Non-LTE processes in the study of radiative transfer in planetary atmospheres

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Introduction

In the study of radiative transfer through planetary atmospheres, the infrared region is of particular importance: for mean temperatures of the order of some hundreds of Kelvins, the main part of the planetary thermal emission lies in this spectral region and the processes of absorption and emission by molecules in the atmosphere at these wavelengths turn out to be fundamental in determining the overall energy balance. In particular, with regards to Earth, the atmospheric thermal emission peaks around 10 $\mu$m and more than 95% of the photons has a wavelength between 5 and 50 $\mu$m; this means that more than 90% of the energy irradiated by the planetary surface is transported by photons with energies between 0.05 and 0.25 eV, far below the limit of a typical electronic transition and, instead, characteristic of the roto-vibrational bands of molecules. In the lowest part of planetary atmospheres, where the density is sufficiently large, local thermodynamic equilibrium (LTE) can be assumed for all the molecular degrees of freedom. This greatly simplifies the treatment of radiative transfer, because in this case we already know from statistical physics the population of each excited state and then the characteristic emission and absorption coefficients of molecules. But, higher in the atmosphere, the assumption of LTE no longer holds and the atmospheric optical properties may be dramatically modified. Given that the energy gap between two adjacent rotational levels ($10^{-3} - 10^{-2}$ eV) is smaller or at most comparable with the mean thermal energy for temperatures in the range 100-300 K, these levels keep being in equilibrium up to very high atmospheric layers. The same does not hold for vibrational levels, which have a considerably larger energy gap ($> 0.1$ eV) and at low densities show a significant departure from their equilibrium population. This behaviour is indeed observed in Earth’s atmosphere above about 40 km, as well as in the most external regions of all planetary atmospheres, both during day- and nighttime. In the first case, usually - but not always - the excited levels population is larger than the equilibrium one, due to the action of solar radiation or inelastic collisions with overpopulated species, not adequately balanced by collisional de-excitation processes. During nighttime, the populations are instead usually smaller than those at equilibrium because of the losses due to spontaneous emission of photons, dominant with respect to production of particles in the excited states. This is, however, an over-simplification of the problem; in general it is necessary to separately analyze each case and solve the statistical equilibrium equation for each level out of LTE, taking into account all possible radiative and collisional processes that are responsible of the transitions between levels.

Infrared emission is also commonly used to probe the planetary atmospheres by instruments on satellite, that is, to measure their thermal structure and composition. In the lower part of the atmosphere the assumption of LTE holds but to analyze the middle and upper parts of planetary atmospheres the consideration of non-LTE processes is required. Besides, non-LTE has often the advantage that, being the energy levels significantly excited by solar radiation, the infrared signal of the faint upper atmosphere is larger, allowing to probe this regions too.

This work focuses on the study of infrared radiative transfer in planetary atmospheres under
non-LTE conditions; it is divided in two parts: the first one contains the theoretical basis, whereas in the second one the theory is applied to the case of the carbon monoxide emission in Titan’s atmosphere. To properly understand the role of molecules in the absorption and emission of radiation, a preliminary study on the molecular system is necessary. For this reason, Part I begins with a general review of the basics regarding the rotational and vibrational degrees of freedom of nuclei (Chapter 1), focusing on the diatomic case and describing the main results about polyatomic molecules. We then analyze the interaction of molecules with radiation and derive the selection rules for vibrational and rotational transitions, which explain the typical shape of molecular bands (Chapter 2). Chapter 3 contains the basic theory of radiative transfer, with its fundamental equations and a first discussion of the non-LTE problem. To deal with non-LTE, we need to know the mechanism at the basis of the collisional processes that control the excited levels population. We therefore pay a special attention to the study of vibrational energy transfer in inelastic molecular collisions, reviewing the fundamental theoretical approaches, from the classical Landau-Teller approach to the full-quantum SSH theory, and analyzing the usual experimental technique used to get the characteristic rate constants of these processes (Chapter 4).

The treatment of the radiative transfer problem under non-LTE conditions requires the simultaneous resolution of the statistical equilibrium equation for the considered excited levels and of the equation of radiative transfer in the corresponding roto-vibrational bands. The rate of radiative excitation depends in fact on the mean intensity in each point, that in turn is linked to the population of excited levels in the whole atmosphere. In the most general case, besides, the problem being non-linear, the absorption coefficient itself depends on the excited states population. We study this topic in Chapter 5, writing down the fundamental equations of the non-LTE problem and showing its solution in the linearized two-level case. Part I ends with a brief review of the retrieval problem, that is the inversion of atmospheric emission measurements to obtain the actual concentration of molecular species. We describe this in Chapter 6, where we also study the typical procedure of numerical inversion that is be used in Part II.

In the second part of this work, we dealt with the specific case of CO in Titan’s atmosphere, for which non-LTE effects are determinant. During the last 20 years, many works have focused on the atmospheric concentration of CO on Titan, giving contradictory results, and, in particular, no measurement of the CO abundance above 300 km has been done yet. Developing a non-LTE model for CO allows the analysis of VIMS (Visual & Infrared Mapping Spectrometer, on board Cassini) daytime measurements at 4.7 μm, where the non-LTE behaviour of CO is evident. Such a study is particularly awaited as a confirmation of photochemical models of Titan’s atmosphere, that predict a uniform concentration of CO in the whole atmosphere. Given that CO is the main reservoir of oxygen in Titan’s atmosphere and its presence is linked to water, the matter is of astrobiological interest too.

In Chapter 7 we set the problem in Titan’s atmosphere and develop the non-LTE excitation/deexcitation model for the first two CO vibrational levels. We consider the contribution of absorption of radiation in the fundamental, first hot and first overtone bands and evaluate the possible contribution of different collisional processes. This study is complicated by the lack of experimental rates for specific processes and for some of them an estimate is given and discussed later. We then present the solution of the non-LTE problem obtained through a non-LTE population algorithm based on Lambda iteration resolution strategy, eventually coupled to a Curtis-Matrix type approach. The code run on the basis of the collisional model developed in this work.

In the last Chapter we analyze some spectra acquired by VIMS in the 4.7 μm region for
daytime conditions. The purpose of this analysis is the retrieval of the CO concentration in Titan’s upper stratosphere and mesosphere. The atmospheric emission is simulated using a non-LTE line-by-line radiative transfer code, coupled to an inversion method based on the strategy of maximum likelihood. The low signal-to-noise ratio and the low spectral resolution of the instrument considerably complicate the data analysis. CO abundance profiles are obtained and discussed in the light of photochemical models predictions. Finally possible improvements to the non-LTE model and their potential effects on the retrieved CO profiles are discussed.
Part I

Theoretical basis
Chapter 1

Molecular rotational-vibrational energy levels

To truly understand the processes involved in the radiative transfer in planetary atmospheres it is useful to start from the study of rotational and vibrational levels of molecules: this chapter has, indeed, the purpose of reviewing the physics of the problem and summarizing the main results. We will analyze more in detail the simple case of the diatomic molecule and give some hints about the polyatomic case.

1.1 Diatomic molecules

Let us then start with the study of a diatomic molecule, neglecting for now relativistic effects, for the sake of simplicity. Considering a system composed by n electrons with coordinates $R_i$ and two nuclei of masses $M_a$ and $M_b$ with coordinates $R_a$ and $R_b$, its hamiltonian will be:

$$ H = \sum_i \frac{P_i^2}{2m_e} + \frac{P_a^2}{2M_a} + \frac{P_b^2}{2M_b} + U(R_i, R_a, R_b) + V(R_a, R_b) \quad (1.1) $$

where

- $U(R_i, R_a, R_b) = \sum_i \sum_{j>i} \left[ \frac{e^2}{|R_i - R_j|} + \frac{Z_a e^2}{|R_i - R_a|} + \frac{Z_b e^2}{|R_i - R_b|} \right]$
- $V(R_a, R_b) = \frac{Z_a Z_b e^2}{|R_a - R_b|}$

$H$ is the kinetic energy of the electrons and nuclei, and $U$ and $V$ are the electrostatic potential energy due to the electron-electron, electron-nucleus, and nucleus-nucleus interactions, respectively. $m_e$ is the electron mass, and $Z_a$ and $Z_b$ are the number of protons in each nucleus. The difficulty in finding the eigenvalues for this hamiltonian is given by the coupling between electronic degrees of freedom and the nuclear ones. Because of the large difference in the masses of electrons and nuclei, in most cases we can easily make an adiabatic approximation (that is, in the characteristic time of an electronic orbit, the nuclear wave function does not vary in a significant way) and solve the electronic problem with the nuclei fixed in space, keeping nuclear coordinates as parameters. Before discussing this approximation and its meaning more in detail, it is useful to make some changes in coordinates, moving first in the reference system situated in the center of mass of the nuclei, and referring then the electronic coordinates to the molecule fixed system: in this way the electronic problem can be solved writing all operators (like orbital angular momentum $L$) as a function of the new coordinates $(\xi, \eta, \zeta)$.

So, let us make the first change of coordinates $(R_a, R_b, R_i) \to (R_{cm}, R, R')$, where $R = R_b - R_a$ is the position of the second nucleus with respect to the first, $R_{cm}$ is the
position of the center of mass and \( \mathbf{R}_e' \) are the positions of the electrons referred to the center of mass of the nuclei. Writing again the hamiltonian as a function of the new coordinates and of the conjugate momenta, there appears a new term linked to electronic momenta, also called polarization term:

\[
H = \frac{1}{2M} \dot{\mathbf{R}}_{cm}^2 + \frac{1}{2\mu} \dot{\mathbf{R}}^2 + \frac{1}{2\mu_e} \sum_i \dot{\mathbf{P}}_i^2 + \frac{1}{2(M_a + M_b)} \sum_{i,j} \mathbf{P}_i' \cdot \mathbf{P}_j' + U(\mathbf{R}_e', \mathbf{R}) + V(R) \tag{1.2}
\]

where \( M = M_a + M_b + N_e m_e \) is the molecular mass, \( \mu = \frac{M_a M_b}{M_a + M_b} \) and \( \mu_e = \frac{m(M_a + M_b)}{M} \) are the reduced masses of nuclei and electrons, and \( N_e = Z_a + Z_b \).

At this point we shall refer the electronic coordinates to the molecule-fixed system (the \( \zeta \) axis along the line joining the two nuclei, the axes \( \xi \) and \( \eta \) in the perpendicular plane) and make then another change in coordinates \((\mathbf{R}_{cm}, \mathbf{R}, \mathbf{R}_e') \rightarrow (\mathbf{R}_{cm}, \mathbf{R}, \mathbf{r}_i)\). Describing the rotation with the use of Euler angles, we have that \( \mathbf{r}_i = \mathcal{R}(\theta, \varphi, \chi) \mathbf{R}_e' \), where \( \theta \) and \( \varphi \) indicate the direction of the internuclear axis, whereas \( \chi \) is the angle formed with a fixed direction perpendicular to the symmetry axis.

As it is simply a rotation, which leaves all scalar products unchanged, the structure of the electronic terms in the hamiltonian does not change and can be directly rewritten in the new coordinates and momenta\(^1\). What does change is the term connected with the relative momentum of nuclei, because our independent variables are now different: if we express the momentum in spherical coordinates, \( \mathbf{P}_\theta \) and \( \mathbf{P}_\varphi \) are linked to the partial derivatives along \( \theta \) and \( \varphi \) but, whereas these were at first calculated keeping fixed the electronic coordinates in space, now the same derivatives have to be calculated without varying the molecule-fixed coordinates; in a certain sense, together with the nuclei, we are now rigidly moving the electrons too. The calculation of the new angular momenta is quite laborious\(^2\) and we will not tackle it here, referring for the complete analysis to the books by Brown ([4]) and Judd ([5]).

The result of this procedure leads to the new hamiltonian and, replacing the momenta with \(-i\hbar \nabla\) and ignoring the part referring to the translational motion of the center of mass, we have:

\[
H = H_e + H_v + H_r; \quad H_e = -\frac{\hbar^2}{2\mu_e} \sum_i \nabla_i^2 - \frac{\hbar^2}{2(M_a + M_b)} \sum_{i,j} \nabla_i \cdot \nabla_j + U(r_i, R) \\
H_v = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) + V(R) \quad H_r = \frac{\hbar^2}{2\mu R^2} |\mathbf{J} - \mathbf{L}|^2 \tag{1.3}
\]

We may therefore single out three different parts of the hamiltonian: \( H_e \) is the electronic hamiltonian, with the potential term \( U \) depending on the separation \( R \) between the nuclei; \( H_v \) regards the nuclear vibrational degree of freedom and \( H_r \) is the rotational part of the hamiltonian.

If we fix the distance \( R \) between the nuclei, we can study separately the electronic hamiltonian; let us highlight some of its general characteristics. First of all, as we are not in presence of a central field, the total angular momentum \( \mathbf{L} \) of the electrons is not conserved, contrary to the atomic case. Nevertheless, we have a symmetry for rotation around the internuclear axis \( \zeta \), therefore the projection of \( \mathbf{L} \) on this axis is conserved and we can use the absolute value \( \Lambda \) of this projection in order to classify the system eigenstates: we will have states with

\(^1\)It is important to underline that we are not moving to the rotating system, but simply instantaneously projecting the momenta on it.

