_j}\frac{1}{\left(\frac{1}{j^2}-\frac{1}{i^2}\right)^3}\frac{1}{j^3}\frac{1}{i^3}g$
- g is the Gaunt factor
- Oscillator strengths decrease when the upper level quantum level increases

1.5.1 Atomic species

Electronic transitions for the hydrogen atom

- Transitions “series” correspond to transitions between 2 levels of same lower level
- Lyman series corresponds to transitions between the ground state and other levels
- For Ly α, $\lambda = 121.5\,\mathrm{nm}$, and other lines in the series have shorter wavelengths: series in the UV
- The transitions between the second and higher levels make up the Balmer series. The line $n = 3 \rightarrow n = 2$ is called H α with $\lambda = 656.3\,\mathrm{nm}$ (visible, red). It is often the most intense line in the visible spectrum (A and B stars, ionised nebulae)
- Other series (Paschen, Brackett, Pfund, etc) are in the IR

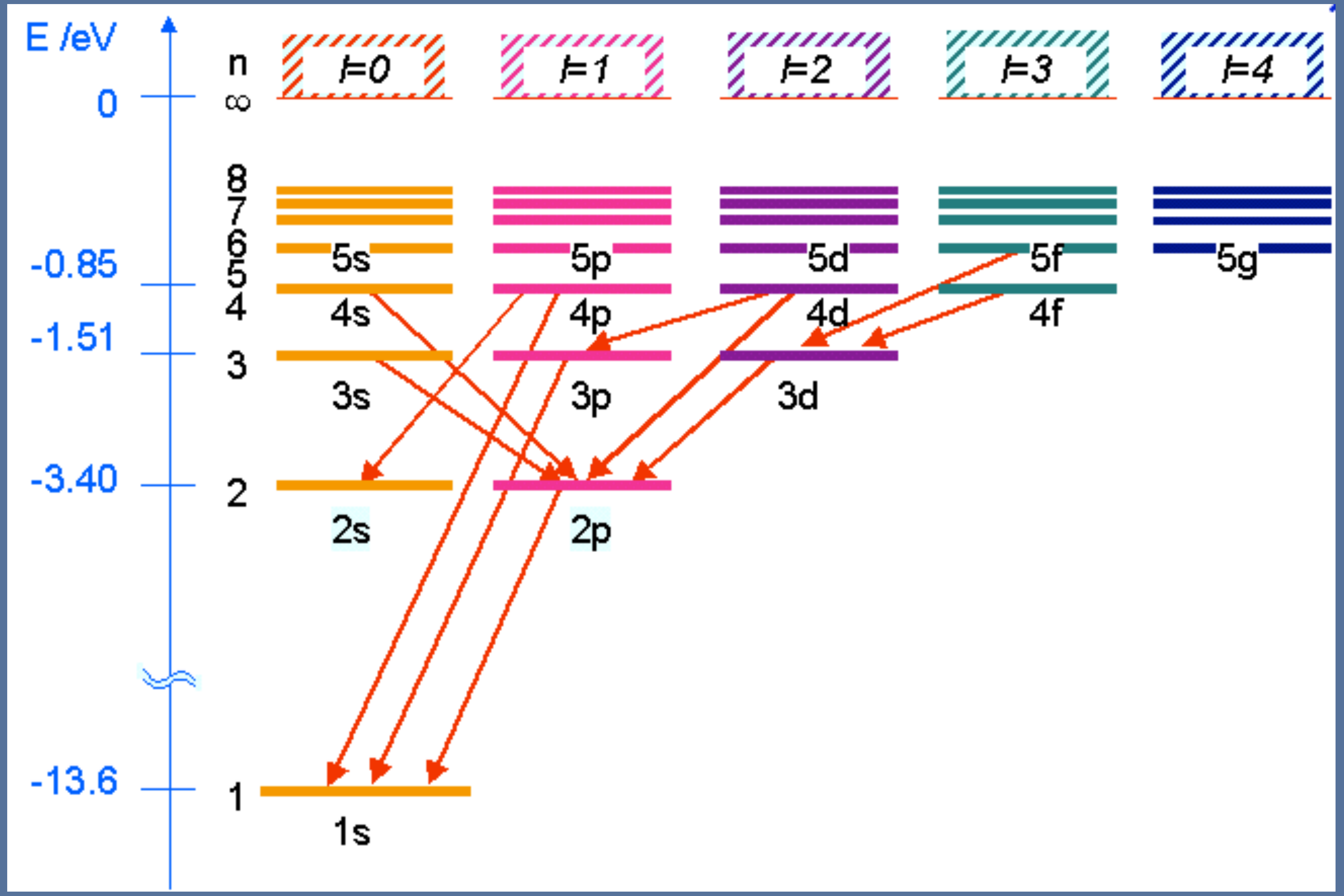


1.5.1 Atomic species

Electronic transitions for the hydrogen atom

- It is also possible to represent transitions on a Grotrian diagram.
- Because of the selection rules ($\Delta l = \pm 1 \quad \Delta l \neq 0$), only certain transitions are allowed.
- The transition $2s \rightarrow 1s$ is forbidden. It corresponds to the emission of two photons with the sum of their energies equal to that of Ly α
- Levels with the same n are degenerate

Grotrian diagram (term diagram)



takes selection rules into account

1.5.1 Atomic species

Fine and hyperfine structure

- If relativistic effects are included (close to the nucleus, the electron velocity is close to light speed) as well as spin-orbit coupling, the level energies are slightly shifted:

$$E_{nl} = -Z^2 \frac{R_y}{n^2} \left(1 + \frac{(Z\alpha)^2}{n^2 \left[\frac{n}{j+1/2} - \frac{3}{4} \right]} \right)$$

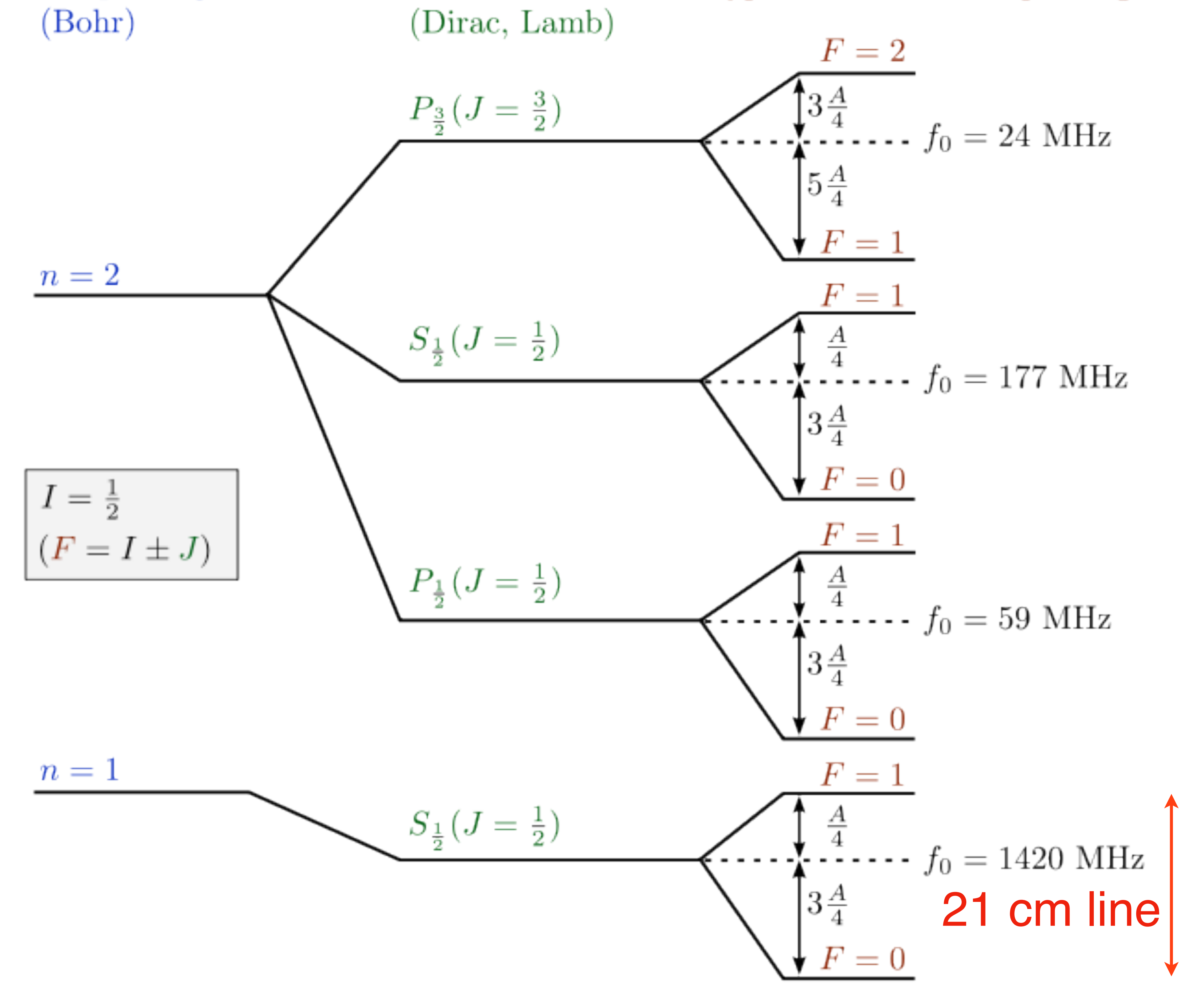
  j is the quantum number associated to the total angular momentum $J = L + S$. Each state is $2j+1$ times degenerate

- This additional level splitting gives rise to fine structure. It is maximal for small n (because the electron is close to the nucleus) or for large Z

1.5.1 Atomic species

Fine and hyperfine structure

- The coupling between the electron and the nuclear spin induces another splitting: hyperfine structure
- For hydrogen, there is a very important transition between two hyperfine levels of term $S_{1/2}$ for $n = 1$. It is the 21 cm line in the radio domain, with which one can trace neutral H emission in the Universe.
- This is a forbidden transition with Einstein A coefficient of $2.9\,10^{-15}\,\mathrm{s}^{-1}$ (excited level lifetime: ~ 10 Myears). Its natural linewidth is very small
- Because of the great number of H atoms, this line is very strong
- This transition was detected for the first time in 1951
- For most other astrophysical applications, this splitting can be ignored



1.5.1 Atomic species

Multi-electron atoms

- As for H, eletrons will occupy levels of main quantum number n, of orbital angular momentum l and projection m, and of spin s.
- There are however differences with respect to the case with only one electron
  - Because of Pauli's principle, two electrons cannot occupy the same quantum state
  - The presence of other electrons modifies the charge distribution and changes the energy levels of electronic states
- The state of an atom is given by the occupation of the orbitals and the term symbol

1.5.1 Atomic species

Multi-electron atoms

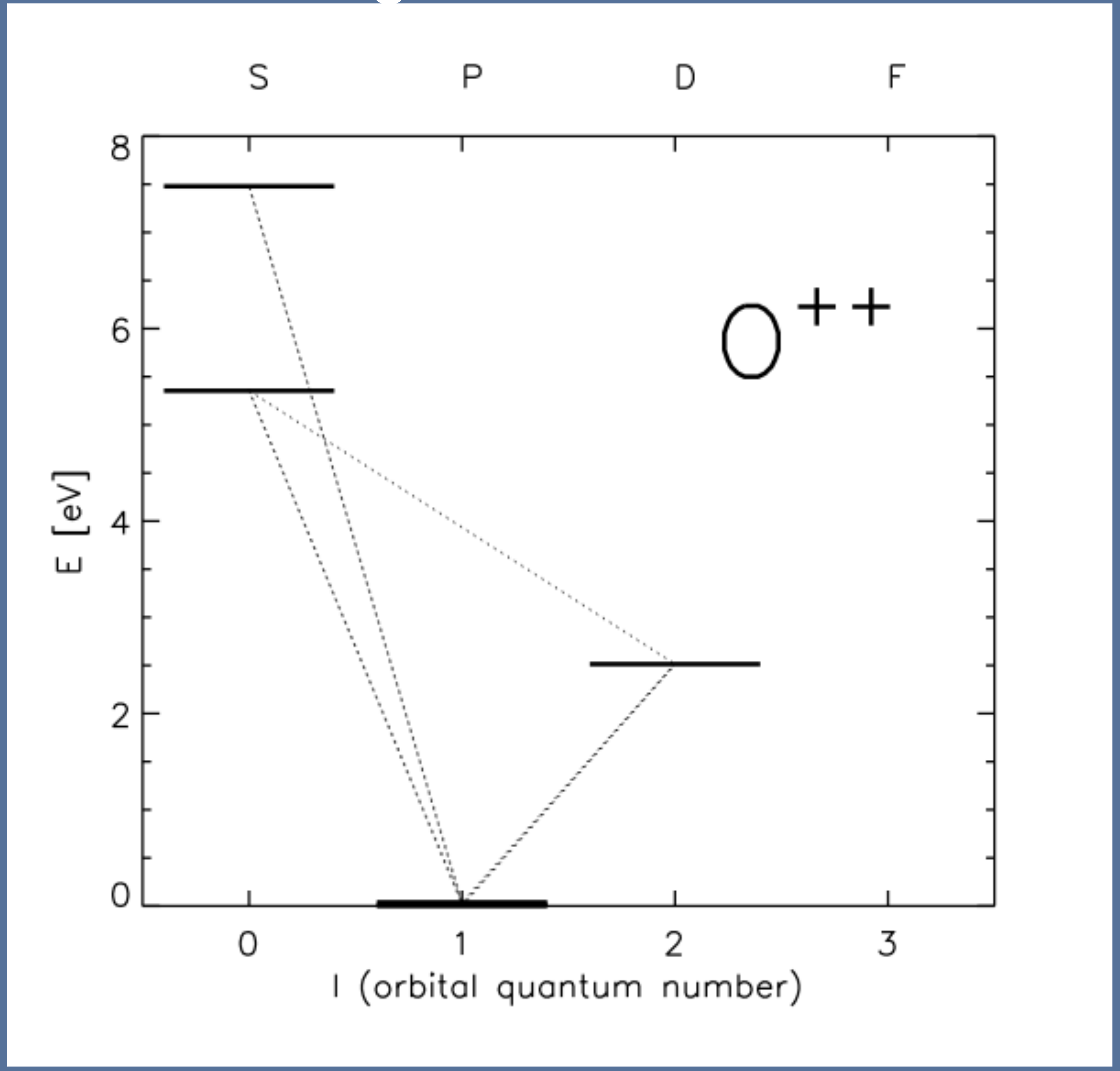
- Examples of occupations of the orbitals
  - Lithium, $Z = 3$, ground state $1s^2\ 2s^1$
  - Oxygen, $Z = 8$, ground state $1s^2\ 2s^2\ 2p^4$
- For a given occupation of the orbitals, there can be several electronic configurations leading to different values for the total spin S, the total orbital angular momentum L, and for J the total angular momentum. These configurations are called “term symbols”.
- For fully occupied shells, we have ${}^1S_0$ terms that do not contribute to electronic excitation. We then focus on external shells.

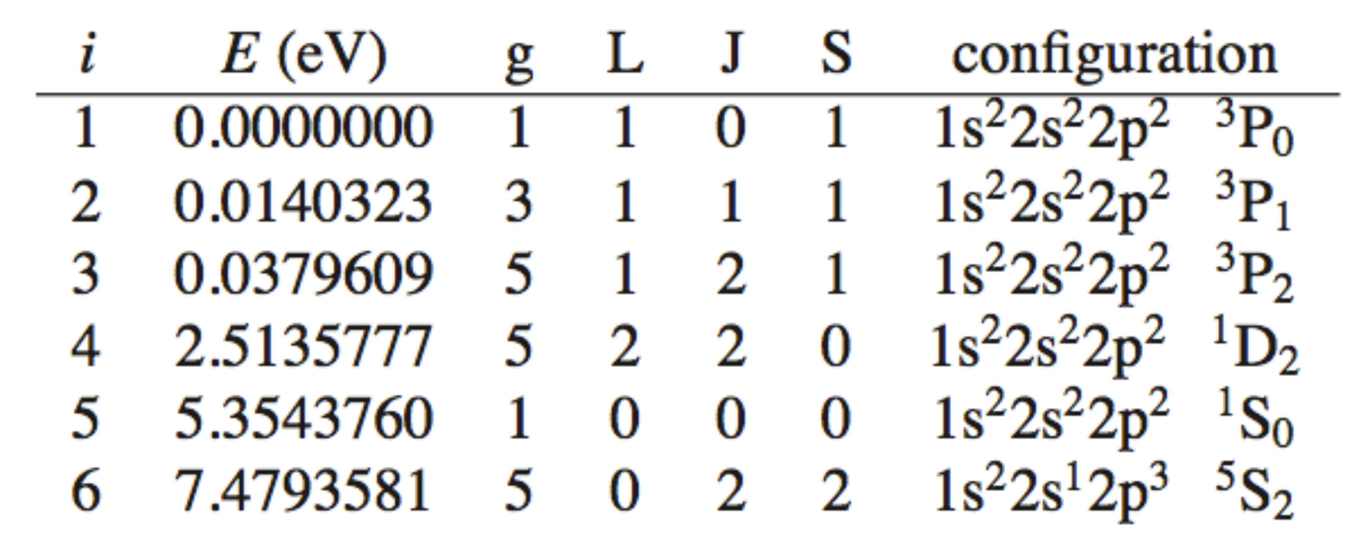
1.5.1 Atomic species

Multi-electron atoms

- Example of doubly ionised oxygen
- 6 electrons: $1s^2\ 2s^2\ 2p^2$
- Spectral terms : ${}^1\mathrm{D}_2,\ {}^3\mathrm{P}_0,\ {}^3\mathrm{P}_1,\ {}^3\mathrm{P}_2,\ {}^1\mathrm{S}_0$
- Hund's rules are used to find the lowest energy levels
- Transition ${}^1D_2 \rightarrow {}^3P_2$ is the transition [OIII] $\lambda = 0.5\,\mu\mathrm{m}$. This is a forbidden line often observed in ionised nebulae like planetary nebulae. The word "forbidden" here means that there is no authorised dipole transition, but quadrupole transitions are allowed, for which A_{ji} is very weak (compared with the A_{ji} of dipolar transitions)

Term diagram for O^{2+}





i	E (eV)	g	L	J	S	configuration	
1	0.0000000	1	1	0	1	$1s^2 2s^2 2p^2$	${}^3P_0$
2	0.0140323	3	1	1	1	$1s^2 2s^2 2p^2$	${}^3P_1$
3	0.0379609	5	1	2	1	$1s^2 2s^2 2p^2$	${}^3P_2$
4	2.5135777	5	2	2	0	$1s^2 2s^2 2p^2$	${}^1D_2$
5	5.3543760	1	0	0	0	$1s^2 2s^2 2p^2$	${}^1S_0$
6	7.4793581	5	0	2	2	$1s^2 2s^1 2p^3$	${}^5S_2$

C.P. Dullemond

1.5.2 Molecular species

- Observed molecular lines or generally not due to electronic transitions but rather to vibrations or rotation of the molecule
- Excited vibrational and rotational energy levels have much lower energies than electronic levels and therefore molecular transitions occur at much longer wavelengths than electronic transitions

1.5.2.1 Rotational transitions

Linear molecules

- For linear molecules like CO, the expression of the rotational energy levels is particularly simple
- There is only one quantum number, J which is the rotational quantum number
- The energy levels are given by: $E = \dfrac{\hbar^2}{2I} J(J+1) = B\, J(J+1)$
  - I is the moment of inertia of the molecule along the rotation axis. For CO, $I = 1.46\, 10^{-39} \mathrm{g\, cm^2}$
  - The statistical weights of the rotational levels are $2J+1$
  - The rotation constant is $B = \dfrac{h}{8\pi^2\, c\, I}$
- Because of centrifugal distortion, there are correction terms in the expression of E (modification of the moment of inertia at high J)

1.5.2.1 Rotational transitions

- Selection rules: allowed transitions are such as $\Delta J = \pm 1$
- The transition frequencies ν therefore verify:

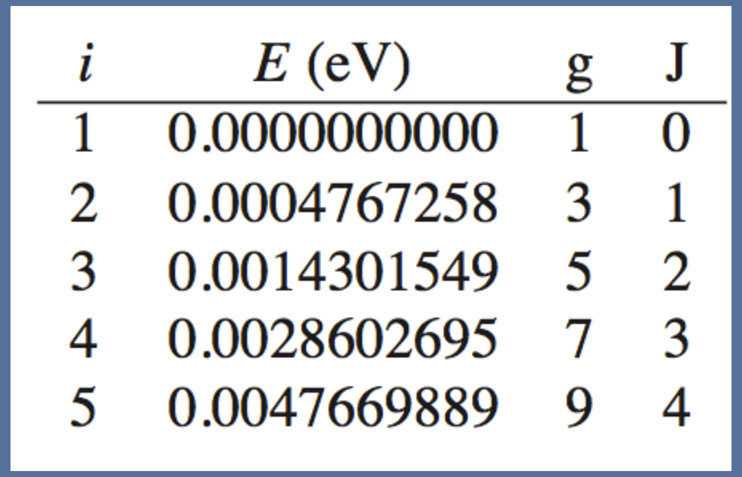
$$h\nu = \frac{\hbar^2}{2I}\left[J\left(J+1\right) - \left(J-1\right)J\right] = \frac{\hbar^2}{I}J$$

  The transitions frequencies linearly increase with J

- The rotational spectrum of linear molecules is very simple: we have a "rotational ladder".

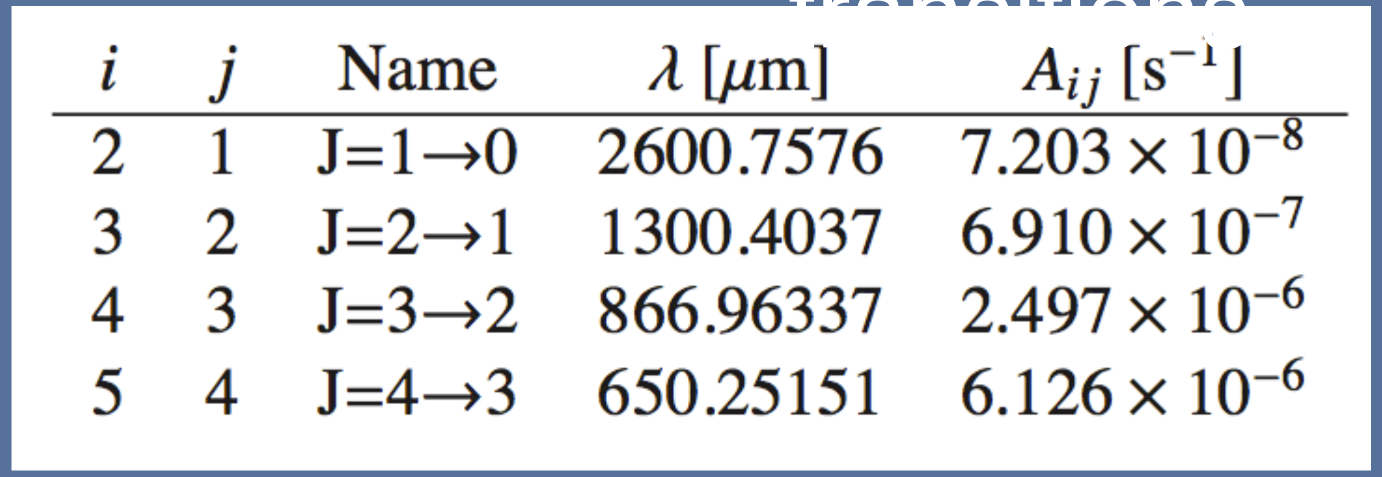
1.5.2.1 Rotational transitions

- For CO, rotational transitions $J : 1 \rightarrow 0$ and $J : 2 \rightarrow 1$ occur in the millimeter domain.
- These are typically the most intense lines coming from cold interstellar and circumstellar matter in this wavelength domain.
- In the ISM, CO largely dominates the spectral emission in the (sub)mm because it is the most abundant molecule after H_2: CO abundance is about 10^{-4} times that of H_2

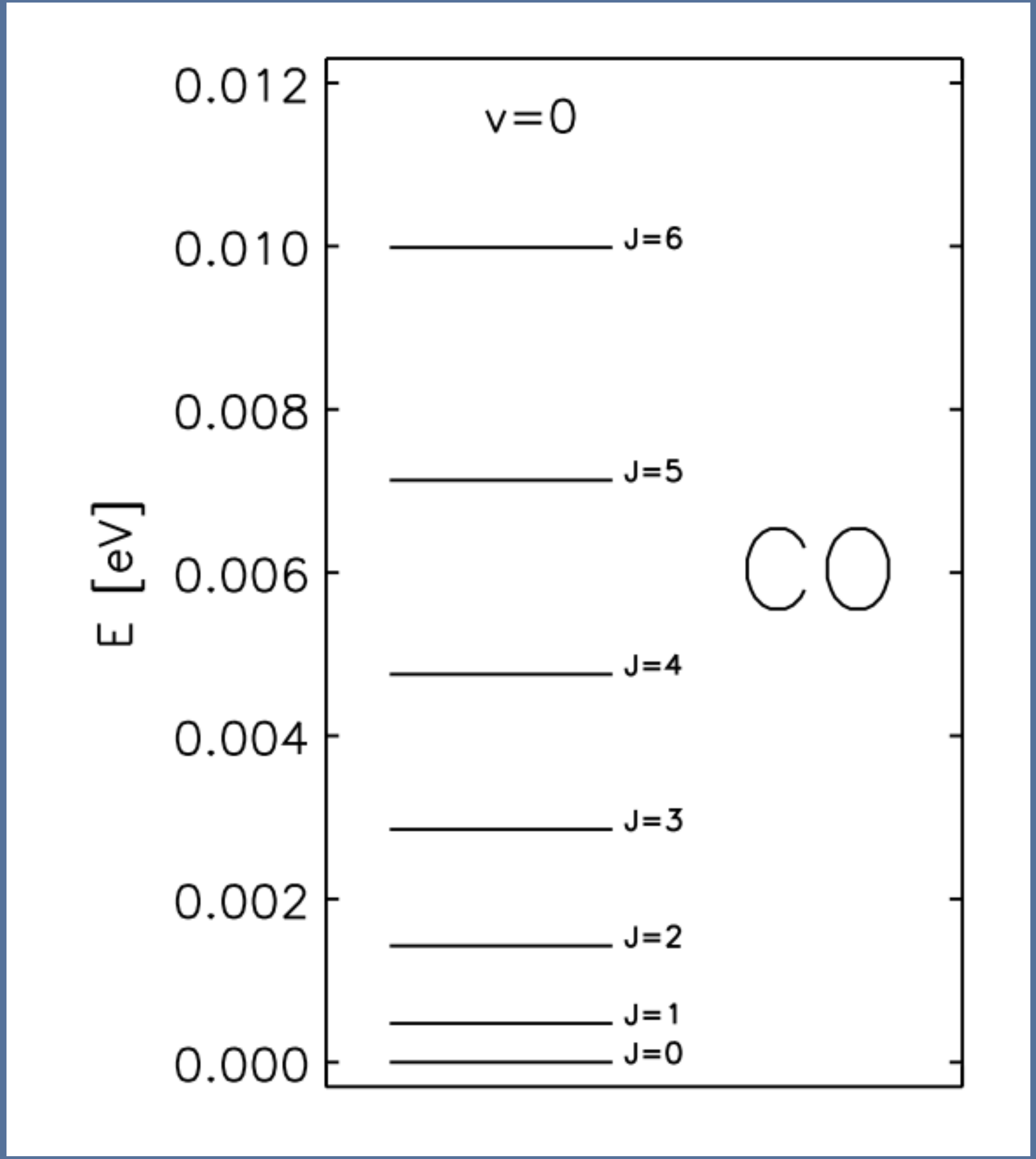


i	E (eV)	g	J
1	0.0000000000	1	0
2	0.0004767258	3	1
3	0.0014301549	5	2
4	0.0028602695	7	3
5	0.0047669889	9	4

CO rotational transitions



i	j	Name	λ [μm]	A_{ij} [s^{-1}]
2	1	J=1→0	2600.7576	7.203×10^{-8}
3	2	J=2→1	1300.4037	6.910×10^{-7}
4	3	J=3→2	866.96337	2.497×10^{-6}
5	4	J=4→3	650.25151	6.126×10^{-6}



C.P. Dullemon

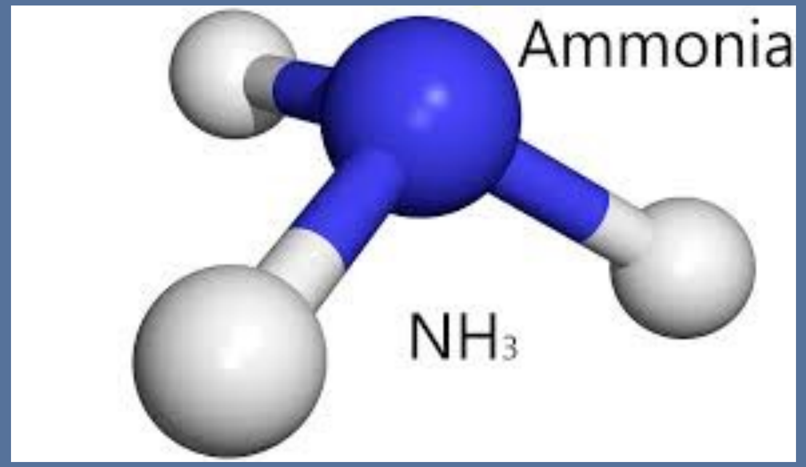
1.5.2.1 Rotational transitions

- Why are H_2 rotational lines not much stronger than those of CO (considering the fact that there is 10000 times mode H_2 than CO?)
    - H_2 is a symmetric molecule abd as a consequence, it does not have a permanent electric dipole. Such a molecule does not produce dipolar radiation when spinning. Although H_2 does not have dipolar transitions, it does have quadrupolar transitions which have much smaller A_{ij}. Molecular hydrogen lines are therefore very weak.
    - Another point is that H_2 has a much smaller mass (than CO) with a much smaller moment of intertia ($I = 4.7\,10^{-41}\,\mathrm{g\,cm^2}$). The excitated quantum levels are at much higher energies, ie high temperatures are needed to populate these levels. Selection rules for quadrupole transitions are $\Delta J = \pm 2$.
    - The H_2 rotational transition with the longest wavelength (the least energetic) is at $\lambda = 28.2\,\mu\mathrm{m}$, ie in the MIR
- Other linear di- or tri-atomic molecules like CS, OH, HCO^+, HCN, etc. are commonly observed

1.5.2.1 Rotational transitions

non-linear molecules: symmetric tops

- For non linear molecules, we need to define rotational constants for 3 axes (3 moments of inertia)
- Symmetric top molecules have two equal rotational constant
- Molecules must have at least a 3-fold axis of symmetry
- for example: NH_3