\(^2\)The main difficulty of this operation consists of the fact that we are considering angular momenta with respect with two different systems, the one fixed in space and the molecule-fixed one.
\( \Lambda = 0, 1, 2, \ldots \) which are usually indicated with the capital greek letters \( \Sigma, \Pi, \Delta, \) etc. We then have a further symmetry for reflection with respect to a plane containing the \( \zeta \) axis: in the reflection the energy does not change, but the direction of the projection of angular momentum does. The states with \( \Lambda \neq 0 \) are then doubly degenerate, whereas the \( \Sigma \) state is an eigenstate of the reflection operator with possible eigenvalues \( \pm 1 \) (this property is shown referring at it as the \( \Sigma^+ \) or \( \Sigma^- \) state). Experimentally, we see that the fundamental state of the majority of stable diatomic molecules is a \( \Sigma^+ \) state. In the following we will refer to the eigenstates of the electronic hamiltonian as \( \ket{n\Lambda} \), thus showing the energy level and the projection of electronic angular momentum; we then have:

\[
H_e \ket{n\Lambda} = E_{en}(R) \ket{n\Lambda} \quad \text{and} \quad L_\zeta \ket{n\Lambda} = \Lambda \ket{n\Lambda} \tag{1.4}
\]

At this point let us go back to our problem. We may consider separately on the other two parts of the total hamiltonian \( H_e \) and \( H_r \), and then look for the solutions to the complete system as linear combinations of tensor products between the eigenstates of the three hamiltonians. Given the large mass difference between electrons and nuclei, a simpler analysis is sufficient: in a famous 1927 work ([7]), Born and Oppenheimer showed that, expanding the complete hamiltonian in powers of \( (m_e/M_n)^{1/4} \), at the lowest order we can neglect everything but \( H_e \); at the second we shall take into account \( H_v \), too, at the fourth \( H_r \), and only at successive orders will the interaction terms between the three parts matter. We might then look for a solution to the system considering only the diagonal elements of \( H \) in the basis constituted by the eigenstates of \( H_e, H_v \) and \( H_r \). Let us write \( \ket{\Psi} = \ket{n\Lambda \alpha} \ket{v} \), where \( \ket{\alpha} \) is an eigenstate of the total angular momentum of the molecule and \( \ket{v} \) is an eigenstate of \( H_v \):

\[
\bra{\Psi} (H_e + H_r + H_v) \ket{\Psi} = E_{n\alpha} \bra{n\Lambda \alpha} \ket{\alpha} \bra{\alpha} \ket{v} \tag{1.5}
\]

multiplying both terms by \( \bra{\Psi} \ket{n\Lambda} \) and expanding the left one,

\[
\bra{\Psi} \ket{n\Lambda} (H_e + H_r + H_v) \ket{n\Lambda \alpha} \ket{v} =
= \left[ E_{en}(R) + \frac{\hbar^2}{2\mu R^2} \bra{\Psi} \ket{n\Lambda} \left( J^2 + L^2 - 2 J \cdot L - \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) \right) \right] \ket{n\Lambda \alpha} \ket{v}
+ \frac{h}{2\mu R^2} \bra{\Psi} \ket{n\Lambda} \left( J^2 + L^2 - 2 J \cdot L - \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) \right) \ket{v}.
\tag{1.6}
\]

Now, the operator \( J \) does not act on the electronic state and \( J^2 \ket{\alpha} = J(J+1) \ket{\alpha} \); if we expand \( L^2 - 2 J \cdot L = L_\xi^2 + L_\eta^2 + L_\zeta^2 - 2 J_\xi L_\xi - 2 J_\eta L_\eta - 2 J_\zeta L_\zeta \), we can ignore the terms linear in \( L_\xi \) and \( L_\eta \) because they only couple states with different \( \Lambda \); then \( J_\zeta \ket{\alpha} = \Lambda \ket{\alpha} \), given that the only contribution to the angular momentum along \( \zeta \) is due to the electronic component.\(^3\)

Finally simplifying the term containing the radial derivative applied to the electronic eigenstate, we obtain:

\[
\left[ \frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right) - J(J+1) \frac{\hbar^2}{2\mu R^2} - W(R) + E_{env} \right] \ket{v} = 0 \tag{1.7}
\]

with

\[
W(R) = E_{en}(R) + V(R) - \frac{\hbar^2}{2\mu R^2} \Lambda^2 - \frac{\hbar^2}{2\mu R^2} \bra{n\Lambda} (L_\xi^2 + L_\eta^2) - R^2 \frac{\partial}{\partial R^2} \ket{n\Lambda}
\]

We can see that the energy \( E_{en}(R) \) of the electronic state becomes here part of an effective potential that keeps the two nuclei bined, together with the term of Coulombian repulsion and

\(^3\)We are neglecting the intrinsic momentum of nuclei.
other terms linked to the electronic state: it is just this potential that governs the vibrational motion of the two nuclei and the corresponding energy levels. To draw theoretically the exact form of $W(R)$ requires elaborated numerical simulations even for rather simple molecules and, in the analysis of vibrational levels of molecules, approximate forms of $W(R)$ have historically been used, getting the characteristic parameters from experimental data.

If the system only makes small oscillations around the equilibrium point $R_e$, we may expand the potential $W(R)$ around it, keeping only terms till second order in the small displacement and solving the equation for the wave function $\langle v | \psi \rangle = \Psi_v(R)$, assuming $W(R) = \frac{1}{2}k(R - R_e)^2$, with $k = \left. \frac{d^2 W(R)}{dR^2} \right|_{R=R_e}$. Let us solve equation (1.7) with a harmonic potential, considering the reduced wave function $u_v(R) = R\Psi_v(R)$ and changing variable to $\rho = R - R_e$:

$$\frac{d^2 u}{d\rho^2} + \frac{2\mu}{\hbar^2} \left[ E_v - \frac{1}{2} k\rho^2 - \frac{\hbar^2}{2\mu} J(J + 1) \right] u = 0$$

expanding the rotation term till the second order $\frac{1}{(R_e + \rho)^2} = \frac{1}{R_e^2} \left[ 1 - \frac{2\rho}{R_e} + \frac{3\rho^2}{R_e^2} + ... \right]$ and calling $B \equiv \frac{k^2}{2\mu R_e^2}$ the equilibrium rotational constant,

$$\frac{d^2 u}{d\rho^2} + \frac{2\mu}{\hbar^2} \left[ E_v - \frac{1}{2} k\rho^2 - BJ(J+1) + 2B \frac{J(J+1)}{R_e} - 3 \frac{B}{R_e^2} J(J+1) \rho^2 \right] u = 0$$

In order to reduce eq. (1.9) to the equation of the one-dimensional harmonic oscillator, we can apply a last substitution $\sigma = \rho + a$ and look for $a$ such as to make the coefficient of the first degree term vanish. Choosing $a = \frac{2BJ(J+1)}{kR_e^2 + 6BJ(J+1)} R_e$, we then obtain:

$$\frac{d^2 u}{d\sigma^2} + \frac{2\mu}{\hbar^2} \left[ E_v - E_{\text{rot}} + E_{\text{nr}} - \frac{1}{2} k' \sigma^2 \right] u = 0$$

with $E_{\text{rot}} = BJ(J+1)$; $E_{\text{nr}} = \frac{2B^2J^2(J+1)^2}{kR_e^2 + 6BJ(J+1)}$; $k' = k + \frac{6B}{R_e^2} J(J+1)$.

The only difference with the case of the one-dimensional harmonic oscillator is given by the boundary conditions: for the $u(\sigma)$ of the oscillator we have $u = 0$ for $\sigma \to \pm \infty$, whereas in our case $u = 0$ for $\sigma = -(R_e + a)$ and $\sigma \to \infty$. Since the wave function will be non-vanishing only in a small region around $R_e$, we can state that the solutions will be the same, with negligible error, and so the energies will be those of a one-dimensional harmonic oscillator with constant $k'$:

$$E_v = \left( v + \frac{1}{2} \right) \hbar \nu' + E_{\text{rot}} - E_{\text{nr}}, \text{ with } \nu' = \frac{1}{2\pi} \sqrt{\frac{k'}{\mu}}.$$

We may consider the case of low rotational levels, for which the vibrational energy is much higher than the rotational one, and keep only the first order of $\nu'$ and $E_{\text{nr}}$, expanding in the small term $BJ(J+1)/kR_e^2$; we then obtain:

$$E_{\nu,J} = \left( v + \frac{1}{2} \right) \hbar \nu + BJ(J+1) - \frac{[BJ(J+1)]^2}{2\pi^2 kR_e^2}$$

The first two terms are clearly the energies of an harmonic oscillator with constant $k$ and of a rigid rotator with moment of inertia $I = \hbar^2/2B$, whereas the third term represents a first correction due to the fact that the rotator is not actually rigid but undergoes a stretch with the growth in the angular momentum (and in fact, increasing $J$, the energies are lower than those of a rigid rotator because the moment of inertia is growing).

The treatment we followed till now gives a first approximate measure of the roto-vibrational levels of a diatomic molecule, although the precision of such approximation is obviously limited.
by the excessively simplified assumption of harmonic potential; other forms of the potential $W(R)$, closer to the real interaction, have been tried historically and give a correction to the energy levels. A case worth of mentioning is the Morse potential, that we can see in Figure 1.1:

$$W(R) = D \left[1 - e^{-\alpha(R-R_e)}\right]^2 - D$$

![Morse potential graph](image)

Figure 1.1: The Morse potential for characteristic values of the CO molecule: $D = 11.02\, eV$, $\alpha = 2.32 \times 10^8\, cm^{-1}$, $R_e = 1.13 \times 10^{-8}\, cm$.

The Morse potential allows a more precise analysis; first of all, it correctly tends to a finite value for $R \to \infty$, although for $R \to 0$ it does not actually diverge as it should\(^4\). Moreover, differently from the harmonic potential case, now we only have a finite number of possible eigenvalues for the energy. The energies of the system with the new potential, which we will not derive here (see the original work by Morse [8], its solution by Pekeris [?] or the book by Pauling and Wilson [2], are as follows:

$$\frac{E_{\nu J}}{\hbar c} = \left(v + \frac{1}{2}\right) w_e - x_e w_e \left(v + \frac{1}{2}\right)^2 + B_e J(J+1) - D_e J^2(J+1)^2 - \alpha_e \left(v + \frac{1}{2}\right) J(J+1)$$

(1.12)

where

$$w_e = \frac{a}{2\pi c} \sqrt{\frac{2D}{\mu}} \quad x_e = \frac{\hbar c w_e}{4D} \quad B_e = \frac{\hbar}{\hbar c} = \frac{\hbar}{8\pi^2 \mu R_e^2 c}$$

$$D_e = \frac{4B_e^2}{\hbar c w_e^2} \quad \alpha_e = 6 x_e B_e \sqrt{\frac{B_e}{x_e w_e}} \left(1 - \sqrt{\frac{B_e}{x_e w_e}}\right)$$

All parameters are in units of $cm^{-1}$, which will become familiar units in the next chapters. The meaning of the two additional terms can be understood even without a quantitative analysis. The quadratic term in $v$ is due to the anharmonicity of the potential: given the form of the Morse function, for large oscillations the restoring force is lower than that of the harmonic

\(^4\)But the error made here is completely negligible, because in this region the Morse potential has a quite high value and the wave function practically vanishing.
case and, therefore, there is a negative correction to the energy level that grows increasing \( v \). The last mixed term is connected with this effect as well and with the asymmetry of the potential: since the restoring force is lower for large \( R \), the wave function will be larger in the region with \( R > R_e \) and consequently the mean moment of inertia will be larger than the one at equilibrium distance; for this reason we have another negative correction to the energy that grows with \( v \) and \( J \).

In Figure 1.2 we can see a comparison between the eigenfunctions obtained with a Morse potential and an harmonic approximation.

**Multiplet terms**

Till now we have been studying the case of the diatomic molecule without considering electronic spin and the validity of this analysis is quite general because the majority of diatomic molecules has the singlet state \( ^1\Sigma^+ \) as fundamental state. But if the fundamental state of a molecule has total spin \( S \neq 0 \) or if we are dealing with an excited state, it is necessary to take into account the relativistic effects and the spin part of the system hamiltonian. We are not interested here in a detailed analysis of this situation, yet it deserves to give some hints to the modifications that the energy levels undergo in some particular situations. The general case is in fact extremely complicated and it is therefore useful to restrict the discussion to a few limiting situations, known as *Hund’s coupling cases* (see [6]).

In the atomic hamiltonian, the presence of the spin produces the additional term of spin-orbit coupling \( \propto L \cdot S \), which eliminates the degeneracy on \( S \) and is treated as a perturbation to the levels of the non-relativistic hamiltonian. Going back to the diatomic molecule, the situation is more complicated because we have different effects to deal with as perturbations and the treatment will be different depending on which effect dominates on the others and which quantum numbers are “more or less good” (that is, which among the various angular momenta are better or worse conserved). The quantum number \( \Lambda \), corresponding to the projection of the electronic angular momentum on the molecular axis, is strictly conserved in the problem with fixed nuclei, and in most cases it is quite a good approximation to regard it as conserved even in presence of molecular rotation and spin-orbit coupling: the energy gap between levels with different \( \Lambda \) is far larger than the one produced by the other effects. As \( \Lambda \) can still be regarded as conserved and the symmetry with respect to rotation about the molecular axis is still quite a good symmetry, we can speak, in the diatomic case, of *spin-axis coupling*. The separation of the levels due to the term \( L \cdot S \) will be proportional to the mean value of this operator on the electronic state and consequently to the projection of the spin in the direction of molecular axis.