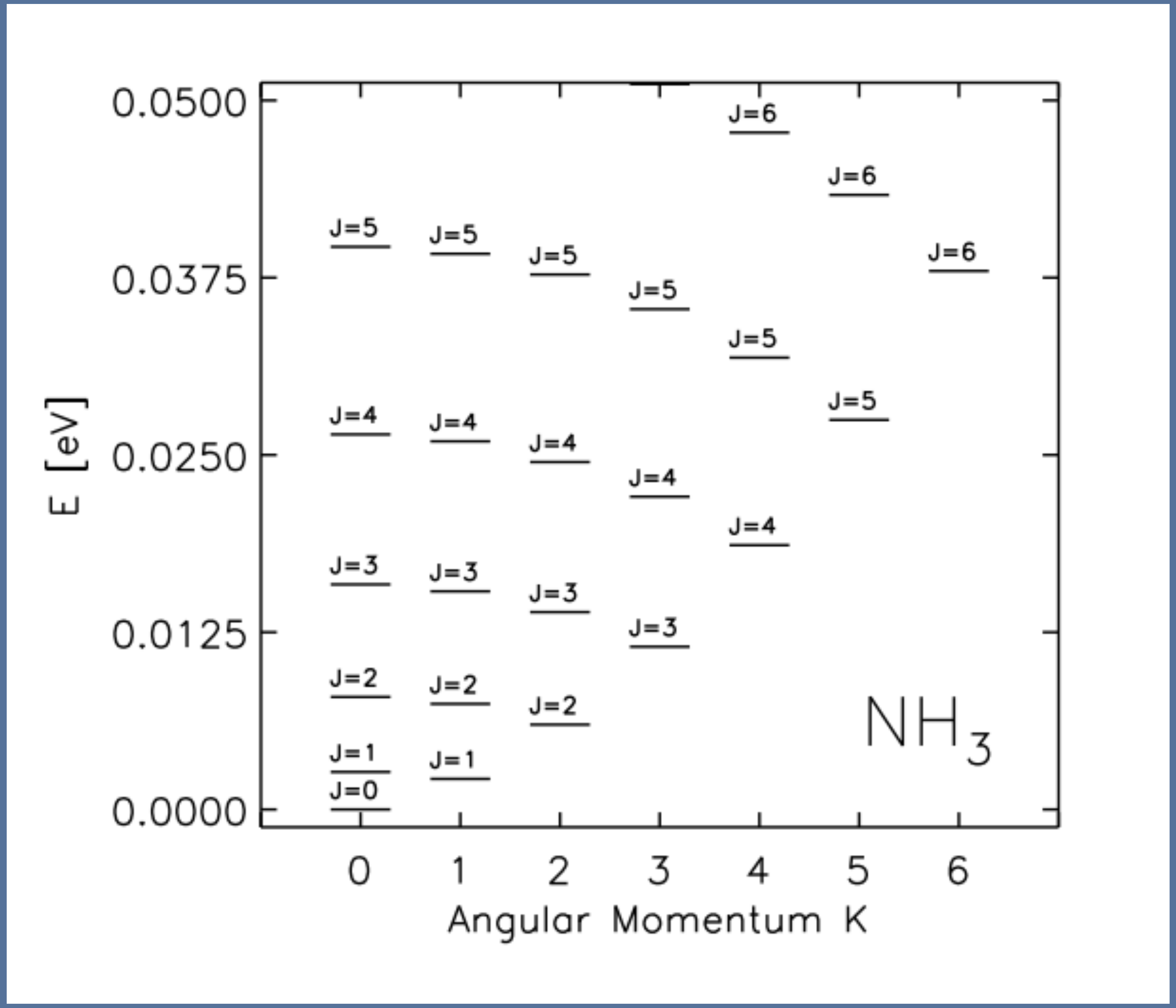


- To describe the rotational levels of such molecules, we need a supplementary quantum number, K, in addition to J.
- Allowed electric dipole transitions are such that $\Delta K = 0$
- If $K > 0$ (non zero), the molecule can be radiatively de-excited down to the lowest level with $J = K$ and can only go back to the ground state ($J = 0$) with collisions (rarely nu quadrupolar transitions)
- Molecules like NH_3 can therefore be used as “thermometers” is those levels are depopulated by collisions

1.5.2.1 Rotational transitions

non-linear molecules: symmetric tops

NH_3 rotational energy levels



C.P. Dullemond

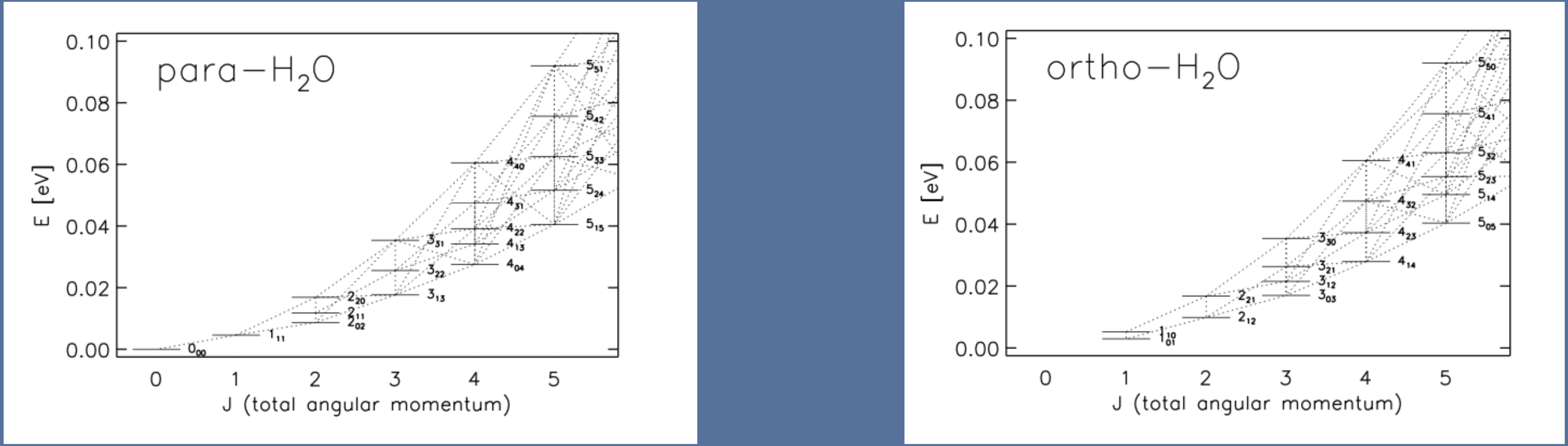
1.5.2.1 Rotational transitions

non-linear molecules: asymmetric tops

- For these molecules, all 3 rotational constants are different.
- Three quantum numbers are used: J, K_+, K_-, also written J, K_a, K_c
- J is the total angular momentum and K_+ and K_- are the projections of the angular momentum on the axes of highest and lowest moments of inertia, respectively.

1.5.2.1 Rotational transitions

H_2O rotational energy levels



C.P. Dullemond

- Because of the presence of two H atoms, there are 2 forms of the molecule, depending on the total spin
  - $S = 0$, para-H2O, statistical weight of 1
  - $S = 1$, ortho-H2O, statistical weight of 3 (triplet state)
- Generally if the temperature is not too low, the ratio ortho/para is 3. There are no radiative transitions between both species, and the conversion has an extremely low efficiency with collisions (more efficient are proton exchanges)

1.5.2.2 Rovibrational transitions

- Molecules can also vibrate: the vibration energy is given in first approximation by $E_v = h\nu_0 \left(\frac{1}{2} + v\right)$, where v is the vibrational quantum number (harmonic oscillator)
- The line frequencies are $h\nu_{ij} = h\nu_0\,(v_i - v_j)$
- In principle, we do not exactly have a perfect harmonic oscillator, and there are some higher order terms (Morse potential)
- All transitions from $v = i + 1$ to $v = i$ have the same energy and are called "fundamental transition" (for CO, this corresponds to $\lambda = 4.7\mu\mathrm{m}$)
- The transitions $v = i + 2 \rightarrow v = i$ (around $\lambda = 2.3\mu\mathrm{m}$) are called overtone transitions. These transitions are possible for an anharmonic oscillator (otherwise, only $\Delta v = \pm 1$ are allowed.
- Vibrational transitions are in the IR in general.

1.5.2.2 Rovibrational transitions

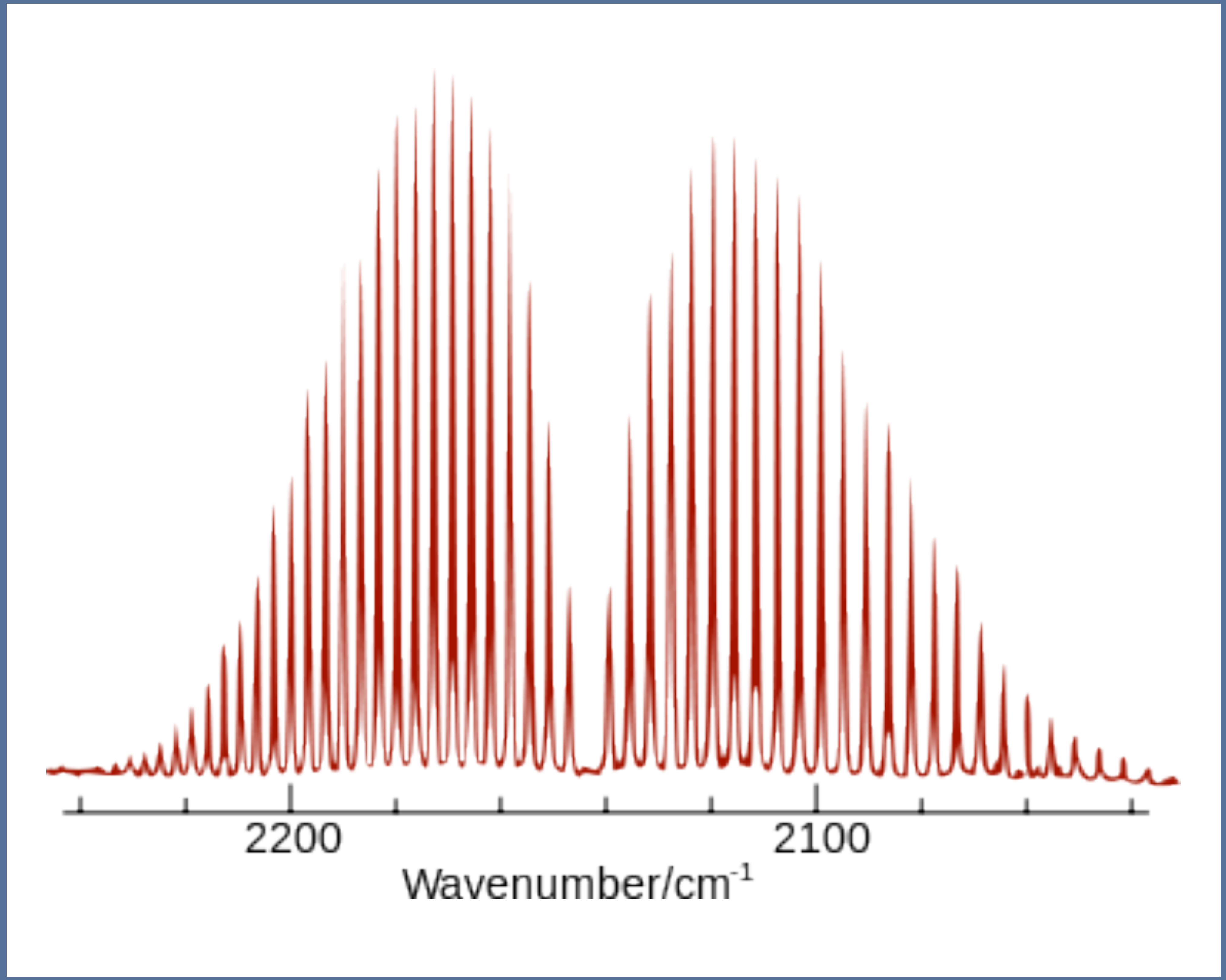
- When molecules can rotate in addition to vibrating, we have rovibrational transitions.
- In this case, all Δv are possible. The selection rules for the rotation are $\Delta J = 0, \pm 1$.
- If CO is in a vibrationally excited state, for example $v = 1, J = 4$, the molecule can radiatively de-excite towards $v = 0\ J = 4$, $v = 0\ J = 5$ and $v = 0\ J = 3$.
- Transitions with $\Delta J = +1$ are P-branch transitions, those with $\Delta J = 0$ are Q-branch transitions, and those with $\Delta J = -1$ are R-branch transitions.
- The energy levels are: $E_{v\,J} = h\nu_0\,(v + \frac{1}{2}) + \frac{\hbar^2}{2I}\,J\,(J + 1)$
- The second term is small with respect to the first one, so that rovibrational transition frequencies are close to $\nu_0\,(v_i - v_j)$.
- The transitions $\Delta v = \pm 1 \quad \Delta J = 0$ are forbidden for linear molecules

1.5.2.2 Rovibrational transitions

- Because of the rotational structure, we obtain a series of lines for the R-branch and another for the P-branch (and one fundamental line for the Q-band if it exists)

- For the R-band ($\Delta J = -1$) the photon is slightly more energetic whereas for the P-branch, part of the vibrational energy is used to rotate the molecule faster, so the photon is less energetic

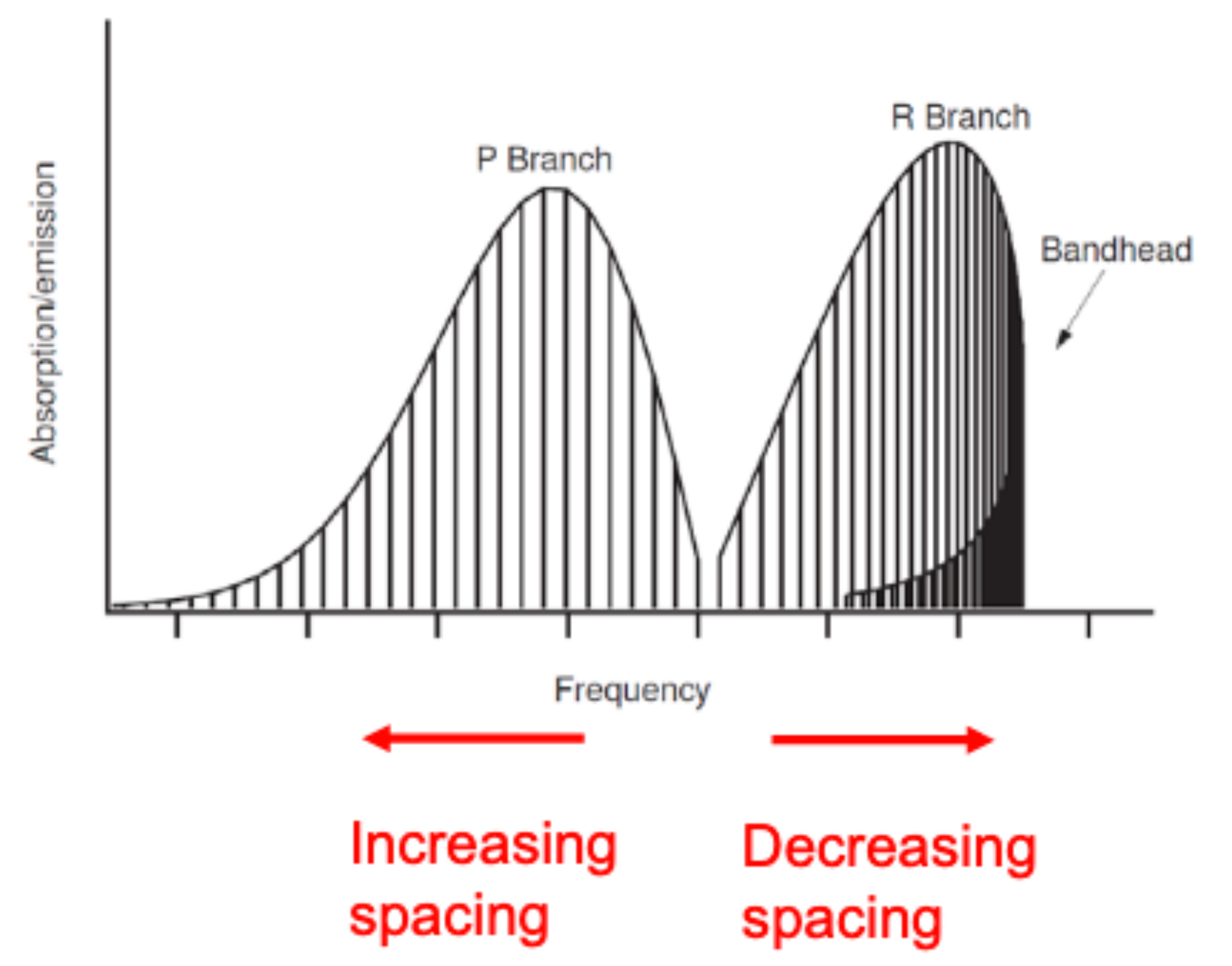
CO rovibrational spectrum



1.5.2.2 Rovibrational transitions

- In fact, the rotational constant is slightly smaller for $v = 1$ than for $v = 0$ because of the distorsion of the molecule. Because of this for the R-band, transitions get closer and closer (whereas the spacing increases for the P-branch)

- At some point the spacing in the R-branch goes down to zero → many lines are in close proximity: this is called a band head



1.6 Necessary data

- To solve radiative transfer, we need the following data
    - Frequencies of the transitions (and selection rules)
    - Einstein coefficients
    - Level energies and degeneracies
    - Partition function in the LTE case (or recalculate it)
    - For non-LTE calculation, the collisional coefficients are needed
- Where to find these data?
    - Most of them are available in databases

1.6 Necessary data

Atomic data

The Opacity Project	http://cdsweb.u-strasbg.fr/topbase/topbase.html
The Iron Project	http://cdsweb.u-strasbg.fr/tipbase/home.html

Molecular data

The Cologne Database for molecular spectroscopy (CDMS)	https://cdms.astro.uni-koeln.de/classic/
The JPL molecular spectroscopy database	http://spec.jpl.nasa.gov
The HITRAN database	http://www.cfa.harvard.edu/hitran

Collisional data

The Chianti database	http://www.chiantidatabase.org
The Lamda database	http://www.strw.leidenuniv.nl/~moldata
The Basecol database	http://basecol.vamdc.eu

2. Line profiles

2.1 Doppler broadening

2.1.1 Thermal Doppler broadening

- When a collection of atoms/molecules with velocities due to thermal motions absorbs or emits photons corresponding to a transition of energy $h\nu_0$, the frequency of the photons is shifted by an amount $d\nu = \nu - \nu_0 = \nu_0 \frac{\upsilon_z}{c}$, where υ_z is the velocity component of atoms or molecules along the line of sight (positive towards the observer) and c the speed of light
- If the distribution of particles is a Maxwellian, the number of particles able to absorb or to emit at frequency ν per frequency interval is

$$\frac{dN_z}{d\nu} = \frac{dN_z}{d\upsilon_z}\frac{d\upsilon_z}{d\nu} = \frac{c}{\nu_0} N \left(\frac{M}{2\pi kT}\right)^{\frac{1}{2}} \exp\left(-\frac{M\upsilon_z^2}{2kT}\right)$$

- NB in astrophysics, objects evolve over timescales much longer than the time to reach Maxwell equilibrium, so the above relation is valid in most cases. In jets or in the solar corona however, other particle distributions will apply.

2.1.1 Thermal Doppler broadening

- The absorption coefficient at ν can be written:

  $$\alpha_\nu = \frac{h\nu}{4\pi} N_i B_{ij} \left(1 - \exp\left(-\frac{h\nu}{kT_{\rm ex}}\right)\right) \frac{1}{\sqrt{\pi}\Delta\nu_D} \exp\left(-\left(\frac{\nu-\nu_0}{\Delta\nu_D}\right)^2\right)$$ with $\Delta\nu_D = \frac{\nu}{c}\sqrt{\frac{2kT}{M}}$

  the Doppler linewidth, also called the thermal linewidth

- The line profile is therefore

  $$\phi(\nu) = \frac{1}{\sqrt{\pi}\Delta\nu_D} \exp\left(-\left(\frac{\nu-\nu_0}{\Delta\nu_D}\right)^2\right)$$, which is evidently a Gaussian and the absorption coefficient at line centre is $$\alpha_{\nu_0} = \frac{h\nu_0}{4\pi} N_i B_{ij} \left(1 - \exp\left(-\frac{h\nu_0}{kT_{\rm ex}}\right)\right) \frac{1}{\sqrt{\pi}\Delta\nu_D}$$

- α_{ν_0} depends on $\Delta\nu_D$ (which can be of the order of $10^{10}\ \mathrm{s}^{-1}$ in the visible for lines at $10^4\ \mathrm{K}$)

2.1.1 Thermal Doppler broadening

- The optical depth at the centre of a line is a parametre which can rather easily be deduced from observations, and which is used to derive the number of atoms/molecules along the line of sight, as we will see later

- It is important to note that the thermal Doppler broadening depends on the mass of the particle that emits the line. For heavy molecules, the broadening is less than for lighter ones.

- The line profile can also be written $\phi(\nu) = \frac{c}{a\,\nu_0\sqrt{\pi}} \exp\left(-\frac{c^2\,(\nu-\nu_0)^2}{a^2\,\nu_0^2}\right)$

  with $a = \sqrt{\frac{2kT}{M}}$ is the linewidth in m/s or in km/s

2.1.2 Turbulent Doppler broadening

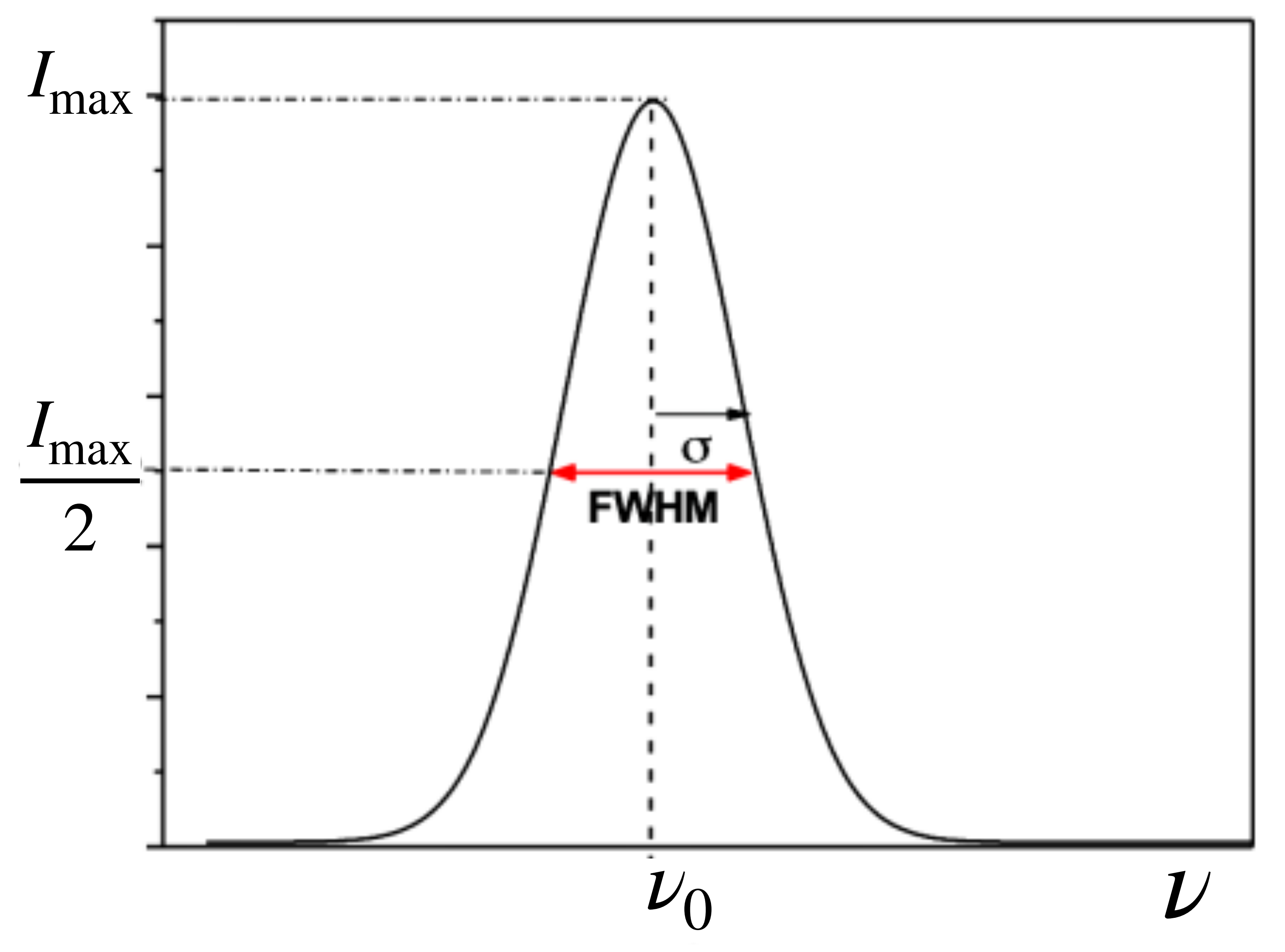
- Particles in astrophysical media are also subject to turbulence
- Turbulence is still poorly constrained: it encompasses pseudo-random motions of gas cells
- Turbulence is usually treated as an additional velocity dispersion
- It is generally assumed that the probability distribution for velocity is a Gaussian with a width that is independent of the particule mass and of the temperature
- We would need a good model of microturbulence to be able to evaluate the velocity dispersion precisely

2.1.2 Turbulent Doppler broadening

- The total broadening is thus written as: $\Delta\nu_D = \frac{\nu_0}{c}\left(\frac{2kT}{M} + v_{\mathrm{turb}}^2\right)^{\frac{1}{2}}$
- or also: $a = \sqrt{a_{\mathrm{th}}^2 + a_{\mathrm{turb}}^2}$, with a the total linewidth, $a_{\mathrm{th}} = \sqrt{\frac{2kT}{M}}$ the thermal component and a_{turb} the turbulent component.
- In principle, if we can measure the linewidths for two species of very different mass, it is possible to derive ar the same time T and v_{turb} (but we have to make sure that the emission of both species comes from the same region).

2.1.3 Full width at half maximum

- For Gaussian lines, the full width at half maximum (FWHM) is given



$$\exp\left(-\left(\frac{\Delta\nu}{\Delta\nu_0}\right)^2\right) = 0.5 \quad \Rightarrow \quad \text{FWHM} = 2\sqrt{\ln 2}\,\Delta\nu_D$$

2.2 Collisional broadening

- Collisional broadening is also called pressure broadening
- The expression can be derived using atomic physics
- Here we just give an outline to understand where it comes from
    - We take as example an atom that can emit at frequency ν_0
    - If the molecule is disturbed by a collision, this shortens the lifetime of the level, ie the decay rate is increased.
    - This will increase the uncertainty in the emitted/absorbed energy, so that photons at a frequency $\nu_0 \pm \Delta\nu$ can also be absorbed or emitted

2.2 Collisional broadening

- The corresponding line has a Lorentzian profile $\phi(\nu) = \frac{1}{\pi} \frac{\gamma_{\mathrm{coll}}}{(\nu - \nu_0)^2 + \gamma_{\mathrm{coll}}^2}$
- γ_{coll} is the damping constant, in units of frequency
- This parameter is not easy to calculate, contrary to Doppler broadening
- The reason is that the way the collision disturbs the emission of a molecule very much depends on the details of the collisional process and the nature of the collision partner.
- γ_{coll} is typically tabulated, for example in the HITRAN database, for each line, with a pressure of 1 atm and a temperature of 296 K.

2.2 Collisional broadening

- For another temperature and another pressure, γ_{coll} can be calculated using the following formula: $\gamma_{\mathrm{coll}}(p,T) = \gamma_{\mathrm{coll}}(p_0,T_0)\,\frac{p}{p_0}\left(\frac{T_0}{T}\right)^n$, with $p_0 = 1\,\mathrm{atm}$ and $T_0 = 296\,\mathrm{K}$.
- The linear dependence in p comes from the fact that for infinitely short collisions and at constant temperature, the number of collisions that each atom/molecule undergoes per second increases with density
- n is given in HITRAN. It is typically between 0.5 and 1. If it is 0.5 and we have a perfect gas ($p = \rho kT$) and if the density ρ is constant, we have $\gamma_{\mathrm{coll}} \propto \sqrt{T}$. This can be understood because the velocity of the particles varies in $\sqrt{T}$, ie γ_{coll} varies like a collisional rate (number of collisions per second). In fact, the velocity at which collisions take place affect γ_{coll}, and n deviates from 0.5 in general

2.2 Collisional broadening

- HITRAN gives 2 values for the damping constant, $\gamma_{\rm self}$ and $\gamma_{\rm air}$
  - $\gamma_{\rm self}$ is used for collisions between identical atoms/molecules (of the same type)
  - $\gamma_{\rm air}$ is used for collisions in a standard molecular mix corresponding to the Earth atmosphere
- The general formula for the collisional broadening by a mix of air and of the molecule is: $\gamma_{\rm coll}(p,T) = \left[\gamma_{\rm air}(p_0,T_0)\,\frac{p-p_s}{p_0} + \gamma_{\rm self}(p_0,T_0)\frac{p_s}{p_0}\right]\left(\frac{T_0}{T}\right)^n$

  where p_s is the partial pressure of the molecule.

2.2 Collisional broadening

- Pressure broadening mainly takes place in dense environments like stellar and planetary atmospheres
- In planetary atmospheres, it usually dominates over Doppler broadening
- In interstellar and circumstellar gas like molecular clouds or protoplanetary disks, pressure broadening rarely plays a role

2.3 Natural width

- Because of the uncertainty principle, energy levels have a finite width ΔE given by $\Delta E \Delta t \gtrsim \hbar$, with Δt the level lifetime
- Short-lived states have large uncertainties in the energy
- This means that photons that have a frequency slightly different than ν_0 can also be emitted by the atom/molecule
- Typically, photons emitted in a transition from this level to the ground state will have a range of possible frequencies: $\Delta \nu \sim \dfrac{\Delta E}{h} \sim \dfrac{1}{2\pi \Delta t}$

2.3 Natural width

- Δt is linked to the Einstein coefficients A_{ij}
- If A_{ij} is very large, as for allowed transitions, the upper energy level of the transitions have a very short lifetime and a broad natural linewidth
    - This is the case for resonance lines (line for which the lower level is the ground state)
- For metastable states, which are the upper levels of forbidden transitions, the lifetime is large, and also for the ground state, which can only be depopulated by absorption. These leads to narrow linewidths.

2.3 Natural width

- The line profile is given by $\phi(\nu) = \frac{1}{\pi} \frac{\delta}{\delta^2 + (\nu - \nu_0)^2}$, with δ the damping constant
- Like for collisional broadening, the line profile is a Lorentzian
- Natural linewidth is rarely observed except in some cases in the line wings.
- Other broadening processes usually dominate

2.4 Voigt profile

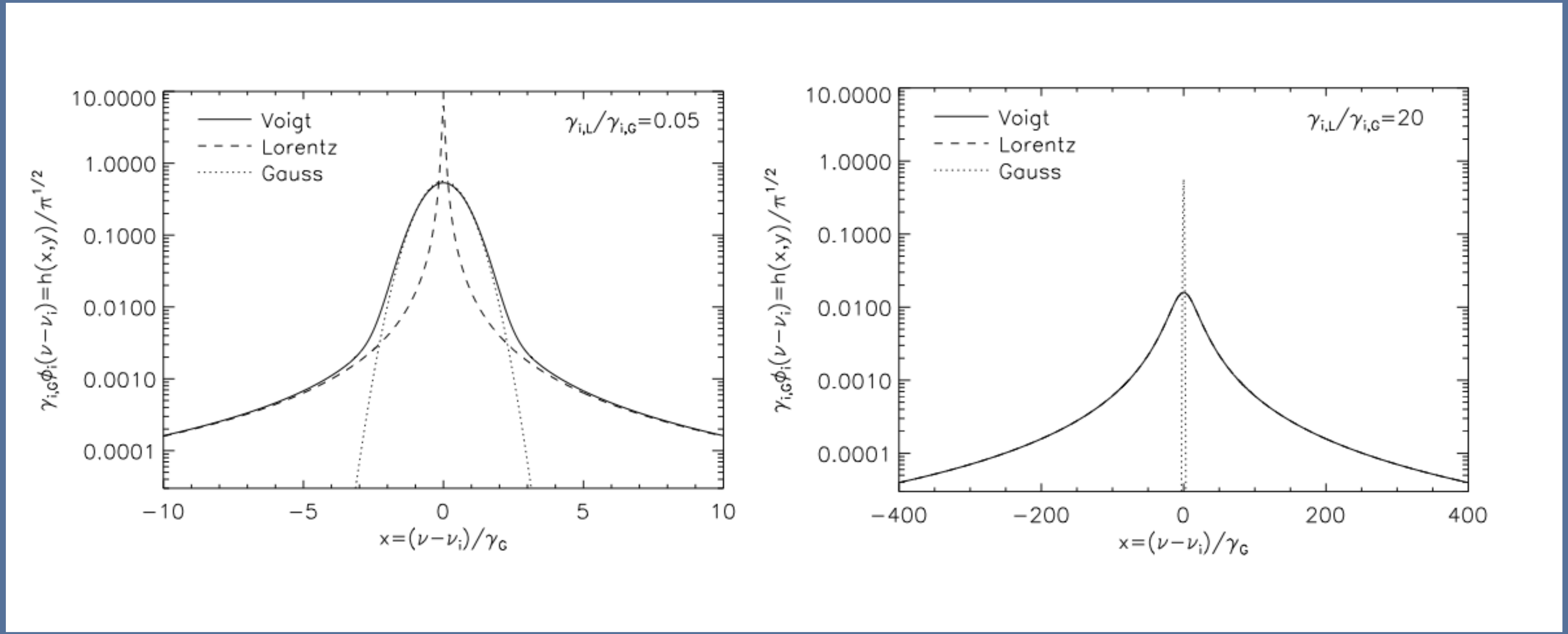
- When more than one broadening processes are present, the combined effect is the convolution of the different profiles
- Combining two Gaussian profiles or two Lorentzian profiles is easy
    - The combination of Doppler and microturbulent broadenings gives a Gaussian profile of width $a = \sqrt{a_{\mathrm{th}}^2 + a_{\mathrm{turb}}^2}$: $\phi_G(\nu) = \frac{c}{a\nu_0\sqrt{\pi}} \exp\left(-\frac{c^2(\nu-\nu_0)^2}{a^2\nu_0^2}\right)$
    - The combination of natural and pressure broadenings gives a Lorentzian profile $\phi_L(\nu) = \frac{1}{\pi}\frac{\delta}{\delta^2 + (\nu-\nu_0)^2}$ with $\delta = \delta_{\mathrm{coll}} + \delta_{\mathrm{nat}}$ the total linewidth