We may now single out two limiting cases: following Hund, we will call coupling case a) the one for which the contribution given by the spin-axis interaction is far more important of that given by molecular rotation (and then \( \Delta E_{LS} \gg \Delta E_{rot} \)), and coupling case b) the opposite situation in which the larger effect is due to rotational motion. Case a) is the one most commonly encountered, whereas case b) better represents the \( \Sigma \) states (for \( \Lambda = 0 \) the spin-axis interaction vanishes at first order).

If we write \( H = H_0 + H_{LS} + H_{rot} \), in case a) we will treat \( H_{rot} \) as a perturbation to the eigenstates of \( H_0 + H_{LS} \); on the contrary in case b) the perturbation will be given by the term \( H_{LS} \) with respect to \( H_0 + H_{rot} \).

In case a), the \( 2S + 1 \) unperturbed eigenstates corresponding to the same \( \Lambda \) are separated by the spin-axis interaction depending on the value of \( \Omega \), projection on the axis of the sum of \( L \) and \( S \) (\( \Lambda - \Xi \leq \Omega \leq \Lambda + \Xi \), where \( \Xi \) is the projection of \( S \)): the level separation is proportional to \( \Omega \) and each energy eigenvalue can be written as \( E_{n\Lambda}(R) + A_\Lambda(R)\Omega \). The
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Figure 1.2: Comparison between eigenfunctions obtained with the Morse potential and with a simple harmonic potential (keeping fixed the energy of the first level); the first two excited vibrational levels are shown: the error made assuming the harmonic eigenfunction is larger for larger intermolecular distance and increases with the vibrational excitation. The eigenfunctions for the Morse potential have been obtained from the numerical resolution of the Schrödinger equation.

Rotational levels will be obtained through the calculation of the diagonal matrix element of $H_{\text{rot}} = B(J - L - S)^2$ for a given state $|n\Omega\rangle$ and, with a treatment completely analogous
to the case without spin, we obtain, at the lowest order (see [1]):

$$E_{\Omega, \nu} = A_{\nu} \Omega + \left( \nu + \frac{1}{2} \right) \hbar \nu + B \left[ J(J + 1) - \Omega^2 \right]$$  (1.13)

In case b), $\Omega$ is no more a good quantum number, because the effect of rotation is more important: we shall calculate the perturbation given by the spin-axis coupling to the rotational eigenstates of a system without spin and with total angular momentum $K = J - S$ (the orbital part, electronic and nuclear, of the total angular momentum $J$). In this way we obtain the energies of the perturbed levels:

$$E_{\nu KJS} = \left( \nu + \frac{1}{2} \right) \hbar \nu + BK(K + 1) + A'_{\nu} \Lambda \frac{(J - S)(J + S + 1)}{2K(K + 1)}$$  (1.14)

So, differently from the previous case, the separation between two levels with different $K$ now depends also on the value of the total spin of the molecule.

1.2 Some results about polyatomic molecules

So far we have analyzed the roto-vibrational energy levels in the special case of diatomic molecules, but many cases of interest for the study of radiative transfer in planetary atmospheres are represented by molecules composed by more than two atoms: for them, a systematic study of the roto-vibrational levels is far more complicated. In order to have a first look at this more general topic, it is convenient and useful to study separately the vibrational and rotational degrees of freedom, neglecting in a first analysis the interactions between them.

Rotational levels

In the diatomic case we only had a single moment of inertia $I = \mu R_e^2$, because we were considering a simple rigid body. In the polyatomic case, instead, all the three moments of inertia in the system of principal axes (which we choose as molecule-fixed system) are in general non-vanishing; let us call $I_a$, $I_b$ and $I_c$ the moments along the three directions $\xi$, $\eta$ and $\zeta$ in that coordinate system.

If the molecule has a symmetry axis with order higher than two, the problem is simpler because the two moments of inertia with respect to directions perpendicular to that axis are equal ($I_a = I_b \neq I_c$) and we speak of a symmetric top molecule: this holds for example for the $NH_3$ molecule, which possesses an axis of order 3, but not for $H_2O$ which is symmetric only for a $\pi$ rotation. We may rewrite the hamiltonian of the system as a function of the projections of the angular momentum on the three principal axes: it can be proved that the three operators $J_\xi$, $J_\eta$ and $J_\zeta$ obey to the canonical commutation rules for angular momenta, apart from an anomalous sign$^5$, and have therefore the same eigenvalues of the components of angular momentum in the fixed system. So, for the symmetric top we have:

$$H_{rot} = \frac{\hbar^2}{2} \left( \frac{J_\xi^2}{I_a} + \frac{J_\eta^2}{I_b} + \frac{J_\zeta^2}{I_c} \right) = \frac{\hbar^2}{2I_a} J^2 + \frac{\hbar^2}{2} J_\zeta^2 \left( \frac{1}{I_c} - \frac{1}{I_a} \right)$$  (1.15)

At this point it is easy to find the rotational energies, because we can take into consideration simultaneous eigenstates of $J^2$ and of $J_\zeta$: If $J(J + 1)\hbar^2$ are the eigenvalues of the squared

$^5$The following relation holds: $[J_\alpha, J_\beta] = -i\epsilon_{\alpha\beta\gamma} J_\gamma$, (see [1]).
1.2. SOME RESULTS ABOUT POLYATOMIC MOLECULES

module of angular momentum and $K\hbar$ those of the projection on $\zeta$, we find that the rotational energies are:

\[
E_{JK} = \frac{\hbar^2}{2I_a} J(J+1) + \frac{\hbar^2}{2} K^2 \left( \frac{1}{I_c} - \frac{1}{I_a} \right) \tag{1.16}
\]

So the levels with the same $J$ that were first $(2J+1)$-fold degenerate are now splitted in energy depending on the value of $K$ and only a residual degeneracy remains for $K \neq 0$ ($E_{JK} = E_{J-K}$).

In the asymmetric top case there is no general analytic solution, because the hamiltonian is function of all three components of angular momentum, which do not commute with each other: the structure of levels in this case is particularly complicated and for this reason the infrared spectrum of asymmetric tops, like water vapour, is very rich.

Vibrational levels

Regarding vibrational levels, even if we are limiting our discussion to the harmonic problem, the complication in the polyatomic case is given by the fact that, in the general case, we have $3N - 6$ degrees of freedom ($3N - 5$ for linear molecules), where $N$ is the total number of nuclei: we have $3N$ variables $\rho_i$ that measure the displacement of each nucleus with respect to its equilibrium position, to which we shall subtract three degrees of freedom regarding the motion of the center of mass and other three for the global rotation of the molecule (two in the linear case), which do not represent vibrational modes. At this point let us look for the normal modes of the system and the corresponding characteristic frequencies: in order to do that it is sufficient to reason in the classical way and then quantize the energies of each oscillator.

The kinetic energy of the system is $T = 1/2 \sum_i M_i \dot{\rho}_i^2$; normalizing the coordinates so that $\rho'_i = \sqrt{M_i} \rho_i$ we obtain an even simpler form for $T = 1/2 \sum_i \dot{\rho}'_i^2$. If we expand the potential till the second order in $\rho'_i$, the first order vanishes because it is referred to the equilibrium position and we can write $V = 1/2 \sum_{ij} b_{ij} \rho'_i \rho'_j$, with $b_{ij} = \left. \frac{\partial^2 V}{\partial \rho'_i \partial \rho'_j} \right|_0$. Therefore, the equations of motion are: $\ddot{\rho}'_i + \sum_j b_{ij} \rho'_j = 0$. The frequencies of the normal modes and their configurations follow from the search of eigenvalues and eigenvectors of the matrix $\hat{B}$ of the coefficients $b_{ij}$:

\[
\sum_j b_{ij} A_j - (\nu/2\pi)^2 A_i = 0 \tag{1.17}
\]

Each normal mode is treated as if it was a one-dimensional oscillator and has therefore the same energy spectrum; the total energy of the system is then:

\[
E_{\{v_\alpha\}} = \sum_\alpha \left( v_\alpha + \frac{f_\alpha}{2} \right) \hbar v_\alpha \tag{1.18}
\]

Where the $v_\alpha$ are the vibrational quantum numbers of the oscillator corresponding to the frequency $v_\alpha$ and with degeneracy $f_\alpha$ in its fundamental state. The degeneracies are linked to the symmetry properties of the molecule: a molecule that does not possess axes of symmetry with order higher than two has no degeneracy of vibrational levels.

Interaction between rotational and vibrational motions

With a separated treatment of the vibrational and rotational motions we certainly make an error, because the oscillations with respect to equilibrium positions will be perturbed in a rotating system, being subject to the quantum analogous of the Coriolis force. The interaction between the two motions is even more evident when the considered vibrational level possesses
a non-vanishing mean value of the angular momentum. A clear example of this can be seen in the degenerate transverse mode of a triatomic linear molecule, like $CO_2$: classically speaking, if the motion along the two directions perpendicular to molecular axis have a relative phase of $\pi/2$, we have that the three nuclei make a rotational motion about the symmetry axis $\zeta$, then with a non-vanishing angular momentum about it.

Only degenerate vibrational levels can have a non-vanishing mean value of angular momentum. If we in fact consider a non-degenerate level and apply the operator of time inversion, we find that the energy of the state remains unchanged and then the state itself (being the only one with that energy), whereas the angular momentum changes sign: it follows that the mean value of the angular momentum on our state has to vanish in order to remain unchanged after this operation; the same conclusion is not valid for a degenerate level, because applying the operator of time inversion we will not in general find the same state. For asymmetric top molecules, as they only have non-degenerate vibrational levels, we will not need - at least at the lowest order - to consider this correction, whereas the rotational hamiltonian for symmetric top molecules has to be modified to include the vibrational angular momentum too:

$$H_{\text{rot}} = \frac{\hbar^2}{2I_a} (J - J^{\text{vb}})^2 + \frac{\hbar^2}{2} (J_\zeta - J^{\text{vb}}_\zeta)^2 \left( \frac{1}{I_c} - \frac{1}{I_a} \right)$$

(1.19)

Where $J^{\text{vb}}$ is the vibrational angular momentum. In this way the degeneracy of the vibrational states is partly removed, and they are now splitted in energy depending on the mean value of $J^{\text{vb}}$ on them.
Chapter 2

Spectra and line shapes

In Chapter 1 we studied the roto-vibrational energy levels of molecules, focusing on the simplest diatomic case and then having a quick look at polyatomic molecules. The purpose of that study is to allow, at least in a qualitative way, understanding the molecular spectra in the infrared region. At this point then it only remains to understand, starting from the quantum theory of time-dependent perturbations, which transitions between the roto-vibrational levels are allowed and to derive an expression for the transition probabilities, on which will depend the intensity of spectral lines. In the second part of the chapter we will, instead, analyze the broadening of lines due to different effects, which is essential in order to move from the ideal problem of the single absorber/emitter to the real situation that we will find in the atmosphere.

2.1 Transition probabilities and selection rules

To reach most of the results we need\(^1\), with regards to the problem of the interaction between molecules and electromagnetic field, a semiclassical approach is sufficient. We mean here that we need a quantum-mechanical approach only for the description of the molecular system, studying its interaction with a classical radiation field. Let us briefly sum up the problem and its solution with the method of time-dependent perturbations, before considering its application in order to derive the selection rules.