2.4 Voigt profile

- Combining a Lorentz and a Gauss profile implies convolving both profiles, which is not trivial: $\phi(\nu) = \int_0^\infty \phi_G(\nu')\,\phi_L(\nu_0 + \nu - \nu')\,d\nu'$
- This is called a Voigt profile
- In numerical radiative transfer, calculating this integral each time a line profile has to be evaluated is costly. Humlicek (1982, JQSRT, 27, 437) has developed a fast numerical procedure to approximate the Voigt profile. The code is publically available. It calculates a function $h(x, y)$ with $x = \dfrac{\nu - \nu_0}{a}$ and $y = \dfrac{\delta}{a}$
- The Voigt profile is then given by $\phi(\nu) = \dfrac{h(x, y)}{\sqrt{\pi}\,a}$

2.4 Voigt profile

- The following figures show the profile in 2 limiting cases



C.P. Dullemond

- If thermal/microturbulent Doppler broadening is small with respect to pressure/natural broadening $(\frac{a}{\delta} \ll 1)$ the profile is similar to a Lorentzian (right panel)

- If thermal/microturbulent Doppler broadening is large with respect to pressure/natural broadening $(\frac{a}{\delta} \gg 1)$ the Gaussian profile dominates near the line centre, but wings of the Lorentzian profile can reappear far from the line centre (left panel)

2.4 Voigt profile

- In diffuse media like the interstellar medium or circumstellar disks, the distance at which the Lorentzian profile reappears can be so large that we can ignore this effect
- However, this has to be evaluated on a case by case basis
- For dense media like stellar or planetary atmospheres, the Gaussian component is generally too small to play a role
- Typically, for forbidden lines, the natural linewidths is very small. Moreover these lines are only found in very diffuse media so that the collisional damping constant is also very small. In this case, the Doppler profile dominates
- For allowed transitions, the Doppler profile dominates in the line centre (up to roughly 3 Doppler widths) but the line wings have a damping profile (for stellar atmosphere lines, typically)

2.5 Line profiles integrated along the line of sight

- In many cases, all atoms or molecules do not have the same velocity along the line of sight
- This effect is amplified when the resolution of the telescope is limited, ie the telescope PSF/beam encompasses different regions that have different velocities

- Several velocity components can be seen in this case
- This can give rise to rather complex profiles, which give nevertheless precious information on gas kinematics, the nature of an astrophysical object and its dynamical evolution

2.5.1 Integrated spectrum for an accretion disk

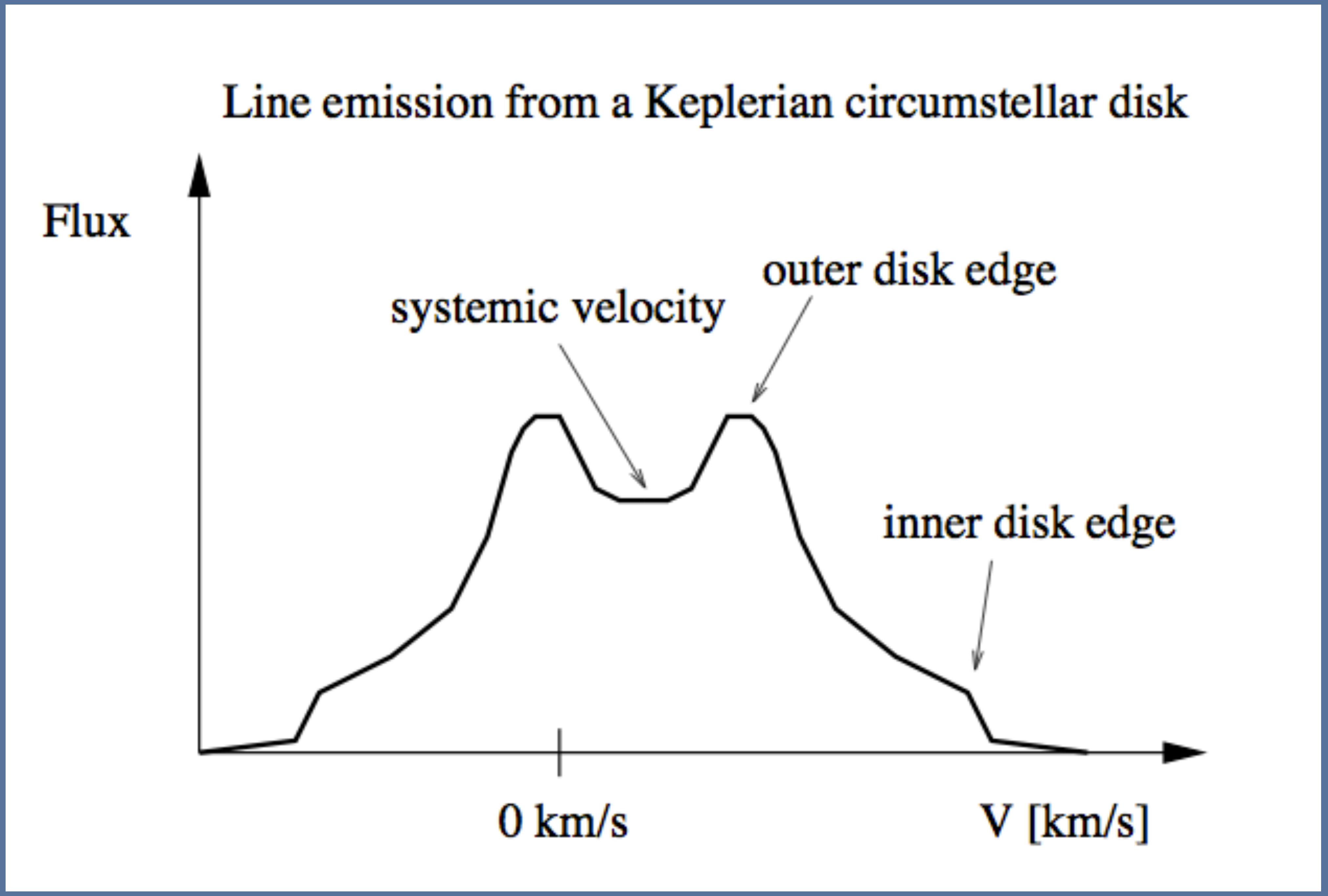
- Disks undergo differential rotation following a keplerian profile: the gas close to the star rotates with a higher velocity and temperature than the gas on external orbits
- If the disk is seen face-on, its orbital velocities cannot be measured by Doppler effect
- If the disk is inclined with respect to the line of sight, the lines have a characteristic profile with two peaks

HD163296 / ESO

2.5.1 Integrated spectrum for an accretion disk

- The emission of the external disk produces the line centre, whereas the emission from the internal disk regions produces the line wings

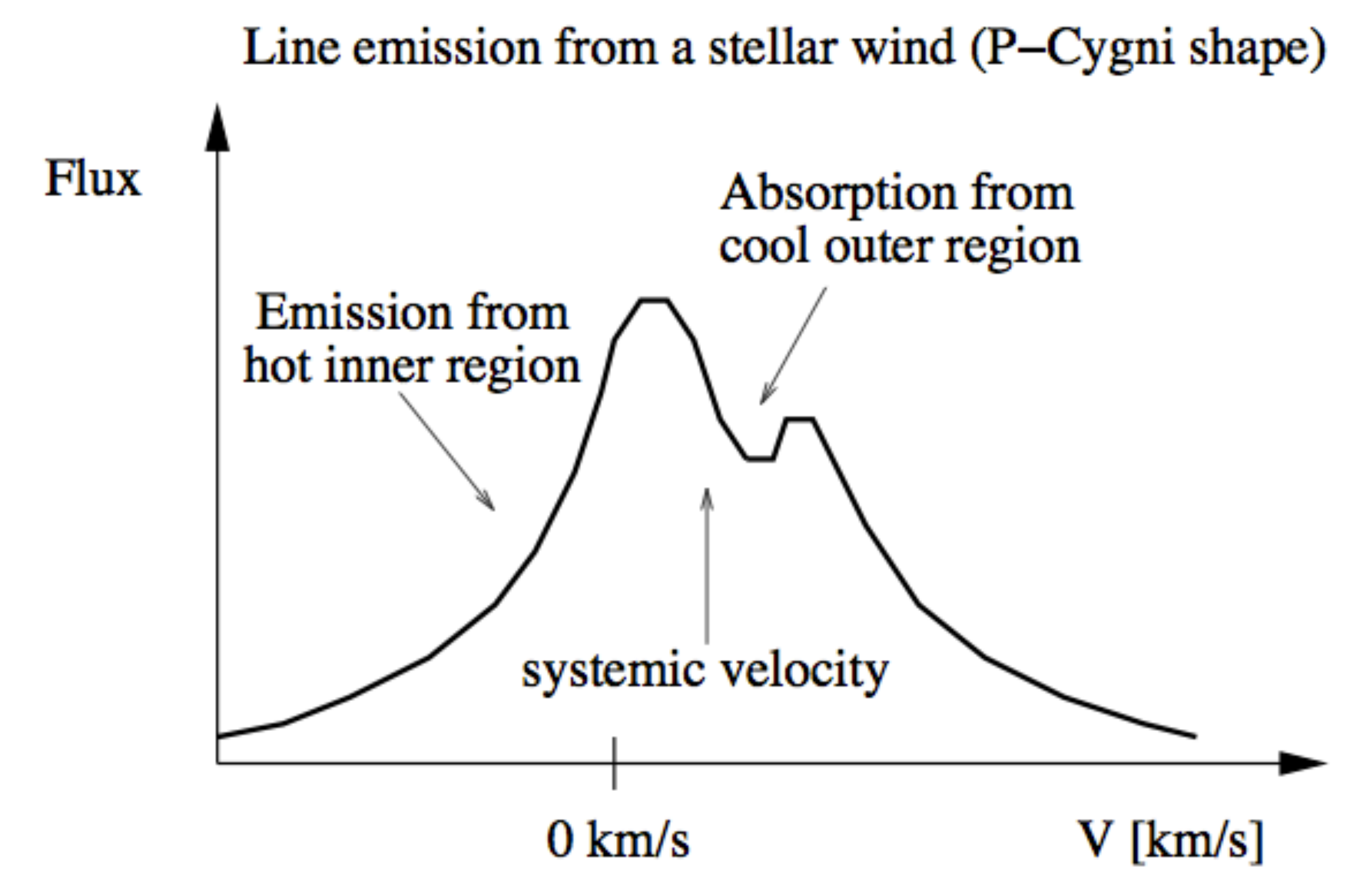
- Inclining the disk towards more edge-on views, the line becomes broader, until the inclination is so large that external disk regions start obscuring the star and disk internal regions



C.P. Dullemond

2.5.2 P-Cygni profile of a stellar wind

- Let us consider a star with a stellar wind of spherical symmetry
- We also assume that the wind accelerates with increasing distance from the star and that the temperature decreases with radius
- The gas close to the star is hot and subsonic: it produces an intense and broad emission
- Other regions of the stellar wind are cold and move at blue-shifted velocities: external regions cause an absorption line superimposed on the large emission line

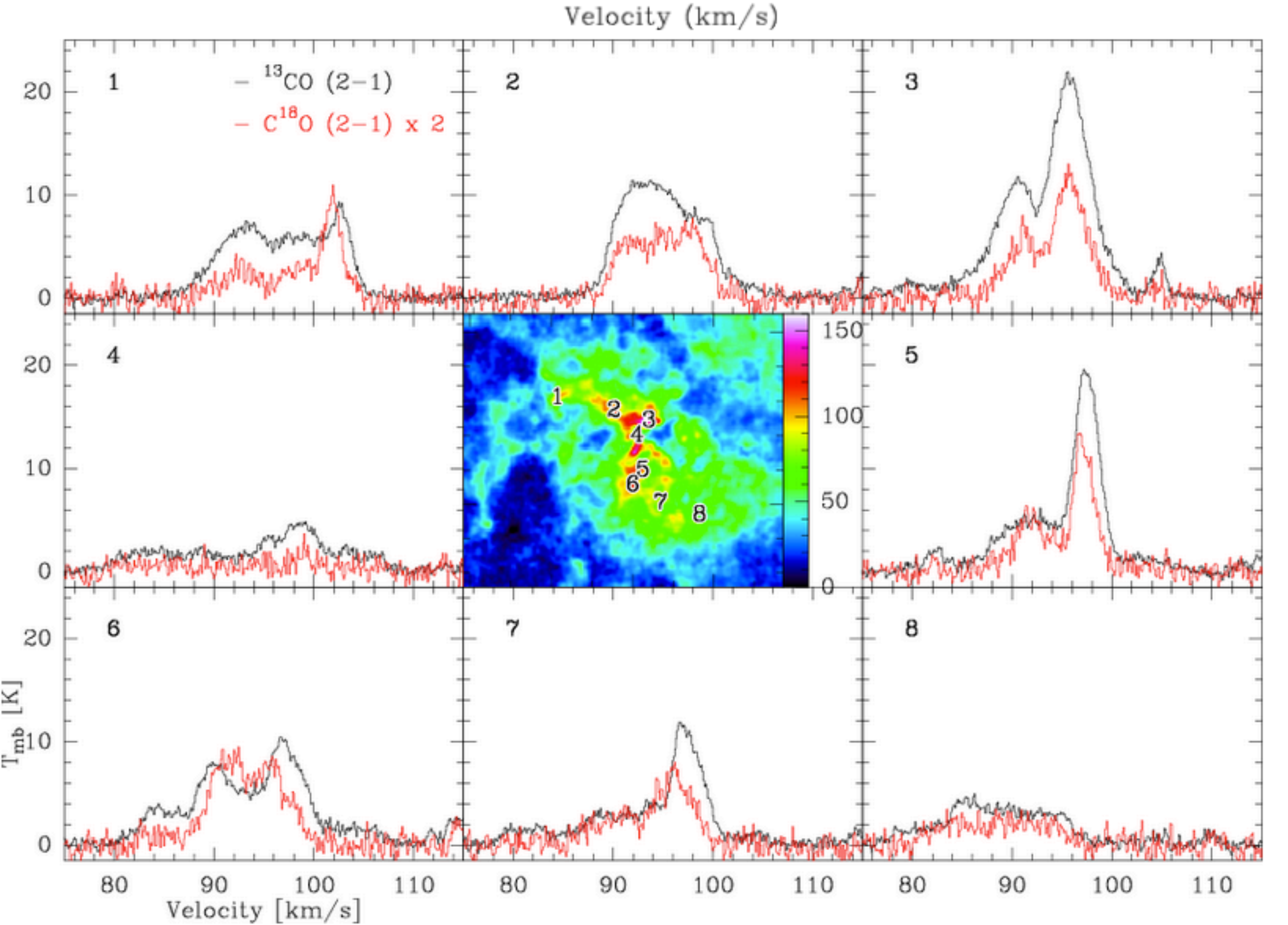


C.P. Dullemond

- This leads to an asymmetric line profile with two peaks, with a blue peak less intense than the red peak
- Such a profile is called a P-Cygni profile

2.5.4 Real spectra

- Real profiles can be extremely complex



Carlhoff, P. *et al.* A&A. 560 (2013) A24

3. Solving line radiative transfer

- In order to solve line radiative transfer, the emissivity and the absorption coefficients (or the source function) have to be determined
- In the expression of the emissivity and absorption coefficient, there are the level populations N_i and N_j
- It is therefore necessary to calculate these populations to solve radiative transfer
- This means determining the excitation state of the atoms/molecules

3.1 Excitation

- Atoms and molecules can change energy level either by photon absorption/emission (raditive excitation) or by energy exchange during a collision with a particle from the ambient medium (collisional excitation).
- Radiative excitation is described by the Einstein coefficients (A_{ji}, B_{ij}, B_{ji}) that we saw at the beginning of the chapter
- Collision excitation is described by collision rates $K_{ij}(T)$
- In general, we use the collisional coefficients C_{ij}, which describe how many times per second a particle goes from level i to level j. They are the equivalent of the Einstein coefficients, but for collisions
  - $C_{ij} = N\ K_{ij}(T)$, with N the density of collisioners
  - Units: C_{ij} is in $\mathrm{s^{-1}}$, and K_{ij} is in $\mathrm{cm^3\ s^{-1}}$

3.1 Excitation

- The number of excitations per second and per unit volume is $N_i\, C_{ij} = N_i\, N\, K_{ij}(T)$
- The number of deexcitations per second and per unit volume is $N_j\, C_{ji} = N_j\, N\, K_{ji}(T)$
- Collisioners are abundant species in the medium: H, e, H_2, depending on the nature of the medium
- Collisional rates are calculated from collisional cross sections σ_{ij}, which depend on energy, i.e. on the particle relative velocity v: $K_{ij} = <\sigma_{ij}\, v>$
- The mean is taken over the velocity distribution function, which is generally a Maxwellian, limited by an energy threshold E_{ij} for collisional excitation (the particle velocity has to be greater than $\sqrt{2\,E_{ij}/m}$, because the transition can only take place if the energy of the incident particle is greater than the energy of the upper level).

3.1 Excitation

- For collisional excitation: $K_{ij}(T) = \int_{E_{ij}}^{\infty} \left(\frac{m}{2\pi\, k\, T}\right)^{3/2} \sigma_{ij}(v)\ \exp\left(-\frac{mv^2}{2\, k\, T}\right) 4\pi\, v^3\, dv$
- For collisional deexcitation:
$$K_{ji}(T) = \int_{0}^{\infty} \left(\frac{m}{2\pi\, k\, T}\right)^{3/2} \sigma_{ji}(v)\ \exp\left(-\frac{mv^2}{2\, k\, T}\right) 4\pi\, v^3\, dv$$
- m is the mass of the collisioning particles
- Note that there are cases where the velocity distribution is not a Maxwellian (e.g. solar flares)
- Generally, we find K_{ij} tabulated for a Maxwellian velocity distribution

3.1 Excitation

- Colisional cross section can be determined experimentally for certain transitions, but experiments are difficult (Bergeat et al., Nature Chemistry, 2015)

- Usually, σ_{ij} (and K_{ij}) can be calculated, but these atomic and molecular calculations are complex, all the more that molecules are complex as well (the difficulty increases with geometry and number of degrees of freedom). Typically, an interaction potential surface between the atom/molecule and collisioner has to be first calculated.

- If one collisioner dominates, it is possible to consider that there is just one collisioner, but in many cases, several have to be taken into account, as for example in molecular media (H_2 and He, or ortho- and para-H_2)

- Since calculations are considerably more complex for H_2 than for He, sometimes the collisional rates with Helium are used, corrected of the mass difference between H_2 and He. It is only an approximation, but is used for lack of better rates

- For each collisional partner pair, there is a set of collisional rates, e.g. CH_3OH-pH_2, CH_3OH-oH_2, CH_3OH-e

3.1 Excitation

- Relation between K_{ij} and K_{ji}: we use microreversibility at LTE, together with the Boltzmann relation
  - $N_i C_{ij} = N_j C_{ji} \quad \Rightarrow \quad N_i K_{ij} = N_j K_{ji}$
  - $\dfrac{N_j}{N_i} = \dfrac{g_j}{g_i} \exp\left(-\dfrac{E_{ij}}{kT}\right)$
  - $\Rightarrow \quad K_{ij} = \dfrac{g_j}{g_i} \exp\left(-\dfrac{E_{ij}}{k\,T}\right) K_{ji}$

Due to microreversibility, this relation remains valid outside LTE

- We can therefore calculate the collisional excitation rate from the collisional de-excitation rate
- Note that the temperature in the relation is the temperature due to the thermal motion of the gas. Turbulent velocity does not contribute, as it is a global motion that plays no role in particle collisions
- The temperature and density dependence is included in the $C_{ij} = N\,K_{ij}(T)$

3.2 Radiative transfer equations in the non-LTE case

- The transfer equation remains unchanged with respect to what was seen in former chapters: $\overrightarrow{n} \cdot \overrightarrow{\nabla} I_\nu(\overrightarrow{x}, \overrightarrow{n}) = j_\nu(\overrightarrow{x}, \overrightarrow{n}) - \alpha_\nu(\overrightarrow{x}, \overrightarrow{n})\, I_\nu(\overrightarrow{x}, \overrightarrow{n})$, with j_ν and α_ν as previously given.

- The term α_ν now depends on direction because the line profile in frequency is ubject to a Doppler shift which depends on the direction (ie on the projection of the velocity along the direction), according to

$$\phi_{ij}(\nu, \overrightarrow{v}) = \phi_{ij}\left(\nu\left[1 - \frac{1}{c}\,\overrightarrow{n} \cdot \overrightarrow{v}\right]\right)$$

- In general, radiative transfer codes work in the referential of the laboratory.

3.2 Radiative transfer equations in the non-LTE case

- The velocity $\overrightarrow{v}$ depends on position $\overrightarrow{x}$. This means that for a given ray in a direction $\overrightarrow{n}$, the Doppler shift (and this the value of ϕ_{ij}) can change along the ray

- As a consequence, the radiation at a given frequency ν can remain unattenuated along a large distance and then suddenly (where the frequency of the line centre ν_{ij} moves closer to ν) because of the Doppler shift, the optical depth increases but can decrease again when the frequency of the line centre moves away from ν: the region in which the ray is optically thick can be limited

- Similarly, a photon emitted at a central frequency ν_{ij} corresponding to the frequency ν of the line in the referential of the laboratory can suddenly become “free” (if it has not been absorbed in the meantime) because the velocity gradient of the gas shifted the line profile away from ν

- Because of the relation between velocity and frequency, spectra are often traced as a function of velocity

3.2 Radiative transfer equations in the non-LTE case

- The radiative transfer equation has a contribution from j_ν and α_ν, which depend on the level populations
- In addition, we need an equation that gives the level populations: this is the equation of statistical equilibrium
- At steady-state, for each level i, the rate at which atoms or molecules are (de)excited away from level i is equal to the rate at which level i is populated again by (de)excitations from other levels

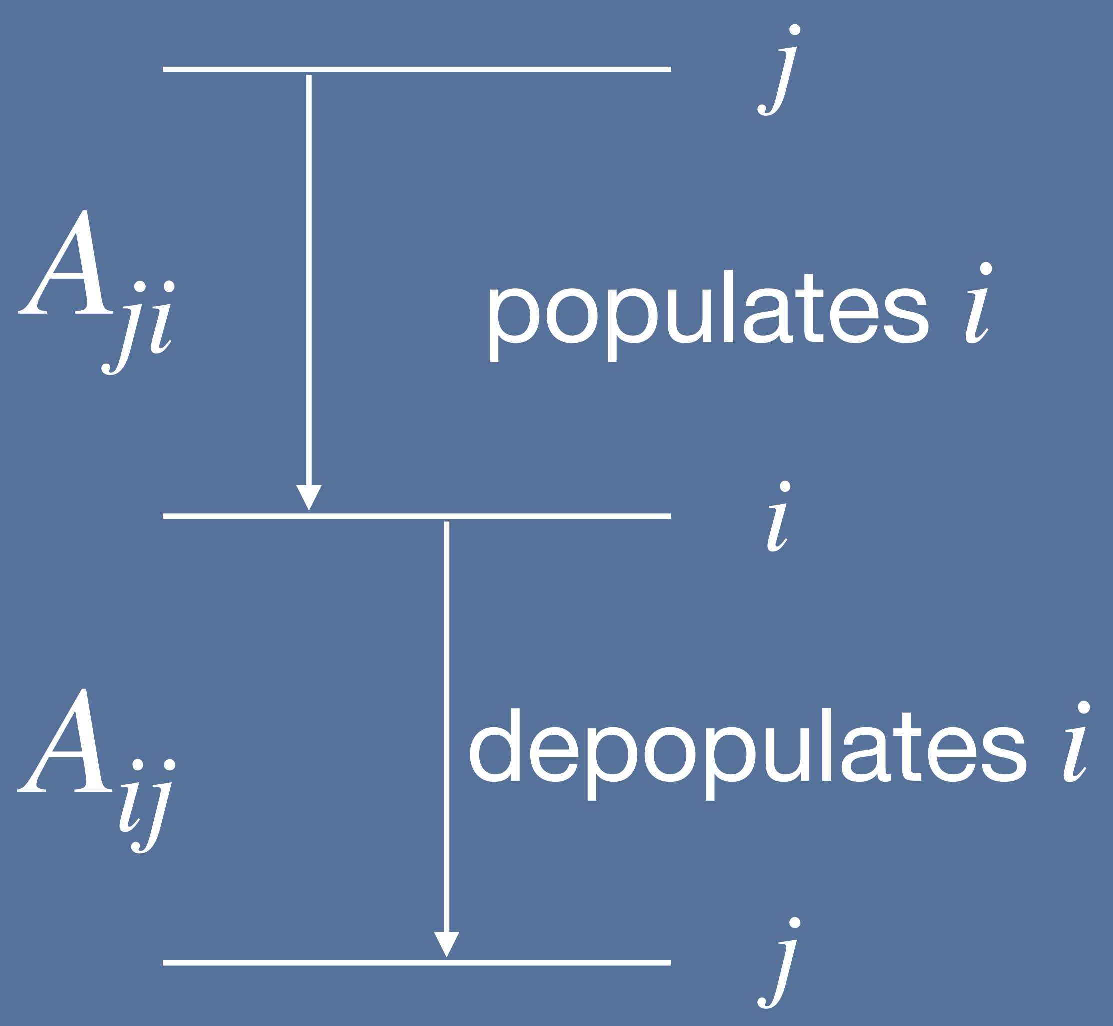
3.2.1 Optically thin case

- We will start with the most simple case, that were the medium is optically thin at all wavelengths, ie the photons emitted by a gas parcel at a given location are not reabsorbed elsewhere in the medium.

- This eliminates the radiative coupling between different regions, so that level populations can be calculated independently at each point of the medium, i.e. locally.

- The equation of statistical equilibrium in this case can therefore be written

$$\sum_{j>i} n_j A_{ji} - \sum_{j<i} n_i A_{ij} + \sum_{i\neq j} [n_j C_{ji} - n_i C_{ij}] = 0$$



3.2.1 Optically thin case

- This equation is verified for all levels i, which makes a system of N_{lev} linear equations, where N_{lev} is the number of considered levels of the atom or molecule
- The equation we have to solve is therefore a matrix equation (which can be easily done using, eg, “Numerical Recipes”)

3.2.2 Critical density

- When radiative deexcitation dominate over collisional transitions that repopulate the level, the level populations can be smaller than their value at LTE
- For a given temperature, we can define a critical density, which is defined as the density above which collisions maintain populations close to their LTE values
- The critical density depends on the transition: certain low energy transitions can be at LTE when higher energy transitions can have populations that largely deviate from LTE
- The critical density is a rather vague concept, but it is useful to determine if at a given density and temperature, non-LTE effects are to be expected and if LTE is a good approximation
- Line intensity ratios can also trace density, by checking whether their are consistent with populations at LTE

3.2.2 Critical density

- For a 2-level system, the critical density can be expressed as follows

$$\frac{N_2}{N_1} = \frac{C_{12}}{C_{21} + A_{21}} = \exp\left(-\frac{\Delta E}{kT}\right)\frac{1}{1 + \frac{A_{21}}{C_{21}}}\frac{g_2}{g_1}$$

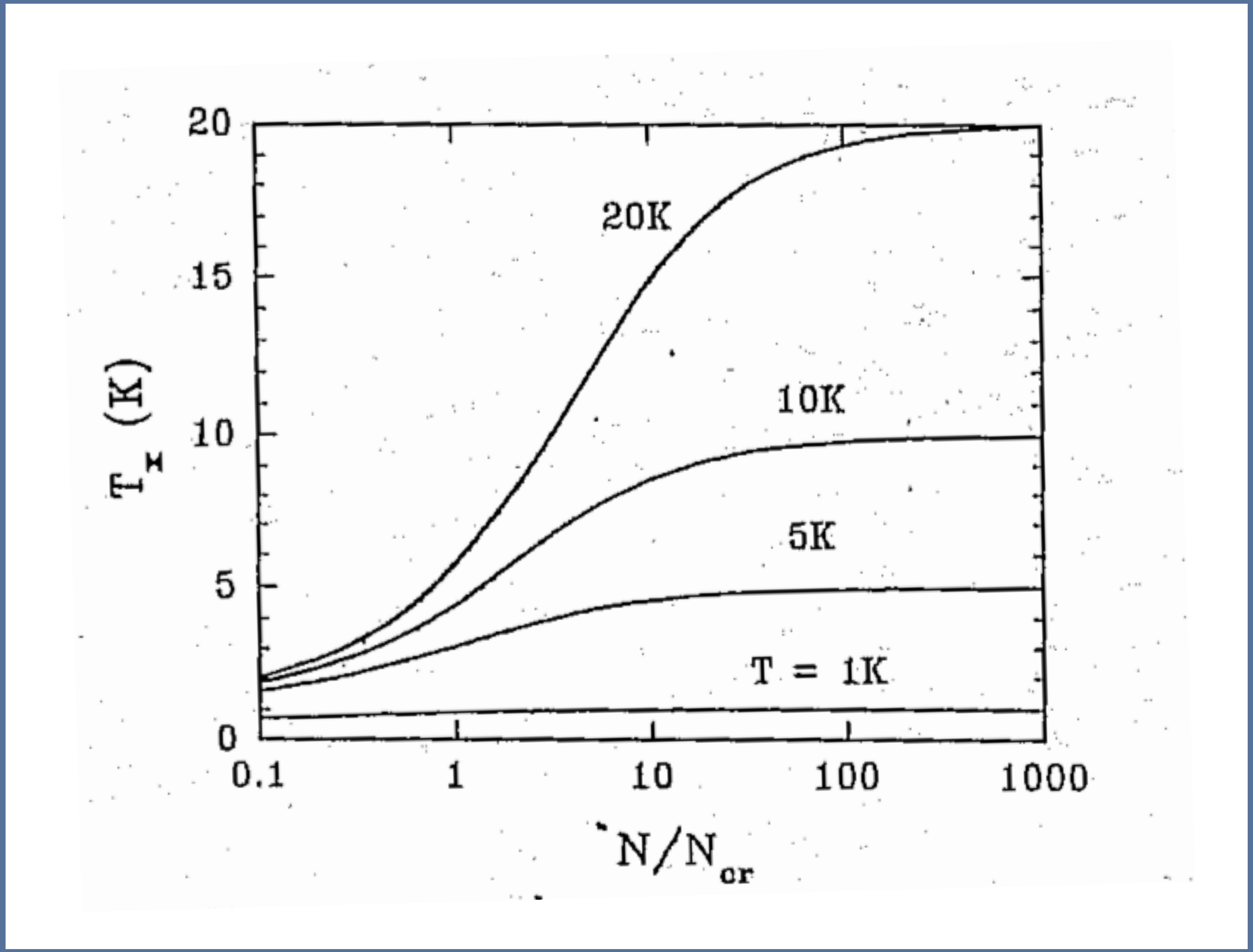
- The critical density is given by $\dfrac{N_{\rm cr}}{N} = \dfrac{A_{21}}{C_{21}}$

- The excitation temperature is then given by $T_{\rm ex} = \dfrac{T}{1 + \frac{kT}{\Delta E}\ln\left(1 + \frac{N_{\rm cr}}{N}\right)}$

- If $N \gg N_{\rm cr}$, $T_{\rm ex} \simeq T\left(1 + \dfrac{kT}{\Delta E}\dfrac{N_{\rm cr}}{N}\right)^{-1}$ and $T_{\rm ex} \to T$

- For complex molecules (in particular non linear molecules) it is more difficult to formulate an expression of the critical density because many transitions can populate or depopulate the levels

3.2.2 Critical density



Elitzur, Astronomical Masers

3.2.3 General case, non optically thin

- In addition to photon emission (by radiative deexcitation), photons can also be absorbed, when the medium is not optically thin

- For a radiation field $I_\nu(\vec{x}, \vec{n})$, the number of photons absorbed by a transition $j \rightarrow i$ is

$$\begin{aligned}\oint \alpha_{ij,\nu}(\vec{n}) \frac{I_\nu(\vec{n})}{h\nu} d\nu \, d\vec{n} &\simeq \frac{1}{h\nu_{ij}} \oint \alpha_{ij,\nu}(\vec{n}) \, I_\nu(\vec{n}) \; d\nu \; d\vec{n} \\ &\simeq \frac{1}{h\nu_{ij}} \oint \frac{h\nu_{ij}}{4\pi} (N_j B_{ji} - N_i B_{ij}) \, \phi_{ij}(\nu, \vec{x}, \vec{n}) \, I_\nu(\vec{n}) \, d\nu \, d\vec{n} \\ &\simeq (N_j B_{ji} - N_i B_{ij}) \frac{1}{4\pi} \oint \phi_{ij}(\nu, \vec{x}, \vec{n}) \, I_\nu(\vec{n}) \, d\nu \, d\vec{n} \\ &\simeq (N_j B_{ji} - N_i B_{ij}) \, J_{ij}\end{aligned}$$