Interaction of light with molecules: semiclassical approach

Let us consider a classical electromagnetic field, described by the vector potential \( \mathbf{A} \) and for which the scalar potential \( \Phi \) is identically zero (the electric and magnetic fields are obtained respectively from \( \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \) and \( \mathbf{B} = \nabla \times \mathbf{A} \)). The hamiltonian for a set of particles with mass \( m_i \) and charge \( \varepsilon_i \) interacting with such electromagnetic field is obtained replacing the momenta \( p_i \) with the new conjugate momenta \( \mathbf{p}_i - \frac{\varepsilon_i}{c} \mathbf{A} \). Besides, as \( \Phi = 0 \), from the orthogonality of \( \mathbf{E} \) and \( \mathbf{k} \) follows that \( \nabla \cdot \mathbf{A} = 0 \); so we obtain:

\[
H = H_0 - \sum_i \frac{\varepsilon_i}{m_i c} \mathbf{p}_i \cdot \mathbf{A}(\mathbf{q}_i, t) + \sum_i \frac{\varepsilon_i^2}{2m_i c^2} \mathbf{A}^2(\mathbf{q}_i, t) = H_0 + H_1(t) + H_2(t) \tag{2.1}
\]

In the above equation \( H_0 \) is the unperturbed hamiltonian; we then have two perturbative terms, one of first and the other of second order in the intensity of the electromagnetic field, both explicitly dependent on time. What we want to calculate here is the first order transition

\(^1\)But not all of them, as we will see further on.
probability between a state $|m\rangle$ and a state $|n\rangle$, per unit time; we will neglect, in a first analysis, the second order term $H_2(t)$. Let us imagine to find the system at time $t_0$ in the eigenstate $|m\rangle$ of the unperturbed hamiltonian and to "turn on" the interaction at this instant; let us move to the interaction representation, making the operators evolve with the unperturbed hamiltonian and the states with the perturbation $H_1$. In this representation the temporal dependence of the operator $H_1$ can be written as:

$$\dot{H}_1(t) = U_0^\dagger (t, t_0) H_1(t) U_0(t, t_0) \quad \text{where} \quad i\hbar \frac{dU_0(t, t_0)}{dt} = H_0 U_0(t, t_0) \quad (2.2)$$

Therefore, the new time evolution operator for the states is $\tilde{U}(t, t_0) = e^{-\frac{i}{\hbar} \int_{t_0}^{t} \dot{H}_1(t') dt'}$. The transition probability between $|m\rangle$ and $|n\rangle$ in the time interval $(t - t_0)$ is given by:

$$P_{m\rightarrow n}(t) = \left| \langle n | \tilde{U}(t, t_0) | m \rangle \right|^2 \approx \left| \langle n | \left( 1 - \frac{i}{\hbar} \int_{t_0}^{t} \dot{H}_1(t') dt' \right) | m \rangle \right|^2 \quad (2.3)$$

In the second passage we approximated the exponential keeping only the first order term in the perturbative expansion: this will be justified if the transition probability between the two states results to be far smaller than unity, whereas if the contrary holds the whole perturbative approach loses its validity. If we now focus on the transition between two different eigenstates of the unperturbed hamiltonian (so that $\langle m | n \rangle = 0$) and we expand the expression of which we are calculating the expectation value, we obtain:

$$P_{m\rightarrow n}(t) = \frac{1}{\mathcal{F}_1^2} \left| \int_{t_0}^{t} \langle n | H_1(t') | m \rangle e^{i(En - Em) t'} dt' \right|^2 \quad (2.4)$$

Since we are here interested in transition excited by radiation, let us consider a plane wave that hits our quantum system and focus on a single Fourier component with frequency $\nu$, amplitude $A$, wave vector $k$ and polarization $e$, whose vector potential is given by:

$$A(x, t) = A/2 \left[ e^{i(kx - 2\pi \nu t)} + e^{-i(kx - 2\pi \nu t)} \right]$$

It is useful here to link the amplitude $A$ of the wave to its intensity, mean value over a period of the Poynting vector: $I(\nu) = \langle \dot{A}^2 \rangle / 4\pi c = \pi A^2 \nu^2 / 2c$. Substituting the expression of $H_1$ in eq. (2.1) in $P_{m\rightarrow n}(t)$, after integration, we obtain:

$$P_{m\rightarrow n}(\nu, \Delta t) = \sum_i \mathcal{F}_i^2 \Delta t^2 \frac{\sin^2 \left[ \pi (\nu - \nu_{nm}) \Delta t \right]}{[\pi (\nu - \nu_{nm}) \Delta t]^2} + \sum_i \mathcal{G}_i^2 \Delta t^2 \frac{\sin^2 \left[ \pi (\nu + \nu_{nm}) \Delta t \right]}{[\pi (\nu + \nu_{nm}) \Delta t]^2} \quad (2.5)$$

where

$$\nu_{nm} = \frac{(E_n - E_m)}{\hbar}, \quad \mathcal{F}_i = \frac{\varepsilon_i A}{2m_i c \hbar} \langle n | (p_i \cdot e) e^{i k \cdot q} | m \rangle \quad \text{and} \quad \mathcal{G}_i (m \rightarrow n) = \mathcal{F}_i^*(n \rightarrow m)$$

We see that the transition probability is composed by two terms: the first, significantly different from zero only for $\nu \sim \nu_{nm}$, represents an absorption process because the initial state $|m\rangle$ energy is lower than that of the final state $|n\rangle$; the second term, instead, is non-vanishing only in a small region around $-\nu_{nm}$ and represents the induced emission of a photon; the double product of the two (the squared module acted on the sum of the terms) has been neglected because they are never simultaneously non-vanishing. At this point we only have to derive the expression for the transition probability per unit time $W_{m\rightarrow n}$. Before going on, it is worth observing that this way of dealing with the problem, which assumes a classical electromagnetic
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field, has a particularly critical point. In fact, it is not easy to understand which is the physical sense of \( \Delta t = t - t_0 \); this is the time for which the perturbation is present and should correspond to the time interval that takes a light packet to reach and go beyond the molecule, but in this way it keeps being ill-defined. In an entirely quantum treatment, in which the electromagnetic field is quantized too, the perturbative calculation makes sense only between \( t = -\infty \) and \( t = +\infty \), because only in this limit it is possible to define the free, non interacting fields. In our case as well, then, the only sense we can give to the expression obtained above is in the limit \( \Delta t \to \infty \) and integrating over all frequencies we obtain a total transition probability per unit time:

\[
W_{m \to n} = \int d\nu \lim_{\Delta t \to \infty} \frac{P_{m \to n}(\nu, \Delta t)}{\Delta t}
\]

(2.6)

Now, the function \( x^{\sin^2|x|} \), if seen as a function of \( \alpha \), has its principal peak with value \( x \) at \( \alpha = 0 \) and the first zero at \( \alpha = \pi/x \), whereas its integral in \( \alpha \) from \(-\infty\) to \( \infty \) always gives \( \pi \), for each value of \( x \). In the limit \( x \to \infty \) the whole function is compressed close to zero, where it assumes a value that tends to infinity, and is then equivalent to a Dirac's distribution \( \delta(\alpha) \) (actually \( \pi \delta(\alpha) \) because its integral over the whole \( \alpha \) axis gives \( \pi \) instead of 1). In our case \( x = \pi \Delta t \), \( \alpha = \nu \pm \nu_{nm} \) and in the limit we will obtain, from the first term in eq. 2.5, a \( \delta(\nu - \nu_{nm}) \), from the second a \( \delta(\nu + \nu_{nm}) \). Now applying the integration in \( d\nu \) and writing the explicit expression for \( A \) in function of \( I(\nu) \), for the two terms of 2.5 we get:

\[
\text{Absorption (} E_n > E_m \text{)} \quad W_{m \to n} = \frac{I(\nu_{nm})}{2\pi\epsilon^2\nu_{nm}^2} \left| \langle m | \sum_i \frac{\varepsilon_i}{m_i} (p_i \cdot e) e^{ikq_i} | m \rangle \right|^2
\]

(2.7)

\[
\text{Ind. emission (} E_n < E_m \text{)} \quad W_{m \to n'} = \frac{I(\nu_{mn'})}{2\pi\epsilon^2\nu_{mn'}^2} \left| \langle m' | \sum_i \frac{\varepsilon_i}{m_i} (p_i \cdot e) e^{ikq_i} | m' \rangle \right|^2
\]

Absorption and induced emission are perfectly equivalent, simply one refers to the case in which the initial state \( |m\rangle \) energy is lower than that of the final state \( |n\rangle \), the other to the opposite case in which the final state \( |n'\rangle \) has the lowest energy. For the sake of clarity and future convenience, let us then consider two states \( |\alpha\rangle \) and \( |\beta\rangle \) such that \( E_\alpha < E_\beta \) and focus on the transitions from \( |\alpha\rangle \) to \( |\beta\rangle \) and vice versa. If the final state of the transition is \( g \)-fold degenerate, we will be interested in knowing the total probability of ending in any of the degenerate states at the final energy, indistinguishable from the energetic point of view: in order to do this it is sufficient to sum on all the final degenerate sub-states, reason for which we make the factor \( g \) explicit and average the matrix element among all the sub-states (the average is indicated by the braces). It is then convenient to define the transition probabilities \( B_{\alpha \to \beta} \) per unit intensity, so that \( W_{\alpha \to \beta} = B_{\alpha \to \beta} I(\nu_{\alpha\beta}) \). Making the last modifications we obtain:

\[
\text{Absorption} \quad B_{\alpha \to \beta} = \frac{g_\beta}{2\pi\epsilon^2\nu_{\alpha\beta}^2} \left\{ \left| \langle \beta | \sum_i \frac{\varepsilon_i}{m_i} (p_i \cdot e) e^{ikq_i} | \alpha \rangle \right|^2 \right\}_{|\beta\rangle}
\]

(2.8)

\[
\text{Ind. emission} \quad B_{\beta \to \alpha} = \frac{g_\alpha}{2\pi\epsilon^2\nu_{\alpha\beta}^2} \left\{ \left| \langle \beta | \sum_i \frac{\varepsilon_i}{m_i} (p_i \cdot e) e^{ikq_i} | \alpha \rangle \right|^2 \right\}_{|\alpha\rangle}
\]

These are known as the Einstein coefficients for absorption and induced emission.
**Spontaneous emission**

One of the limits of our semi-classical treatment is clear when we try to calculate the analogous coefficient for spontaneous emission of a photon, with the corresponding spontaneous decay from \( |\beta \rangle \) to \( |\alpha \rangle \): without an external magnetic field, in fact, the Hamiltonian of our system remains unperturbed and its eigenstates naturally evolve into themselves. No decay is possible. Here appears the necessity of a treatment in which the electromagnetic field is quantized too, considering the complete system Hamiltonian, which includes the matter and the radiation part, as well as their interaction even in the absence of photons. In this new way of seeing the problem, the eigenstates of what we called above the unperturbed Hamiltonian are no more eigenstates of the total one and can evolve: the spontaneous emission corresponds to the transition between the tensor product of the initial state \( |\beta \rangle \) with the vacuum state of the electromagnetic field, which we may indicate as \( |\beta \rangle \pi_{\nu_\alpha} = 0 \), and a final state with our molecule in state \( |\alpha \rangle \) and the field in the one photon state, \( |\alpha \rangle \pi_{\nu_\alpha} = 1 \).

Without going more in depth of the full quantum approach, we still can come to the coefficient \( A_{\beta \rightarrow \alpha} \) of spontaneous emission, with the aid of an elegant statistical approach first proposed by Einstein. Let us consider the transitions between the two states \( |\alpha \rangle \) and \( |\beta \rangle \) for a gas at thermal equilibrium with radiation at temperature \( T \); we can then apply the principle of detailed balance and write:

\[
\frac{n_\beta}{n_\alpha} \left[ B_{\beta \rightarrow \alpha} J(\nu_{\nu_\beta}) + A_{\beta \rightarrow \alpha} \right] = n_\alpha B_{\alpha \rightarrow \beta} J(\nu_{\nu_\beta}) 
\]

Since we are at equilibrium, we have for the populations of the two levels and the radiation (see eq. 3.6):

\[
\frac{n_\beta}{n_\alpha} = \frac{g_\beta}{g_\alpha} e^{-\hbar \nu_{\nu_\beta}/kT}, \quad J(\nu) = \frac{2\hbar}{e^2} \frac{\nu^3}{e^{\hbar \nu/kT} - 1}
\]

From this we get that \( A_{\beta \rightarrow \alpha} = (2h\nu^3/e^2)B_{\beta \rightarrow \alpha} \) and then, making it explicit:

\[
Spontaneous \ emission \quad A_{\beta \rightarrow \alpha} = \frac{2g_\alpha \nu_{\beta}}{h \nu_0^3} \left\{ \left( \beta | \sum_i \frac{\xi_i}{m_i} (p_i \cdot e) e^{ik \cdot q_i} | \alpha \right) \right\}^2 \quad (2.10)
\]

We might object that, since we obtained this expression setting equilibrium conditions, it should not be always valid, but this is a false argument: the coefficients \( B_{\alpha \rightarrow \beta}, B_{\beta \rightarrow \alpha} \) and \( A_{\beta \rightarrow \alpha} \) are characteristic of the single molecule in its interaction with light and thus cannot depend on the statistical properties of the whole particle set; in other words, a single particle does not know what other particles are doing, and so the relation between the coefficients we got above always holds.

**Dipole approximation**

So we now have an expression for all the three Einstein coefficients but, written in this form, it is difficult to say something more about the transition considered. Let us make an approximation, known as the electric dipole approximation, which simplifies the problem and allows us to infer some deductions on the coefficients - called the selection rules - without calculating them. The approximation consists in assuming that the radiation wavelength is far larger than the dimensions of our emitter/absorber, so as to consider the field spatially uniform in the region of interest; practically, this approximation consists in taking only the zero-th order term of the expansion \( e^{ik \cdot q_i} = 1 + ik \cdot q_i + \ldots \). In the case of our interest, we see how this condition is easily satisfied: the molecular dimensions (for not too complex molecules) lie largely below 1 nm, so much smaller than the infrared wavelength (\( \lambda > 1 \mu m \)). At this point we can use the
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commutation relations of \( p_i \), \( e \), \( q_i \) in order to further simplify the matrix element and write it in a more meaningful form.

Since \( p_i = (im_i/\hbar) [p_i^2/2m_i, q_i] = (im_i/\hbar) [H_0, q_i] \), in the dipole approximation we have that:

\[
\langle \beta | \sum_i \frac{\varepsilon_i}{m_i} (p_i \cdot e) | \alpha \rangle = \frac{i}{\hbar} \langle \beta | \sum_i \varepsilon_i [H_0, q_i] \cdot e | \alpha \rangle = \frac{i}{\hbar} (E_\beta - E_\alpha) \langle \beta | D \cdot e | \alpha \rangle
\]  

(2.11)

Where \( D \equiv \sum_i \varepsilon_i q_i \) is the operator corresponding to the total dipole moment of the molecule. For the sake of convenience, we rewrite the expressions obtained above for the absorption and emission coefficients in the dipole approximation:

\[
\text{Absorption} \quad B_{\alpha \rightarrow \beta} = \frac{2\pi g_\beta}{\hbar c} \left\{ \langle \beta | D | \alpha \rangle \cdot e \right\}^2_{(\beta)}
\]

\[
\text{Induced emission} \quad B_{\beta \rightarrow \alpha} = \frac{2\pi g_\alpha}{\hbar c} \left\{ \langle \beta | D | \alpha \rangle \cdot e \right\}^2_{(\alpha)}
\]  

(2.12)

\[
\text{Spontaneous emission} \quad A_{\beta \rightarrow \alpha} = \frac{8\pi^2 g_\alpha \nu_\alpha^2}{\hbar c^3} \left\{ \langle \beta | D | \alpha \rangle \cdot e \right\}^2_{(\alpha)}
\]

At higher order, that is necessary for example if the dipole coefficient vanishes, we will have to take into consideration the term \( k \cdot q_i \) in the expansion of the exponential; the procedure in this case is more complicated, but we still are able to write the resulting expression as a function of the coordinates only: at the second order we then have the contributions of magnetic dipole and electric quadrupole, and so on with the subsequent approximations.

Selection rules for dipole approximation

Taking eq. (2.12) into consideration, we can study the dipole matrix element \( \langle \beta | D | \alpha \rangle \) for each set of molecular quantum numbers: if, for a particular set, the matrix element cannot be different from zero, due to symmetry reasons or other general arguments, we speak of a forbidden transition; we regard as allowed transition in the opposite case where we do not have such arguments and the matrix element may not vanish (although the conditions we are going to find are only necessary and not sufficient). Since we are working at the lowest order, the fact that one transition is forbidden does not mean at all that such transition will never happen, but only that the first order coefficient is zero and the probability for it to happen is small\(^2\).

Now, as we are interested in the infrared region of the spectrum, let us limit our discussion to the molecular rotational and vibrational transitions alone, ignoring the electronic levels. The dipole moment is given by \( D = -e \sum_i R_i + e \sum_i Z_i R_i \) and the following relation with the dipole moment referred to the molecule-fixed system holds: \( D = \mathcal{R}^{-1}(\theta, \varphi, \chi) d \), where \( \mathcal{R}^{-1} \) is the inverse of the rotation matrix that moves the system \( (x, y, z) \) in \( (\xi, \eta, \zeta) \). Let us then write the matrix element of \( D \) between two levels differing only for the rotational and vibrational part \( |\alpha J' \nu'\rangle \) and \( |\alpha J \nu\rangle \), where \( \alpha \) indicates the set of electronic quantum numbers:

\[
\langle \alpha J' \nu' | D | \alpha J \nu \rangle = \langle \alpha J' \nu' | \mathcal{R}^{-1}(\theta, \varphi, \chi) d | \alpha J \nu \rangle = \langle J' | \mathcal{R}^{-1}(\theta, \varphi, \chi) J \rangle \langle \nu' | d | \nu \rangle
\]

(2.13)

In the last step \( \overline{d} \) is the average of the dipole moment \( d \) on the electronic state \( |\alpha \rangle \) and we can now factorize the matrix element because only the rotational state depends on the angular coordinates. Let us first analyze the factor that depends on the vibrational state \( \langle \nu' | \overline{d} | \nu \rangle \). The average value of \( d \) on the electronic state will depend in some way on the

\(^2\)For example, the so-called forbidden lines of elements like atomic oxigen are fundamental in stellar atmospheres and far from non existing!
nuclear configuration and we may expand \( d \) in a Taylor series with respect to the coordinates \( \xi_\kappa \) of the nuclear oscillations normal modes.

\[
d = d_0 + \sum_\kappa d_1^{(\kappa)} \xi_\kappa + \frac{1}{2} \sum_{\kappa,\ell} d_2^{(\kappa,\ell)} \xi_\kappa \xi_\ell + \ldots
\]

(2.14)

Where \( d_0 \) is the permanent dipole moment of the molecule. At least in the simplest cases, expanding only till the first order seems to be quite a good approximation: if we consider a diatomic molecule with \( d_0 \neq 0 \) and raise the separation between the two nuclei (assuming that this operation does not modify the electronic state), the value of \( d \) will depend linearly on the displacement of the nuclei with respect to the equilibrium position. We hypothesize that this fact holds in general and we then stop to the first order of the expansion 2.14. At this point we easily obtain a selection rule for the vibrational states, considering for simplicity the harmonic approximation; for the one-dimensional harmonic oscillator \( \xi = -i \sqrt{\frac{\hbar}{4 \pi m \nu}} (a^\dagger - a) \), where \( a^\dagger \) and \( a \) are the creation and destruction operators for the oscillator, and we have, for a single normal mode:

\[
\langle v' | d_0 + d_1 \xi | v \rangle = d_0 \langle v' | v \rangle - i \sqrt{\frac{\hbar}{4 \pi m \nu}} d_1 \left( \langle v' | a^\dagger | v \rangle - \langle v' | a | v \rangle \right)
\]

(2.15)

We then obtain:

\[
\text{Selection rule on } v \quad \rightarrow \quad \Delta v = 0, \pm 1
\]

(2.16)

We may observe that the first condition (\( \Delta v = 0 \)), corresponding to a pure rotational transition, can be realized only in the case in which the molecule possesses a permanent dipole moment \( d_0 \). This means that, for molecules which, for various reasons, are prevented from having such a permanent dipole, the pure rotational transitions are not allowed: it is the case of those linear molecules that have a further reflection symmetry with respect to a plane perpendicular to the molecular axis, like diatomic omopolar molecules (\( O_2 \), \( N_2 \)) or triatomic linear molecules, for example \( CO_2 \). Even in the case in which the permanent dipole moment of the molecule vanishes, we still can have a rotational transition (coupled to a vibrational one) if the first order variation of the dipole moment with respect to the normal coordinates does not vanish, (that is, \( d_1 \neq 0 \)). In the case of homopolar diatomic molecules, as the only vibrational mode is perfectly symmetric, not only the first, but all terms of the expansion of \( d \) are zero (there can be no privileged direction for the vectors \( d_\kappa \)); that is why those molecules do not have a roto-vibrational spectra (at least at the lowest order, that is in the dipole approximation) and, even though they dominate the Earth’s atmospheric composition, do not absorb nor emit radiation in the infrared region. For the same reason, in the \( CO_2 \) case, there will not be any transition involving the symmetric longitudinal oscillation mode, yet there will with regards to the asymmetric mode and the transversal ones.

The selection rule 2.16 holds in the harmonic case and stopping at the first order the dipole moment expansion, therefore, differently from the rule on the angular momentum we are going to see, it is not exact: considering anharmonic effects or successive orders of the expansion, transition between levels with \( \Delta v = 2, 3, \ldots \) are still possible even in the dipole approximation, although with very small probabilities.

Let us now go back to the 2.13 and take this time the first factor under consideration, \( \langle J' | R^{-1} (\theta, \varphi, \chi) | J \rangle \). To get the selection rules on \( J \) we turn to the Wigner-Eckart theorem\(^3\),

\[\text{Theorem states that the matrix element of a spherical tensor of rank } k \text{ and magnetic number } q \text{ between two states with different angular momentum } (J, m) \text{ and } (J', m') \text{ is proportional to the Clebsch-Gordan coefficient we would have if we summed the two angular momenta } k \text{ and } J \text{ to obtain } J'. \text{ That is, the following holds: } \langle a' J' m' | T_q^{(k)} | a J m \rangle \propto \langle J k m a J' m' \rangle. \text{ See } [10] \text{ for the complete statement and a proof to the theorem.}\]
realizing that the rotation matrix $\hat{R}^{-1}$ corresponds to a spherical tensor\(^4\) of rank 1 and that the angular momentum can then vary at most by unity:

$$\text{Selection rule on } J \quad \rightarrow \Delta J = 0, \pm 1$$ (2.17)

This rule is general and exact in the dipole approximation, as no further assumption had to be used in order to get it. It is possible to refine this rule in the particular case of diatomic molecules: if we apply the space inversion operator $\hat{I}$ to a diatomic molecule, this is equivalent in the molecule-fixed system to a reflection with respect to a plane containing the symmetry axis and its effect on the electronic state is to leave obviously unchanged the state energy, while inverting the sign of the projection of the electronic angular momentum on the axis (then changing $\Lambda$ in $-\Lambda$). If we are in a state $|\alpha\rangle = |n\Lambda = 0\rangle$, that is a $\Sigma$ state, after the spatial inversion we still find the system in the same state, unless a factor $\pm 1$. With regards to the rotational state, the effect of the spatial inversion is to bring in a factor $(-1)^J$, while the vibrational state remains unchanged, depending only on the modulus $R$ of nuclear separation (the space inversion acts only on $\theta$ and $\varphi$). Going back to the matrix element 2.13, and using these last properties of the operator $\hat{I}$:

$$\hat{I} D \hat{I}^\dagger = -D, \quad \hat{I} |\alpha J v\rangle = (-1)^J (\pm 1) |\alpha J v\rangle$$

and then:

$$\langle \alpha J' v' | D | \alpha J v\rangle = \langle \alpha J' v' | \hat{I} \hat{I}^\dagger (\hat{I} D \hat{I}^\dagger) \hat{I} | \alpha J v\rangle = (-1)^{J + J' + 1} \langle \alpha J' v' | D | \alpha J v\rangle$$ (2.18)

Consequently, $J + J' + 1$ has to be even. We have so refined the selection rule on $J$ for diatomic molecules in the $\Sigma$ state (actually for all linear molecules with $\Lambda = 0$):

$$\text{Selection rule on } J \text{ for } \Sigma \text{ states: } \rightarrow \Delta J = \pm 1$$ (2.19)

### 2.2 Vibrational bands

As we saw, every vibrational transition can (or has to, if 2.19 holds) be coupled to a rotational transition. Since all energies depend on $v$ as well as on $J$, for every vibrational transition we have a spectrum formed by different lines depending on the values of $J$ and $J'$. For a transition $v \rightarrow v' = v + 1$ we may distinguish different bands, depending on whether $\Delta J = 0, 1$ or $-1$: the band at the higher energies is the $R$ band, the central one the $Q$ band and the lowest one is the $P$ band. According to the last selection rule we got in the previous section, the Q band will be absent in the great majority of diatomic molecules. Let us write the transition energies we obtain from 1.12:

$$\frac{\Delta E}{\hbar c} = \tilde{v}_e \Delta v - \Delta v(v' + v + 1)x_e \tilde{v}_e + \Delta J(J + J' + 1) \left[ B_e - \frac{\alpha_e}{2} \right] +$$

$$- \frac{D_e}{2} \Delta J(J' + J + 1)^3 - \alpha_e \left[ vJ(J + 1) - v'J'(J' + 1) \right]$$ (2.20)

Neglecting the last two terms, which are minor corrections, the energy difference between two following lines is constant and given by $2B_e$. The existence of the last two terms is yet detectable looking to an experimental spectrum, as they produce some secondary properties of the spectrum: the second-last one is responsible for slowly decreasing the gap between the lines as $J$ grows, whereas the last one causes the separation of the lines in the Q band, which would otherwise not be resolved.

\(^4\)We define as a spherical tensor of rank $k$ an operator that transforms under rotation so as the spherical harmonics $Y_{\ell m}^\ell$ with $\ell = k$. It can be proved that $\hat{R}^{-1}$ transforms like the spherical harmonics with $\ell = 1$ (see [10]).
If we focus on spontaneous emission, the relative intensities of the lines belonging to the same vibrational band will be proportional to the matrix element in eq. (2.12) and to the population of the upper roto-vibrational level in each transition (see Chapter 3). So, at thermal equilibrium, each vibrational band has a characteristic shape, depending on temperature, as we can see in Figures 2.1 and 2.2. In the first one, regarding the CO molecule, we can see only the \( P \) and \( R \) bands, according to the selection rule (2.19); in the other one, which shows a vibrational band of \( CH_3D \), we instead see the closely spaced lines of the \( Q \) band too.

![Figure 2.1: Relative line intensities of the fundamental band of CO at 296 K, due to transition from the first excited to the ground state. Since the diatomic CO molecule is in a \( \Sigma \) state, the \( Q \) band is not present. Data taken from the HITRAN Database [15].](image)

**2.3 Line shapes**

In section 2.1 above, when we calculated the absorption and emission coefficients we integrated over the whole time axis, in the non-interacting fields limit. This assumption determines that the frequency dependence of the absorption coefficient is a delta function. This means that, without other effects (like the ones we are going to study below), the spectral line is infinitely sharp, corresponding to an exact energy gap. Actually, this is not what we find in nature and even for a perfectly isolated emitter the line is never properly a line, but shows a spectral width and a characteristic shape. The reason for this contradiction in our theory is due to the fact that our semiclassical approach is not really adequate to describe what happens. This was already apparent when we wanted to calculate the spontaneous absorption coefficient. However, starting from that point, we use the Griem [12] approach to overcome the apparent paradox and make the existence of the so called natural broadening of lines quite intuitive.