- J_{ij} is the mean intensity integrated over the line profile

3.2.3 General case, non optically thin

- $J_{ij} = \frac{1}{4\pi} \oint \phi_{ij}(\nu, \vec{x}, \vec{n})\, I_\nu(\vec{n})\, d\nu\, d\vec{n}$

  with $\phi_{ij}(\nu, \vec{x}, \vec{n}) = \phi_{ij}(\nu, \vec{v}(\vec{x})) = \phi_{ij}\left(\nu\left[1 - \frac{1}{c}\vec{n}\cdot\vec{v}\right]\right)$

- We now include the absorption term in the statistical equilibrium equation:

$$\sum_{j>i}\left[n_j A_{ji} + (n_j B_{ji} - n_i B_{ij})\, J_{ji}\right] - \sum_{j<i}\left[n_i A_{ij} + (n_i B_{ij} - n_j B_{ji})\, J_{ij}\right] + \sum_{i\neq j}\left[n_j C_{ji} - n_i C_{ij}\right] = 0$$

- This is the full equation of statistical equilibrium for non-LTE line radiative transfer

- This equation is a local equation, which must be solved separately at each location, but it also has aglobal character because of the dependency in J_{ij} which can only be calculated by solving the whole radiative transfer

3.2.3 General case, non optically thin

- We therefore have, as in the case of continuum, a chicken-egg problem
- In order to have the populations, we need the mean intensity, and in order to have the mean intensity, we need the populations (to solve the radiative transfer, we need to know j_ν and α_ν which depend on the populations)
- The source function for the $j \rightarrow i$ is $S_{ij} = \dfrac{j_\nu(\overrightarrow{n})}{\alpha_\nu(\overrightarrow{n})} = \dfrac{n_j A_{ji}}{n_i B_{ij} - n_j B_{ji}}$
- For the total source function, we have to use $S_\nu = \dfrac{\sum j_\nu}{\sum \alpha_\nu}$

3.2.3 General case, non optically thin

Hypotheses made in order to solve these equations

- Hypothesis of complete redistribution: the velocity of atoms and molecules is assumed to be completely randomised between absorptions and emissions, ie the hypothesis of complete redistribution consists in supposing that before or after each atom or molecule absorbs or emits a photon, collisions have already changed its direction.

- This hypothesis is important to solve line RT. Otherwise, we would have to solve the statistical equilibrium equations not only at each grid point, but also for each velocity vector.

- Instead of a 3D problem in $\overrightarrow{x}$, we would have to solve a 6D problem in $\overrightarrow{x}, \overrightarrow{v}$

- Unfortunately the complete redistribution is not always garanteed. In particular in the turbulent ISM, the typical time it takes for an eddy to randomised its velocity is much greater than the $1/A_{ji}$ of the transitions.

- Even in this case, we use the hypothesis of total redistribution, because the full treatment of non-LTE line RT with partial redistribution is not numerically treatable in 3D

3.2.4 Comparison with dust continuum RT

- Line radiative transfer, even without anisotropic scattering, has many traps
- in particular, unless we build a complete model of the object (cf structure of a protoplanetary disk, with chemistry, heating and cooling of gas, RT) we have to assume the gas temperature
- For certain applications and in particular depending on the nature of data to be modelled, it can be worth using approximations like those we have seen (homogeneous medium, LTE) or specific (escape probability).
- In some cases, it is the presence or not of atomic/molecular data that will dictate the methods that we can use. For example, collisional rates are only available for a restricted number of systems. It is illusory to try a non-LTE calculation when collisional rates are not available

3.2.5 Analogy with scattering

- As mentioned before, we talk sometimes about scattering in line RT
- This involves two successive processes, first an excitation (absorption), followed by a deexcitation (reemission) for a pair of levels
- The net effect is to redirect the photon in a new direction
- The process is mathematically equivalent to true isotropic scattering and this is why the word “scattering" is used, although this can lead to confusion
- In fact, the mathematical equivalence is only true for a two-level system. With a system that has multiple levels, the excitation towards the upper level can be followed by a 2-step de-excitation, ie an energetic photon is absorbed but two low-energy photons are emitted. This process is no longer similar to scattering

3.2.5 Analogy with scattering

Example for a two-level system

- combining these 3 equations, we can write: $j_{ul,\nu} = \alpha_{ul,\nu} \, J_{ul}$
- This is equivalent to the isotropic scattering expression previously seen
- The main difference is that J_{ul} is the mean intensity integrated over the frequency (integrated over the line profile): the photons can change frequency within a spectral line for each scattering event
- This is reminiscent of the analogy with scattering for emission/absorption for thermal dust radiative transfer, except that this time, it takes place in a very narrow frequency domain around the line
- The random walk steps due to scattering can have different lengths depending on the frequency (and therefore the optical depth) seen by the photon at a given time

3.2.5 Analogy with scattering

Example for a two-level system

- Another difference with isotropic scattering is that for the two-level system, the opacity $\alpha_{ul,\nu}$ depends on the mean intensity J_{ul}.
    - If J_{ul} is large, most atoms will be in the upper level, so that there will be fewer atoms to excite from the lower level. This decreases $\alpha_{ul,\nu}$
    - If J_{ul} is sufficiently small that $n_u \ll 1$, $\alpha_{ul,\nu}$ can be considered constant
- In certain cases, systems can behave like a two-level systems. This is the case for Ly α recombination lines: an H$^+$ ion which recombines with an electron usually forms an atom in an excited state. Following radiative decay the atom goes back to lower and lower states until it reaches 1s
- If it reaches the 2p state, the only radiative transition downward is Ly α

3.3 Local thermal equilibrium

- A simple case in line radiative transfer is that of LTE. Even if it is not valid, these approximations are very much used
- One of the characteristics of local thermodynamic equilibrium for lines is that level populations are described by a Boltzmann distribution, ie $\frac{n_j}{n_i} = \frac{g_j}{g_i} \exp\left(-\frac{E_{ij}}{kT}\right)$, where T is the thermodynamic temperature in the medium.
- This means that the populations are governed by collisions
- We then obviously have $T_{\mathrm{ex}} = T$ for all pairs of levels (all transitions have levels populated according the same excitation temperature T_{ex} and this temperature is equal to the kinetic temperature of the gas)

3.3 Local thermal equilibrium

- This temperature is often not precisely known
- Sometimes, the assumption is made that $T_{\rm ex}$ is the same for all transitions, but that but that it is different from T. In general, it is smaller (except for masers), which means that the levels are sub-thermally populated
- In what follows, we will keep the notation $T_{\rm ex}$.
- We also assume a homogeneous source model

3.3 Local thermal equilibrium

- We have already seen the solution of the radiative transfer equation in this simple case: $I_\nu = I_\nu(0)\,\mathrm{e}^{-\tau_\nu} + S_\nu\,(1 - \mathrm{e}^{-\tau_\nu})$, with $S_\nu = B_\nu(T_{\mathrm{ex}})$
  - Optically thick case: $I_\nu \sim S_\nu$
  - Optically thin case: $I_\nu \sim \tau_\nu\,S_\nu + I_\nu(0)\,(1 - \tau_\nu)$
  - Optically thin case without background: $I_\nu \sim \tau_\nu\,S_\nu$
- In the Rayleigh-Jeans domain: $T_b = T_{\mathrm{bg}}\,\mathrm{e}^{-\tau_\nu} + T_{\mathrm{ex}}\,(1 - \mathrm{e}^{-\tau_\nu})$
- Outside the RJ regime: $J_\nu(T_b) = J_\nu(T_{\mathrm{bg}})\,\mathrm{e}^{-\tau_\nu} + J_\nu(T_{\mathrm{ex}})\,(1 - \mathrm{e}^{-\tau_\nu})$

3.3.1 Expression of the optical depth

- It is the optical depth term that contains information on the amount of matter
- The interesting case is the optically thin case, otherwise it is rare to be able to determine the optical depth (unless there is a hyperfine structure)
- The optically thick case gives the temperature of the medium (although in non-LTE conditions, this is not the kinetic temperature of the gas)
- We start from $\tau_\nu = \int \alpha_\nu \, ds$ and $\alpha_\nu = \dfrac{h\nu}{4\pi} n_j B_{ji} (\dfrac{n_i B_{ij}}{n_j B_{ji}} - 1)\, \phi(\nu)$
- The populations are given by $\dfrac{n_j}{n_i} = \dfrac{g_j}{g_i} \exp\left(-\dfrac{h\nu}{kT_\mathrm{ex}}\right)$ and we use the relations between the Einstein coefficients: $\dfrac{A_{ji}}{B_{ji}} = \dfrac{2h\nu^3}{c^2}$ and $g_i B_{ij} = g_j B_{ji}$

3.3.1 Expression of the optical depth

$$\Rightarrow \alpha_\nu = \frac{h\nu}{4\pi} n_j \frac{A_{ji}}{2h\nu^3} c^2 \left[\exp\left(\frac{h\nu}{kT_\mathrm{ex}}\right) - 1\right] \phi(\nu)$$

$$= \frac{A_{ji}}{8\pi\nu^2} c^2 \left[\exp\left(\frac{h\nu}{kT_\mathrm{ex}}\right) - 1\right] \phi(\nu)\, n_j$$

- Where n_j is the upper level population
- The optical depth at frequency ν is therefore:
- $\tau_\nu = \int \alpha_\nu \, ds$

$$= \int \frac{A_{ji}}{8\pi\nu^2} c^2 \left[\exp\left(\frac{h\nu}{kT_\mathrm{ex}}\right) - 1\right] \phi(\nu)\, n_j\, ds \quad = \frac{A_{ji}}{8\pi\nu^2} c^2 \left[\exp\left(\frac{h\nu}{kT_\mathrm{ex}}\right) - 1\right] \phi(\nu)\, N_j$$

with N_j the column density of particules in the upper level

3.3.1 Expression of the optical depth

- In general, $\phi(\nu)$ is not perfectly characterised, which hinders the determination of N_j from τ_ν
- On the other hand, we can often more easily determine the frequency integrated optical depth.
- The function $\phi(\nu)$ is non zero over a very small domain around the central frequency of the line (with the linewidth which is negligible with respect to the frequency of the transition, i.e. $\Delta\nu \ll \nu_0$) and the other functions of ν in the expression of τ_ν vary slowly over this domain. We can therefore write

$$\int \tau_\nu \, d\nu = \frac{A_{ji}}{8\pi\nu_0^2} c^2 \left[\exp\left(\frac{h\nu_0}{kT_{\rm ex}}\right) - 1\right] N_j \int \phi(\nu)\, d\nu$$

where ν_0 is the frequency of the transition

3.3.1 Expression of the optical depth

- Because $\int \phi(\nu)\, d\nu$ is normalised, this yields

$$\int \tau_\nu \, d\nu = \frac{A_{ji}}{8\pi\nu_0^2} c^2 \left[\exp\left(\frac{h\nu_0}{kT_{\mathrm{ex}}}\right) - 1\right] N_j$$

- When spectra are expressed as a function of velocity and not frequency, it is interesting to substitute ν by υ, using $d\nu = \nu / c \, d\upsilon$

$$\int \tau_\upsilon \, d\upsilon = \frac{A_{ji}}{8\pi\nu_0^3} c^3 \left[\exp\left(\frac{h\nu_0}{kT_{\mathrm{ex}}}\right) - 1\right] N_j$$

This gives the column density of particles in the upper level, given the velocity integrated optical depth

3.3.1 Expression of the optical depth

- In order to have the species total column density (and not only that of particles in level j), we can use the partition function $N_j = \frac{N}{Z} g_j \exp\left(-\frac{E_j}{kT_{\mathrm{ex}}}\right)$

$$\int \tau_v \, dv = \frac{A_{ji}}{8\pi\nu_0^3} c^3 \left[\exp\left(\frac{h\nu_0}{kT_{\mathrm{ex}}}\right) - 1\right] \frac{N}{Z} g_j \exp\left(-\frac{E_j}{kT_{\mathrm{ex}}}\right)$$

- It is therefore possible to determine the total column density from the velocity (or frequency)-integrated optical depth, knowing the temperature (for exemple with $T_{\mathrm{ex}} = T_{\mathrm{kin}}$)
- Several further simplifying assumptions can then be made: if the line is Gaussian, or optically thin

3.3.1 Expression of the optical depth

- For a Gaussian line (eg Doppler broadening dominates, with a low optical depth, a simple velocity field), we have: $\int \tau_{\mathrm{v}} dv = \sqrt{\frac{\pi}{4 \ln 2}}\, \tau_0 \, \Delta v$

  τ_0 is the optical depth at the centre of the line

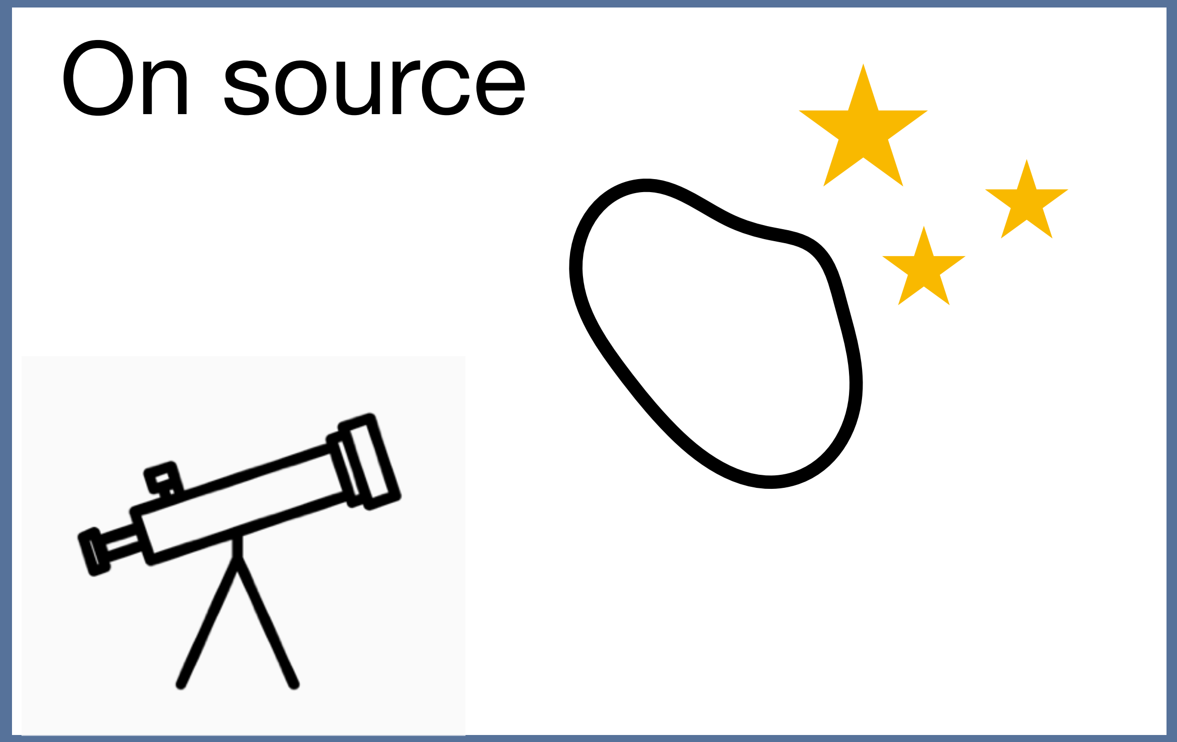
  Δv is the linewidth (FWHM)

- This expression is valid as long as lines are Gaussian. They can be slightly optically thick, but generally, the more optically thick the lines are and the less they are Gaussian.