The natural broadening of lines is however only of theoretical interest (though of great one, as it shows the deepest nature of the light-matter interaction); in a real situation, like the one we will find in planetary atmospheres, natural broadening is completely negligible if compared...
2.3. LINE SHAPES

Figure 2.2: Relative line intensities of a \( \text{CH}_3D \) band at 296 K, due to transition from the the V2 vibrational level to the ground state. Here a strong Q band is visible too. Data taken from the HITRAN Database.

with other effects: as we usually observe a gas composed by many molecules with different velocities in each direction, which besides influence each other through collisions, we will have to consider two further line broadening mechanisms, the doppler broadening and the pressure or Stark broadening.

Natural broadening

Let us imagine that we have a particle in an excited state \( j \) that can spontaneously de-excite to the ground state through emission of a photon, with a probability \( A_{j0} \). For the sake of simplicity we assume that this is the only transition that can take place. Recalling what we said earlier regarding spontaneous emission, the simple fact that our particle may spontaneously de-excite from state \( j \) means that the particle eigenstates are not truly eigenstates of the system hamiltonian; the eigenstates of the system “particle plus electromagnetic field” are instead a linear combination of terms, each one being the tensor product between a particle eigenstate and a field one. In our case, we shall write

\[
    |\Psi(0)\rangle = |j\rangle \otimes |n_{\nu} = 0\rangle
\]

for the initial state of the system, as we have the particle in the excited state \( j \) and no photons, and

\[
    |\Psi(t)\rangle = a(t)|j\rangle|n_{\nu} = 0\rangle + b(t)|0\rangle|n_{\nu} = 1\rangle
\]  

(2.21)

for the evolution of the system state, as we know that at some time we could find it in the ground state with a photon emitted. The coefficients \( a \) and \( b \) are known if we assume that the decay probability of our particle follows an exponential curve, with characteristic constant given by the Einstein coefficient, \( \Gamma = A_{j0} \), so that:

\[
    |a(t)|^2 = e^{-\Gamma t} \quad \sim \quad a(t) = e^{i\omega_{\nu}t}e^{-\Gamma t/2}
\]  

(2.22)
So the coefficient of time evolution is no more only the characteristic exponential of stationary states (here $\omega_0 = E_j/\hbar$), but there is an additional factor due to the possibility of decay. By computing the Fourier transform in time of this coefficient and taking its squared module, we obtain the distribution of possible energy values for our level, which will not be a delta function centered at $\omega_0$, but:

$$f(\omega) = 1/\sqrt{2\pi} \int_0^\infty e^{-i\omega t} e^{i\omega_0 t} e^{-\Gamma t/2} dt = \frac{1/\sqrt{2\pi}}{i(\omega - \omega_0) + \Gamma/2}$$

(2.23)

and then, taking the module and normalizing the distribution to unity:

$$P(\omega) = f^*(\omega) f(\omega) = \frac{\Gamma/2\pi}{(\omega - \omega_0)^2 + (\Gamma/2)^2}$$

(2.24)

What we get is then a Lorentzian distribution, centered at the energy $E_j$ - eigenvalue of the ideal system composed by the particle alone - and with a width given by the spontaneous emission coefficient $A_{j0}$. The emitted photon will then follow the same distribution, thus making the spectral line no more a line, but a feature with a typical Lorentzian shape.

In case of transition between two excited level $j$ and $\ell$, each with many possible spontaneous transitions, it can be proved that the resulting natural line shape will still be a Lorentzian profile, its width given by the sum of all coefficients of all possible transitions from the two levels, that is $\Gamma = \sum_{i<j} A_{ji} + \sum_{i<\ell} A_{\ell i}$.

Doppler broadening

The doppler broadening is simply due to the fact that we usually look at particles which are in motion with respect to the observer and the characteristic frequency they emit or absorb will be detected as a slightly different one. So the photon emitted by a particle in motion toward us will be detected at a higher frequency, whereas a running away particle will emit and absorb at lower frequencies according to us. Of course, a doppler effect may be due to very different motions: we shall distinguish between macroscopic motions linked to atmospheric dynamics or to motion of the whole planet\textsuperscript{5} and microscopic ones, given by the thermal motion of particles. In a usual situation the last one will dominate, given that the typical thermal speed of air particles is of the order of hundreds of meters per second for temperatures above 100 K, whereas air masses never reach such velocities. So let us ignore other contribution to doppler effect and see which is the line shape produced by a thermal population of particles at temperature $T$, absorbing radiation at a frequency $\nu$ (according to the observer). A particle in motion with velocity $v$ in the direction of the line of sight (towards the observer) will see the incoming radiation at a frequency $\nu' = \nu(1 - v/c)$, keeping only the lowest order in the ratio $v/c$. The effective line shape will be given by the convolution of the line profile in the particle reference system, centered at frequency $\nu'$, with the probability that the particle sees the radiation at $\nu'$, instead of $\nu$. The latter is nothing else than a simple gaussian distribution: we are interested in the distribution of velocities only in one direction, the one toward us, along the line of sight. Then we have:

$$\varphi(\nu) = \int_\psi(v) P(v) dv \quad \text{where} \quad P(v) = \frac{e^{-(v/v_h)^2}}{v_h \sqrt{\pi}}$$

(2.25)

\textsuperscript{5}Of course different types of macroscopic motions produce very different features in the absorption spectra: a global motion of a planet toward us will only produce a frequency shift, planetary rotation a shift varying with longitude, whereas local motions linked to winds and turbulence might produce a broadening of the lines.
2.3. LINE SHAPES

Then, if we assume that the line profile is simply a delta function at some frequency \( \delta(\nu - \nu_0) \), the resulting line shape will be:

\[
\varphi(\nu) = \int_{-\infty}^{\infty} \delta(\nu - \nu_0 + \nu_0 \sqrt{\frac{\nu - \nu_0}{v_\text{th}}}) e^{\frac{-(\nu - \nu_0)^2}{v_\text{th} \sqrt{\pi}}} d\nu \propto e^{-\frac{m c^2 (\Delta \nu - \nu_0)^2}{2 k T}} \tag{2.26}
\]

where we made explicit the temperature dependence. What we obtain in this case is then a gaussian line profile that peaks at the characteristic frequency \( \nu_0 \) and has a width proportional to the square root of the temperature: the higher the temperature, the wider the line profile. With a “profile at rest” different from a delta function, the resulting line shape will of course be different, leaving the gaussian one as the limiting case in which only doppler broadening matters.

Stark broadening

Stark (or pressure) broadening is probably one of the richest topics regarding line shapes. A lot of historical literature focuses on this problem, trying to draw approximate theories or measuring experimentally the parameters needed. The reason for this is easily understood: we speak here of the particular profile acquired by a spectral line when the absorbers/emitters are a set of particles colliding with each other and influencing reciprocally their optical properties. The great difficulty of dealing with particles interacting with the radiation field and at the same time perturbed by other particles becomes even more complicated in the case of molecular infrared emission, as we will briefly explain below. A superficial treatment would not be able to give us an insight into the physical sense of this complicated topic; therefore we find it more useful to only explain here the different approaches towards a complete theory and their critical points, referring the reader to the review by Tsao and Curnutte [13] for a comprehensive reading.

First of all, we can understand something from the two mostly used names for this effect: the name pressure broadening confirms us that it has to do with particle collisions, whereas the reference to Stark explains that the mechanism at work here is the perturbation of particle eigenstates and the shift of the relative energy eigenvalues due to an external electric field. Since the problem is very wide, it is useful (if not necessary) to consider two limiting cases: the electric field responsible for the perturbation might be quasi-static and given by a lot of far away particles, or in the opposite case it might be produced by a single particle passing just close to the one we are considering and so be rapidly varying. The first situation is assumed by the so-called statistical broadening theories which consider the modification of the particle optical properties when it is placed in an external static field (so the time-independent perturbation theory is sufficient here), produced by other particles around it. Weighting each field with the probability for it to be produced, this leads to a typical line shape, which in the case of charged perturbers has a typical dependence given by the product of an exponential and a power law (Holtsmark’s profile, see [12]). This perturbation is yet not so important where the only long-range fields are due to molecular dipole moments.

In the typical situation we will find in planetary atmospheres the opposite case of a single perturber is instead of great importance. The perturber is usually another molecule, rapidly passing close to the molecule under consideration: this situation is known as the impact approximation. It assumes that the typical time of each collision is far smaller than the average time between two of them. With this initial assumption, the hamiltonian of the system is now given by the one of eq. 2.1, with two additional terms given by the hamiltonian of the colliding particle

\[ ^6 \] Actually, for a complete treatment, quantum radiation theory is needed here.
and the relative interaction of the two: the latter may be seen as a time-dependent potential term, if we assume that the particles follow classical paths. Solving the problem with time-dependent perturbation theory, we now have an additional perturbative term: the difficulty here is given by the fact that the radiative term and the collision one simultaneously perturb our system, and the second may induce transitions in our molecule as well. The easiest way to avoid this critical point is to set the adiabatic approximation, which states that the state modification due to the collision varies slowly and in particular does not lead to any transition in our molecule. Although this assumption leads to a qualitatively correct result, it is not completely adequate to treat collisions between molecules, as they show many closely spaced rotational levels and collisional transitions between them are quite frequent. The complete theory, which does not assume the adiabatic approximation, is due to Anderson (see the original article [14] or the review by Tsao and Curnutte [13]) and is the one most suited to treat molecular pressure broadening.

We recall here only the fundamental result of the Stark broadening theory, without justifying it: the predicted line profile in the adiabatic approximation is again a Lorentz function, but contrary to the natural broadening case the line center is now shifted with respect to the original position. The complete Anderson’s theory gives the same result, but the parameters that appear in the expression have now to be calculated considering all rotational states of the emitting molecule (we are now allowing for rotational transitions during the collision). The resulting line shape is:

$$\varphi_{j,j'}(\nu) = C \sum_{m_i,m_f} |\langle j_i,m_i|\mu_z|j_f,m_f \rangle|^2 \frac{nv\alpha_{j,j'}}{(\nu - \nu_0 + nv\beta_{j,j'})^2 + (nv\alpha_{j,j'})^2}$$ (2.27)

Where $|j_i,m_i\rangle$ and $|j_f,m_f\rangle$ represent respectively the initial and final rotational states of the emitting molecule, $\alpha$ and $\beta$ are two parameters depending on the collisions and resulting from a sum over all possible $|jm\rangle$ states of the colliding molecule, $C$ is a normalization constant, $\mu_z$ is the molecular dipole moment in the direction $z$, parallel to the photon polarization, and finally $n$ and $v$ represent the density of the colliders and their mean velocity. As we can see, the total line shape is still a Lorentz profile, but this time the central frequency is shifted from the original position. Line shift and Lorentz half-width are both proportional to $nv$ and, if we take as $v$ the mean thermal speed, we may make explicit their dependence on temperature and pressure, obtaining:

$$\delta_{\text{shift}} \propto \beta P/\sqrt{T} \quad \lambda_{\text{half}} \propto \alpha P/\sqrt{T}$$ (2.28)

So, whereas the doppler broadening only depends on temperature, the pressure broadening depends on pressure too, and the temperature dependence at fixed pressure is inverted (the higher the temperature, the narrower the line, at fixed pressure). Of course this is only the main, explicit dependence, because the two coefficients $\alpha$ and $\beta$ may depend on temperature and pressure too.

The “universal” line shape: the Voigt profile

In the previous section regarding doppler broadening, we calculated the line profile seen by the observer in the case in which the one seen by the particle was given by a delta function, and we obtained a simple gaussian profile. But we now know that the typical line shape “at rest”, far from being a delta function, is instead a Lorentz profile, due to pressure broadening. So the more common line shape should be obtained by the convolution of a gaussian with a Lorentz function, that gives:
2.4. EXPERIMENTAL DATA AND HITRAN DATABASE

\[ \varphi(a, x) = \frac{a}{\pi} \int_{-\infty}^{\infty} e^{-y^2} \frac{e^{-(x-y)^2/a^2}}{(x-y)^2 + a^2} dy \]

where \( a = \frac{\lambda_{\text{half}} c}{4\pi v_0 v_{\text{th}}} \), \( x = \frac{\nu - \nu_0}{\Delta \nu_{\text{th}}} \)

This is known as the Voigt profile. In the above expression, \( \lambda_{\text{half}} \) is the Lorentz half width and \( \Delta \nu_{\text{th}} \) is the mean doppler frequency shift. It is not possible to come to an analytical form of this function, that has then to be calculated numerically. It is yet interesting to look at its limits for small and large \( x \): when \( x \to 0 \) the function goes as \( e^{-x^2} \) and we therefore speak of gaussian core; in the opposite limit the dominant part is given by \( a/x^2 \), that is only the Lorentzian wings matter. In Figure 2.3 we can observe the three types of line profile we encountered till now.

![Figure 2.3: Comparison between Gaussian, Lorentz and Voigt profiles. The Voigt one is obtained for convolution between the other two.](image)

2.4 Experimental data and HITRAN Database

Given all the difficulties we find in calculating the energy levels of molecules, even in the diatomic case, and in the calculation of line intensities and pressure broadening, we easily can imagine that an exclusively theoretical approach in the determination of molecular spectra would be the weak link of a radiative transfer theory based on it. Actually, the purpose of the analysis in this and the previous chapter was to give a physical insight into molecular spectra, and not to quantitatively determine the quantities we will need. Fortunately, there is in fact a huge amount of laboratory studies on the optical properties of gases and different databases contain the experimental data. One of the most used in atmospheric physics is the HITRAN database, which collects data regarding more than two millions lines of different atmospheric gases: for each line there is a string containing information on the frequency of the transition, the gas and the isotope, the line intensity, the levels involved and their degeneracies,
and the characteristic parameters of pressure line broadening. The data are referred to fixed temperature (296 K) and pressure (1 atm), and have to be properly scaled when used for atmospheres in different conditions.