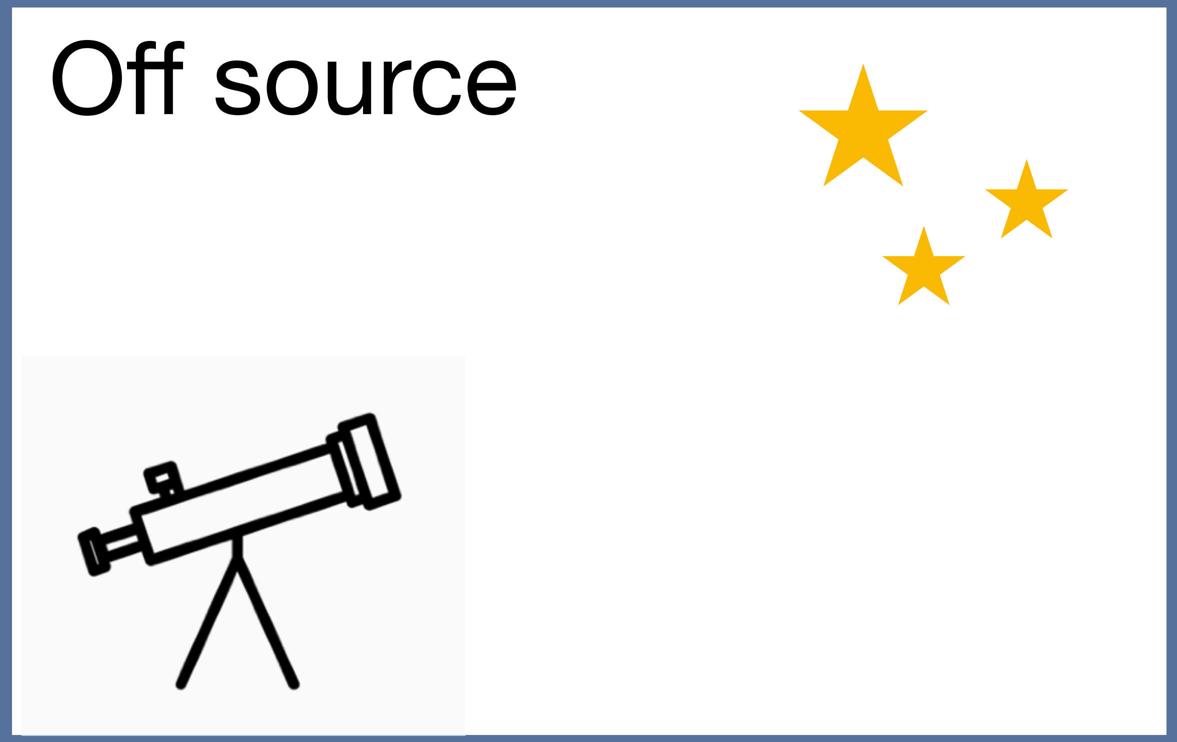
3.3.1 Expression of the optical depth

Application

- Either we can determine the line optical depth directly. An example of this is when the atom/molecule has a hyperfine structure. The relative ratios of the different hyperfine components can give the optical depth: the hyperfine components are in a ratio $g_j A_{ji}$ if the transition is optically thin, but if not, the ratio is different, which allows us to derive the optical depth
- In the general case, the observations give a spectrum which is the difference between an “on source position”, and an “off source” position



$$T_{\mathrm{ON}} = T_{\mathrm{bg}}\,\mathrm{e}^{-\tau_\nu} + T_{\mathrm{ex}}\,(1 - \mathrm{e}^{-\tau_\nu})$$



$$T_{\mathrm{OFF}} = T_{\mathrm{bg}}$$

3.3.1 Expression of the optical depth

Application

- The observed spectrum is $T_b = T_{\mathrm{ON}} - T_{\mathrm{OFF}} = (T_{\mathrm{ex}} - T_{\mathrm{bg}})\,(1 - \mathrm{e}^{-\tau_\nu})$

  Or $T_b = (J_\nu(T_{\mathrm{ex}}) - J_\nu(T_{\mathrm{bg}}))\,(1 - \mathrm{e}^{-\tau_\nu})$

- In the optically thin case: $T_b = \tau_v\,(T_{\mathrm{ex}} - T_{\mathrm{bg}})$, ie T_b and τ_v are proportional

- This leads to $\int T\,dv = (T_{\mathrm{ex}} - T_{\mathrm{bg}}) \int \tau_v\,dv$

$$= (T_{\mathrm{ex}} - T_{\mathrm{bg}})\,\frac{A_{ji}}{8\pi\nu_0^3}\,c^3\left[\exp\left(\frac{h\nu_0}{kT_{\mathrm{ex}}}\right) - 1\right]\frac{N}{Z}\,g_j\,\exp\left(-\frac{E_j}{kT_{\mathrm{ex}}}\right)$$

- $\int T\,dv$ is the line intensity integrated over velocity, ie the area under the observed line. It is measured on the spectrum. If RJ does not apply, we have to replace $T_{\mathrm{ex}} - T_{\mathrm{bg}}$ by $J_\nu(T_{\mathrm{ex}}) - J_\nu(T_{\mathrm{bg}})$

3.3.1 Expression of the optical depth

Application

- If the line is Gaussian, we have directly $T_0 = (T_{\mathrm{ex}} - T_{\mathrm{bg}})\,(1 - \mathrm{e}^{-\tau_0})$ with $\tau_0 = \dfrac{\int \tau_v\, dv}{\sqrt{\dfrac{\pi}{4\ln 2}}\;\Delta v}$ and $\displaystyle\int \tau_v\, dv$ is the expression previously derived.

  T_0 is the intensity at line centre.

3.3.2 Rotational diagrams

- Rotational diagrams are a graphic LTE method to determine the column density
- It is still widely used, even though it might not have a large added value with respect to classical LTE methods
    - This method is more restrictive because it requires additional assumptions with respect to LTE
    - So we have to be careful not to use the method when these assumptions are not verified
    - Goldsmith & Langer 1999, ApJ describe the method in a clear way
- The supplementary assumptions are
    - The transitions are optically thin (formerly, we could assume that they are Gaussian, and not completely optically thick)
    - warm/hot medium for which the background temperature/intensity is negligible, ie $T_{\rm ex} \gg T_{\rm bg}$

3.3.2 Rotational diagrams

- With both assumptions, we can write: $T_b = [J_\nu(T_{\rm ex}) - J_\nu(T_{\rm bg})]\,(1 - {\rm e}^{-\tau}) \simeq \tau\, J_\nu(T_{\rm ex})$
- The intensity integrated under the line is written $\int T\,dv \simeq \int \tau\,dv\; J_\nu(T_{\rm ex})$
- If we now substitute each of these factors with their expression

$$\int T\,dv = \frac{A_{ji}}{8\pi\nu_0^3}\,c^3\left[\exp\left(\frac{h\nu_0}{kT_{\rm ex}}\right) - 1\right] N_j\,\frac{h\nu}{k}\,\frac{1}{\exp\left(\frac{h\nu}{kT_{\rm ex}}\right) - 1}$$

$$= \frac{A_{ji}}{8\pi\nu^2}\,c^3\,\frac{h}{k}\,N_j$$

3.3.2 Rotational diagrams

- The column density in the upper level is expressed in a very simple way as a function of the area under the line $\int T\, dv$

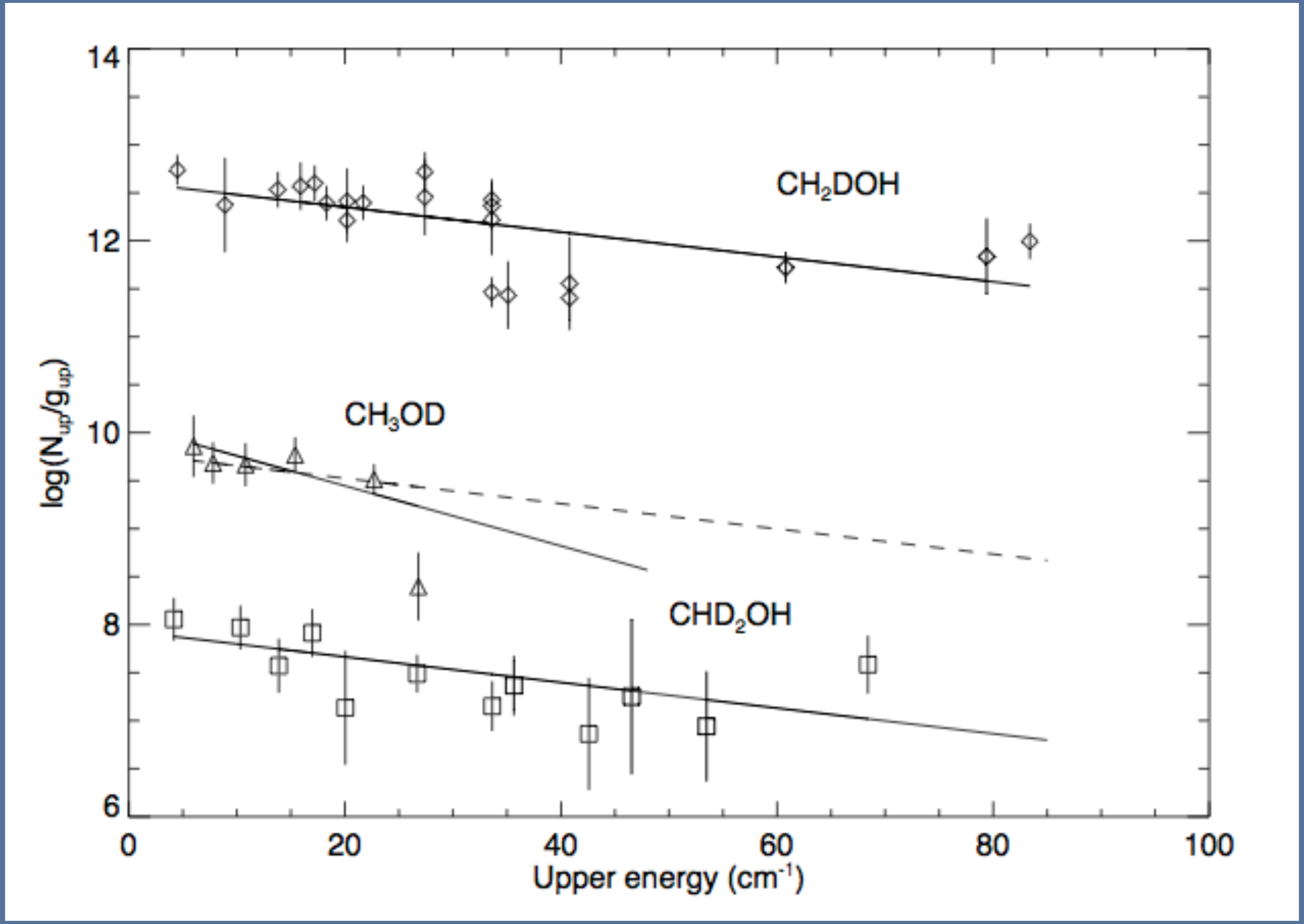
$$N_j = \frac{8\pi\, k\, \nu^2}{hc^3\, A_{ji}} \int T\, dv$$

- What is remarkable in this expression is that it is independent of $T_{\rm ex}$
- In the LTE hypothesis, the column density in the upper level can be expressed with the partition function $N_j = \frac{N}{Z}\, g_j \exp\left(-\frac{E_j}{kT_{\rm ex}}\right)$
- Taking the logarithm of this relation, we have: $\ln\left(\frac{N_j}{g_j}\right) = \ln(N) - \ln(Z) - \frac{E_j}{kT_{\rm ex}}$

3.3.2 Rotational diagrams

- The quantity $\ln\left(\frac{N_j}{g_j}\right)$ is a straight line as function of E_j, the slope of which gives the excitation temperature, and the intercept gives the total column density N
- $\ln\left(\frac{N_j}{g_j}\right)$ is calculated from the expression of N_j as a function of $\int T\,dv$ (see previous slide)
- This method no longer works if we cannot neglect T_{bg} in front of T_{ex}. In this case, N_j is no longer independent of T_{ex}

3.3.2 Rotational diagrams



Parise et al. (2002)

3.4 Escape probability

- There are many cases where the LTE approximation is too coarse.
- Without resorting to solving the whole transfer problem (and its complexity), which implies costly numerical treatment, one can use other simple techniques
- One of the difficulties of line radiative transfer is the coupling between the statistical equilibrium equation at one location (local equation) to the mean intensity, i.e. the radiation field averaged over all directions.
- One approach consists in decoupling these equations by introducing the probability that a photon escapes from the medium after having been emitted.
- This method was proposed by Sobolev (1958)
- It is only an approximation, because in reality the photon might be absorbed and reemitted many times and therefore move everywhere within the source
- This approach gives nevertheless results in good agreement with a more precise and elaborated treatment of radiative transfer

3.4 Escape probability

- For simplicity, we will assume a two-level system. The equations of statistical equilibrium can be written:
  - $\frac{dn_1}{dt} = (-n_1 B_{12} + n_2 B_{21}) J + n_2 C_{21} - n_1 C_{12} + n_2 A_{21}$
  - $\frac{dn_2}{dt} = (n_1 B_{12} - n_2 B_{21}) J - n_2 C_{21} + n_1 C_{12} - n_2 A_{21}$
  - At steady-state we obviously have $\frac{dn_1}{dt} = \frac{dn_2}{dt} = 0$
- If the source is completely optically thick to its own radiation, the mean intensity tends towards the local value of the source function S ($I \rightarrow S$)
- The difference between J and the local source function must then represent the photons escape from the source, and therefore J/S represents the proportion of photons trapped locally

3.4 Escape probability

- If the escape probability is β, the proportion of trapped photons is simply $1 - \beta$.
- The approximation of the escape probability assumes that J can be written $J = S(1 - \beta)$
- β depends on the geometry of the source and of the optical depth
- The important point is that β does not depend on the intensity
- Another point is that the above equation involves the photon absorption probability, instead of the escape probability. The sum of both probabilities is 1 in a simple case of only one line. If there is in addition a continuum or another line that overlaps with the first one, the photon can be lost for the line without escaping the source. The previous equation has then to be modified

3.4 Escape probability

- Introducing the expression of J in the statistical equilibrium equation, we obtain: $\frac{dn_2}{dt} = n_1 C_{12} - n_2 C_{21} - \beta n_2 A_{21}$
- This decouples the mean intensity from the statistical equilibrium equations.
- For a system with more than 2 levels, β depends on the considered transition
- If we have a continuum background intensity, its probability to penetrate in the source is $1 - \beta$

3.4 Escape probability

- Interpretation
  - A deexcitation from level 2 does not always decrease the level population, because the emitted photon can be absorbed elsewhere in the source and excite again the system towards level 2. Only photons escaping the source lead to a change in the populations. The variation rate of the population is the spontaneous decay rate (A_{21}) multiplied by the escape probability β.

3.4 Escape probability

- We now have to estimate the escape probability
- In reality, β depends on the solution of the problem at each location, because S depends on the radiation field
- In order to have an expression of β as a function of the geometry only and the optical depth, but which is independent of the radiation field, approximations have to be made
- Expressions for β as a function of τ for exemple in Elitzur (Astronomical Masers) for different geometries

3.4 Escape probability

- Sobolev approximation, or large velocity gradient (LVG): $\beta = \dfrac{1 - \mathrm{e}^{-\tau}}{\tau}$
- Homogeneous, plan parallel medium: $\beta = \dfrac{1 - \mathrm{e}^{-3\,\tau}}{3\,\tau}$
- Turbulent medium: $\beta = \dfrac{1}{\pi\sqrt{\pi \ln(\frac{\tau}{2})}}$
- Uniform sphere: $\beta = \dfrac{1.5}{\tau}\left[1 - \dfrac{2}{\tau^2} + \left(\dfrac{2}{\tau} + \dfrac{2}{\tau^2}\right)\,\mathrm{e}^{-\tau}\right]$ (Osterbrock)

- We roughly expect that in the limit of low optical depths, $\beta \to 1$ (the medium is transparent and the photon escapes without interactions)
- If the medium is optically thick ($\tau \gg 1$) it can be divided in τ zones of optical depth 1. On average, a photon escapes only if it is produced in the most external region, and the probability it escapes is $1/\tau$

3.4 Escape probability

- Large velocity gradient: the interpretation of this case is that when there is a large velocity gradient in the source the photons emitted by an atom or a molecule at a velocity $\overrightarrow{v}$ cannot be reabsorbed by a molecule at a velocity $\overrightarrow{v}'$ located elsewhere in the source, if $|\overrightarrow{v} - \overrightarrow{v}'| > \Delta v$, where Δv is the linewidth.

- The photon can then escape and the problem becomes entirely local. The Doppler shift is $\Delta \nu_{ij} = \nu_{ij}/c\, \overrightarrow{n}\, (\overrightarrow{v} - \overrightarrow{v}')$

- In practice this method gives good results, even when there are few velocity gradients