Such a database, created by years of experiments and spectroscopic investigation, is the fundamental basis for each study on atmospheric emission, representing the primary input of any line-by-line radiative transfer code.

Figure 2.4: A typical line of the HITRAN Database: here for a CO line in the fundamental band at 2003.7 cm$^{-1}$; this is the 32nd line of the P band. The other numbers are information about line intensity, pressure broadening and quantities describing the upper and lower states of the transitions.
Chapter 3

Radiative transfer theory

So far we studied the roto-vibrational degrees of freedom of molecules and the interaction of a single molecule with light. Now we apply that knowledge to a situation in which not only one, but many absorbers of different species are present at the same time in a medium through which light is propagating, a problem known as the radiative transfer problem. Let us first have a look to the basic definitions needed to develop the theory of radiative transfer and then find out its fundamental equations. At the end of the chapter we will make some considerations about the physics behind the assumption of LTE (Local Thermodynamic Equilibrium), which will be of primary importance in the continuation of the study.

3.1 The specific intensity and its moments

A fundamental quantity in the theory of radiative transfer is the specific intensity $I_w$, often called radiance, defined as the energy flux through a surface $dA$ carried by photons that are moving in a direction contained in the cone of solid angle $d\Omega$ around the vector $\hat{n}$, per unit time $t$ and wavenumber $w$. In symbols:

$$dE = I_w(x, t, \hat{n}) \cos \theta \; dw \; dt \; d\Omega \; dA$$  \hspace{1cm} (3.1)$$

where $\theta$ is the angle between the vector $\hat{n}$ and the normal to the surface $dA$, and $dE$ is the infinitesimal energy that is flowing through our surface in the time $dt$. We now have defined the specific intensity per unit wavenumber $w = 1/\lambda$, which is most frequently used in atmospheric physics; however it could be defined also as a function of wavelength $\lambda = 1/w$ or frequency $\nu = cw$.

Starting from this point, we define some related quantities which are useful in what follows and are essentially the consecutive moments of the specific intensity with respect to the angle $\theta$. The mean intensity at a point is the zero-th order moment and is given by:

$$J_w(x, t) \equiv 1/4\pi \int I_w(x, t, \hat{n}) d\Omega$$  \hspace{1cm} (3.2)$$

This quantity is related to the energy density of the electromagnetic field by the simple relation $u_w = 4\pi/c \cdot J_w$.

Let us now define the net radiative flux $F_w$, the first order moment of the specific intensity with respect to $\theta$. The radiative flux is a vector quantity such that the net energy that is passing through a surface with normal vector $dS$ is given by $F_w \cdot dS$; now the energy coming from all directions is taken into account, but with different signs, the positive direction being
defined by the surface vector. In symbols:

\[ F_w(x, t) = \int I_w(x, t, \hat{n}) \hat{n} \, d\Omega \]  

(3.3)

We can observe that, as required, \( F_w \cdot dS = \int I_w(x, t, \hat{n}) \cos \theta \, dS \, d\Omega \) is indeed the net energy passing through our surface. Like the mean intensity, which is a scalar quantity, is related to the energy density, so the net flux can be related to a vector quantity characteristic of the electromagnetic field, the momentum density \( g_w = 1/c^2 F_w \).

Another important quantity deserves to be mentioned here, that is the radiation pressure \( \mathbf{P}_{\text{rad}} \). Being the second order moment of the specific intensity, the radiation pressure is a second rank tensor whose component \( \tilde{P}_{ij} \) represents the net flux of the i-th component of the momentum of the electromagnetic field through a surface with normal along the j-th axis; then the actual flux of i-th momentum through an arbitrary surface with normal vector \( d\mathbf{S} \) is given by \( \tilde{P}_{ij} \cdot d\mathbf{S}_j \). The radiation pressure is defined as follows:

\[ \tilde{P}_{ij} = 1/c^2 \int I_w(x, t, \hat{n}) n_i n_j d\Omega \]  

(3.4)

To better understand the physical sense of the quantities we have just defined, it is useful to limit the discussion to a one-dimensional geometry, the plane-parallel one, in which the specific intensity is function only of the vertical coordinate \( z \) and of the angle formed by the direction \( \hat{n} \) with the \( z \) axis (or more commonly of the cosine of that angle, called \( \mu \)). For symmetry reasons, the only non-vanishing component of the flux vector is the one along the \( z \) direction, and the pressure tensor takes a much simpler diagonal form. Here are the expressions for the first three moments of specific intensity in this simplified case (for the sake of clarity we will omit the explicit indication of \( x, t \) and \( w \) in the expressions):

\[ J = 1/2 \int_{-1}^{1} I(\mu) d\mu \]  

\[ \langle F \rangle_z = \int_{-1}^{1} I(\mu) \mu \, d\mu \]  

\[ \tilde{P}_{zz} = 2\pi/c \int_{-1}^{1} I(\mu) \mu^2 d\mu \equiv P^{\text{rad}} \]  

\[ \tilde{P}_{xx} = \tilde{P}_{yy} = \pi/c \int_{-1}^{1} I(\mu)(1 - \mu^2) d\mu = 1/2(u^{\text{rad}} - P^{\text{rad}}) \]  

(3.5)

Where we defined \( P^{\text{rad}} \), the \( zz \) component of the pressure tensor, and \( u^{\text{rad}} \) is the radiation energy density; it is of some interest to note that, in case of isotropic radiation (\( I(\mu) = I \)), we have \( P^{\text{rad}} = 1/3u^{\text{rad}} \) and the pressure tensor becomes a multiple of the identity, allowing to speak of a scalar radiation pressure.

It is worth recalling here the expression for the specific intensity in a particular case, i.e. in thermodynamic equilibrium. In this case, as known from statistical physics, all radiation quantities take a simple form, which moreover is dependent only on temperature: specific intensity, obviously isotropic, is expressed through the so called Planck function, which descends from the distribution function of a boson gas with zero chemical potential. We write it here, per unit wavenumber:

\[ \text{Planck function: } B_w = \frac{2hc^2}{e^{hcw/kT} - 1} \]  

(3.6)
3.2 The equations of radiative transfer

We can now write the fundamental equation of radiative transfer, which tells us how a light packet\(^1\) will evolve, when it propagates in a medium composed by particles that can absorb, emit or scatter photons. We might think that, in order to study the problem of radiative transfer, a treatment in terms of intensity only would not suffice, as we are always dealing with a propagating electromagnetic field, which is a vectorial quantity, and the two polarizations of the field may in general evolve in different ways. Moreover, we may consider that if we had to sum two strictly monochromatic waves with a defined phase relation, we could not just sum their intensities, but should first sum the amplitudes and only then square the result to obtain the effective intensity. At least about the second problem, we do not have to worry: if we had to sum the radiation emitted by, let us say, two molecules, we would of course need a complete treatment in terms of oscillating vector fields, taking into account interference effects; but as we are now dealing with a great number of independent and randomly distributed particles, we are assured that there is no phase coherence between all the photons belonging to the light packet we are considering and so we will not have any problem in summing their intensities instead of the amplitudes\(^2\).

The other problem we mentioned above has, instead, no general simple solution and the quantities we introduced in the previous section would not suffice to deal with it. In the case of polarized light\(^3\) and with the most general scattering function, the two polarization components evolve in different manners and to treat this problem we need a more general formalism that takes explicitly into account polarization. We define and briefly introduce such a formalism in Section 3.4. For now it will suffice to say that thermal absorption and emission do not distinguish between different polarization states (of course a single particle does, but not a statistically relevant ensemble of particles) and so their evolution will not differ. The most general scattering situation, as we said, would be a problem, but if we limit ourselves to single scattering of unpolarized light or to simple scattering functions that do not distinguish between polarization states, a description in terms of intensity will be sufficient. For more comments about this topic we refer to Section 3.4. Now let us go back to our starting point, assuming that the specific intensity \(I_{\omega}(\mathbf{n})\) is the one quantity completely describing the radiation at a point \((x, t)\).

If we know the specific intensity \(I_{\omega}(\mathbf{n})\) at a certain point and we want to find out the specific intensity at another point along the ray path, at an infinitesimal distance \(ds\) in the direction of propagation \(\mathbf{n}\), we have to take into consideration the absorption, emission and scattering of radiation by the material contained in the infinitesimal volume \(dV = dA \, ds\), crossed by the light ray: simply, the difference between the energy per unit time going out the infinitesimal volume (which is the intensity at the new point \(I_{\omega}(x + dsn, t + ds/c, \mathbf{n})\) times the area \(dA\)) and the energy entering it is given by the difference between the energy emitted and absorbed (or deviated in other directions)\(^4\) per unit time in that volume. We can write:

\[
dA \cdot [I_{\omega}(x + dsn, t + ds/c, \mathbf{n}) - I_{\omega}(x, t, \mathbf{n})] = dV \cdot (\text{emission} - \text{extinction})
\]

---

\(^1\)With light packet we mean here that we have enough photons to allow us speaking about them in a statistical way. Doing so, the quantum probabilities defined in Chapter 2 become statistical probabilities.

\(^2\)With the more general formalism we will introduce in Section 3.4, this fact is referred to as the additivity of the Stokes parameters.

\(^3\)We know that natural light, like that emitted from the sun or from an ensemble of molecules in our atmosphere, is not polarized, but reflected or scattered sunlight is: this is to say that the most general problem is of some interest, if we had to deal with multiple scattering or reflection from the surface.

\(^4\)We will speak of extinction referring at the same time to both the processes of absorption and scattering, which are both responsible of decreasing the intensity in the considered direction.
If we rewrite this difference in terms of partial derivatives with respect to space and time and write more explicitly the emission and extinction terms, we obtain the fundamental equation of radiative transfer:

Fundamental equation of radiative transfer

\[
\left( \frac{1}{c} \frac{\partial}{\partial t} + \mathbf{n} \cdot \nabla \right) I_w(x, t, \mathbf{n}) = \varepsilon_w(x, t, \mathbf{n}) - \alpha_w(x, t, \mathbf{n}) I_w(x, t, \mathbf{n})
\]  

(3.7)

The time derivative is necessary only in case of rapidly varying (relativistic) phenomena, but is completely negligible otherwise, for example in what is related with atmospheric physics. We will neglect this term from now on and also ignore the direct temporal dependence of all quantities, so considering a stationary state, as we will not be dealing with atmospheric dynamics. The emission term appearing on the right-hand side of this equation is called emissivity. Dimensionally, this is an intensity emitted per unit length of ray path. The other term corresponds to extinction and is proportional to the incoming radiation. The constant of proportionality \( \alpha_w \) is the extinction coefficient, also called opacity, which is the inverse of a length: this is the characteristic length of extinction of the light packet, that is the mean free path of photons before being deviated or absorbed. Both these coefficients can be divided in two parts, the first being the sum of all processes of real absorption and emission due to the interaction with matter (that is, a photon is effectively destroyed or emitted in the interaction) and the second representing the scattering processes:

\[
\varepsilon_w = \eta_w + \int \sigma_w(n', \mathbf{n}) I_w(n') \, dY' \quad \quad \alpha_w = \chi_w + \int \sigma_w(n, n') \, dY' \quad \quad (3.8)
\]

We see that the scattering parts explicitly depend on radiation, whereas the thermal coefficients \( \eta_w \) and \( \chi_w \) do not; we will find out in Chapter 5 that these coefficients may depend on the intensity as well.

Equation (3.7) can be rewritten in a different form that requires the definition of two quantities of primary importance, the source function \( S_w \) and the optical depth \( \tau_w \). Let us first rewrite the equation, dividing by the absorption coefficient \( \alpha_w \) and substituting the new quantities:

\[
\frac{dI_w(x, n)}{d\tau_w} = I_w(x, n) - S_w(x, n)
\]

where \( S_w = \frac{\varepsilon_w}{\alpha_w} \) and \( \tau_w(x, x') = \int_0^{\|x-x'\|} \alpha_w(x + s \mathbf{n}, \mathbf{n}) \, ds \)

(3.9)

We can see that the source function is simply the ratio between emission and absorption coefficient; its special role in radiative transfer theory is clear if we note that we can obtain a trivial solution of eq. (3.7) if we put \( I_w = S_w \), and the source function is then in a certain sense the characteristic radiance of each point. We will see in section (3.6) the connection of the source function with the concept of thermodynamic equilibrium and the particular form it takes in that situation. With regards to the optical depth, we can note first of all that it is a dimensionless number, being the product of the path made by the light packet and the absorption coefficient of the matter crossed (which, as we said before, has dimensions of the inverse of a length). We could say, the optical depth measurements the light path in unit of the mean free path of photons: a small optical depth between two points \( A \) and \( B \) means that the atmosphere is substantially transparent between \( A \) and \( B \) at those frequencies and we can
clearly see the light emitted at $A$ if we look at it from $B$; if instead $\tau_w(A, B) \gg 1$ almost all the original photons emitted at $A$ will have been absorbed in the path reaching $B$ and the light we will see will have been emitted at other points along the ray path.

Before going on with the study of emission and extinction, let us write down for completeness the first two moments of the equation of radiative transfer with respect to the angle $\theta$, which involve the moments of the specific intensity we mentioned in the first section. We obtain the first moment integrating eq. (3.7) over the solid angle, that gives:

$$\nabla \cdot \mathbf{F}_w(x) = \int [\varepsilon_w(x, n) - \alpha_w(x, n)I_w(x, n)] \, d\Omega \quad \leftrightarrow \quad = 4\pi \alpha_w(x) [S_w(x) - J_w(x)] \quad (3.10)$$

Where the second equality follows if emissivity and opacity are isotropic (as is the case if we are not in presence of anisotropic scattering$^5$; in this case the divergence of the flux at a point is proportional to the difference between the local source function and the mean radiance.

Multiplying eq. (3.7) by $n$ and integrating again over the solid angle, we obtain:

$$\nabla \cdot \tilde{\mathbf{P}}_w(x) = 1/c \int [\varepsilon_w(x, n) - \alpha_w(x, n)I_w(x, n)] \, n \, d\Omega \quad \leftrightarrow \quad = -\alpha_w(x) \mathbf{F}_w(x)/c \quad (3.11)$$

The second equality holds as before in case of isotropic emissivity and opacity.

Let us now study more in depth the absorption, emission and scattering coefficients that are fundamental to characterize the equations above.

3.3 Molecular absorption and emission

In Chapter 2 we described the absorption and emission processes between two excited roto-vibrational states of a molecule in terms of the three Einstein coefficients $B_{12}$ (absorption), $B_{21}$ (induced emission) and $A_{21}$ (spontaneous emission). In the previous section we instead established the equations necessary to follow the evolution of a light packet crossing air with characteristic overall emission $\eta_w$ and absorption $\chi_w$ coefficients. Now we want to relate these two (referring to air composed by many different gases, each with his own transition frequencies and line intensities) to the Einstein coefficients of the single transitions we defined in Chapter 2. This subject in general would be really complicated, because of the very different types of radiative processes that can occur: there are spectral and spatial regions where absorption by atoms or ions is important, and as well could be important the electronic excitation of molecules, photodissociation, recombination.. However, we will specialize our discussion to the case where the only absorption and emission processes involve transitions between roto-vibrational levels of molecules. This situation is generally representative in the study of planetary atmospheres.

$^5$There is the possibility of anisotropy without scattering contribution too, but it regards situations with fast motions or strong static electromagnetic fields, which are far from what we are going to study.
So, as we said, the overall absorption and emission coefficients are the sum of all contributions by all molecules, and we can write the term referring to each gas as the number density of that gas $n_g$ multiplied by a coefficient characteristic of the single molecule.

\[
\chi(w) = \sum_{g=1}^{N_{\text{gas}}} n_g k_g(w) \quad \eta(w) = \sum_{g=1}^{N_{\text{gas}}} n_g \xi_g(w) \tag{3.12}
\]

$k_g(w)$ has dimensions of an area, like a cross section. For each gas we have to sum over all possible transitions between its excited states: we will call in general $u$ the upper state of the transition and $d$ the lower one. Let us begin with the absorption term. Since this term is the one that will be multiplied by the specific intensity, we should include in its expression both the Einstein $B$ coefficients, the one for absorption and the one for induced emission, because it has to be multiplied by the intensity too. In this way we treat induced emission in a certain sense as a ”negative absorption”. We have:

\[
k_g(w) = \frac{h c w}{4\pi} \sum_u \sum_d \left[ \frac{n_d}{n_{\text{gas}}^u} B_{du} \Psi_{du}(w) - \frac{n_u}{n_{\text{gas}}^d} B_{ud} \Psi_{ud}(w) \right]
\]

The first part is the one of absorption and the other refers to induced emission. $\Psi$ is the line profile of the transition and we can assume that, for the same two levels $u$ and $d$, the profile is the same, for the absorption, induced emission and spontaneous emission case\(^6\). The factor $h c w$ is there because we want this expression, when multiplied by the intensity, to give an energy per unit time (so that multiplying by number density we obtain an energy per unit volume and unit time); since the Einstein coefficients $B$ represent the number of photon absorbed per unit intensity, we need to multiply by the photon energy to obtain what we want\(^7\).

Now, we know from Section 2.1 that $B_{ud} = (g_u / g_d) B_{du}$ ($g$ is the statistical weight of the level), so we can rewrite the expression above in a more compact form, substituting the symbol $f_\ell$ for the population ratio of the level $\ell$ considered with respect to the whole gas $g$ population, $f_\ell = n_\ell / n_{\text{gas}}$:

\[
k_g(w) = \frac{h c w}{4\pi} \sum_u \sum_d \left( f_d - \frac{g_d}{g_u} f_u \right) B_{du} \Psi_{du}(w) \tag{3.13}
\]

This expression takes even a simpler form if all levels are in thermodynamic equilibrium at a temperature $T$:

\[
k_g(w) = \frac{h c w \left(1 - e^{-h c w / k T}\right)}{4\pi Z_g} \sum_u \sum_d g_d e^{-E_d / k T} B_{du} \Psi_{du}(w) \tag{3.14}
\]

Where $Z_g$ is the rotovibrational partition function of gas $g$. The equilibrium expression is greatly simplified because we already know all population ratios: we will see in Section 3.6 when we can restrict ourselves to this simpler case.

Turning to the emission coefficient, the situation is completely analogous, with the exception that we have now to consider the Einstein coefficient for spontaneous emission $A_{ud}$.

---

\(^6\)Only in particular situations can the line profile differ between absorption and emission, but this is not the case in atmospheric physics (for example in case of strong doppler effects the two profile differ, but this requires very fast motions).

\(^7\)The factor $1/4\pi$ is there because $B$ is defined in relation with the mean intensity $B J = \int B \Omega d\Omega / 4\pi$. 
3.4. SCATTERING

\[ \xi_g(w) = \frac{hcw}{4\pi} \sum_u \sum_d f_u A_{ud} \Psi_{du}(w) = \frac{h^2 c^3 w^4}{2\pi} \sum_u \sum_d g_u f_u B_{du} \Psi_{du}(w) \]  \hspace{1cm} (3.15)

Where the second equality holds because of the relations between the Einstein coefficients derived in Section 2.1. We write the equilibrium expression for \( \xi_w \) too, for future convenience:

\[ \xi_g(w) = \frac{h^2 c^3 w^4 e^{-hcw/kT}}{2\pi Z_g} \sum_u \sum_d g_d e^{-E_d/kT} B_{du} \Psi_{du}(w) \]  \hspace{1cm} (3.16)

### 3.4 Scattering

In the previous section we wrote extensively about the molecular absorption and emission coefficients, but we did not say anything about the scattering process. The complete theory is complicated and we will not go deeply in its treatment, yet we will introduce the theoretical formalism needed to deal with the general problem and then we will recall some known results and some empirical approaches, useful when we have not enough information about the physical characteristic of particles responsible for scattering.

To understand how to completely describe a generic radiation, let us consider first a strictly monochromatic wave. In the most general case, we know that the electric field rotates at frequency \( \nu \) following an ellipse in the plane perpendicular to the direction of light propagation: the wave is said to be elliptically polarized. To determine such a wave we need to know the (bidimensional) complex amplitude vector but, as we can make one of the complex components vanish redefining the time origin, we actually only need three independent quantities. We can write the field as:

\[ E(x, t) = \Re \left[ A e^{i(kx - \nu t)} \right] \quad \text{with} \quad A = \begin{pmatrix} a \\ be^{i\delta} \end{pmatrix} \]

Equivalently we may describe this wave with the intensity, the ellipticity of the polarization ellipse and its orientation (and its handedness, that is if the motion of the field is clockwise or counterclockwise).

When we do not have a strictly monochromatic wave, which is only an ideal situation, we are not able to draw a polarization ellipse. If we consider the case of a quasi-monochromatic beam, with a slowly varying amplitude \( A(t) \), we will need other quantities to describe its polarization. These quantities are the four Stokes parameters, which measure the polarization degree of the most general radiation. Let us choose two directions perpendicular to the line of sight, \( l \) and \( r \), with respect to which we calculate the two polarization components. The Stokes parameters are defined as:

\[ I = \langle E_l E_l^* + E_r E_r^* \rangle \quad Q = \langle E_l E_r^* - E_r E_l^* \rangle \quad U = \langle E_l E_r^* + E_r E_l^* \rangle \quad V = i\langle E_l E_l^* - E_r E_r^* \rangle \]  \hspace{1cm} (3.17)

Where the average is made over a time interval much longer than the period of the wave. Apart from the first two parameters, which are clearly the intensity and the difference of the two polarizations intensities, the other two may result a bit cryptic at a first sight. They will be much clearer with a few examples of monochromatic light: the adimensional Stokes parameters, obtained dividing by the intensity \( I \), are \((1, \cos 2\alpha, \sin 2\alpha, 0)\) for linear polarization at an angle \( \alpha \) with respect to the \( l \) axis and \((1, 0, 0, \pm 1)\) for circular (righthanded/lefthanded)...
polarization. In a general case, the relation \( I \geq \sqrt{Q^2 + U^2 + V^2} \) is valid and we can define a degree of polarization as the ratio \( \sqrt{Q^2 + U^2 + V^2}/I \), ranging from 0 (unpolarized light) to 1 (a completely polarized state). As we could have guessed from the two examples above, we can define a degree of linear polarization \( (\sqrt{Q^2 + U^2}/I) \) and a degree of circular polarization \( (V/I) \) too.

For a more comprehensive treatment of this topic we refer to the text by Bohren and Huffman [19]. The transfer equation has to be transported in the Stokes space, but maintains the same structure as defined in Section 3.2, replacing \( I \) with the 4-index vector composed by the Stokes parameters. The thermal absorption is a scalar in the Stokes parameters space, whereas thermal emission gives contribution to the first component only (unpolarized light). The scattering part of extinction is the one responsible for making the different polarizations evolve in different ways and is then represented here by a \( 4 \times 4 \) matrix. In Section 3.2 we defined the scattering opacity as a parameter depending on the two directions of incoming and scattered light. We now rewrite it as a matrix in the Stokes space, assuming that we can separate the dependence on wavenumber and directions:

\[
\sigma_{w;ij}(n, m) = \sigma_w P_{ij}(n, m)/4\pi
\]

\( P_{ij}(n, m) \) is known as the phase function. The simplest possibility is the one of isotropic scattering, in which case the phase function is equal to the identity. The phase function contains important information on the scattering process and the point in scattering theory is then to determine its form and the frequency dependence contained in \( \sigma_w \), starting from the physical properties of scattering particles, like dimension, shape, refractive index. The best known approximation for this problem is probably the one of Rayleigh scattering, which gives a solution valid in the assumption of spherical homogeneous scatterers and in the limiting case of \( x = 2\pi r/\lambda \ll 1 \) (\( \lambda \) being the wavelength and \( r \) the particle radius). The result obtained by Rayleigh is:

\[
\sigma_w = \frac{2}{3}(2\pi \gamma^2)^2 \quad P_{ij}(\theta) = \frac{3}{4} \begin{pmatrix} 1 + \cos^2 \theta & -\sin^2 \theta & 0 & 0 \\ -\sin^2 \theta & 1 + \cos^2 \theta & 0 & 0 \\ 0 & 0 & \frac{1}{2} \cos \theta & 0 \\ 0 & 0 & 0 & \frac{1}{2} \cos \theta \end{pmatrix}
\]  

(3.18)

For spherical dielectric scatterers also a complete formal theory exists, due to Mie, but we will not cite its results here. Let us only say that the dependence of \( \sigma_w \) on frequency has not a simple relationship with the particle radius, nor is this relationship monotonic. But we can say that, for increasing particle sizes, this dependence tends to be weaker and the \( \sigma_w \) to flatten with respect to the small particles limit.

A rigorous treatment of the scattering problem is far beyond our purposes here, being not the central point of this work. The only case we will be interested in is single scattering of solar (unpolarized) light and simple isotropic scattering, for which we only need to consider the first of the Stokes parameters, our familiar specific intensity.

In Part II we will try a simple analysis of such a contribution to the atmospheric emission, but for a complete derivation of the correct scattering functions, a deeper study on the physical properties of the particles responsible for scattering and of their distribution is needed. In this

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8We are here assuming coherent scattering, that is the outgoing photon has exactly the same energy of the incoming one. In a more general case we would have to define a redistribution function \( \phi(w, w') \) which tells us how the frequency is being modified.

9The phase function is usually normalized so that the 11 component gives unity when mediated over the solid angle.

10Assuming the phase function is equal to the identity in the Stokes space.
work we only simulated the aerosol scattering with a semi-empirical relation, fitted to the available data. Such an approximate approach, first proposed by Ångström (see [20]), assumes that the scattering coefficient $\sigma_w$ has a simple power dependence on frequency, of the type:

$$\sigma_w = \sigma_0 \left( \frac{w}{w_0} \right)^\alpha$$

The exponent $\alpha$ is called the Ångström parameter and depends on the mean particle size $r$: a typical trend of this parameter respects the Rayleigh prediction in the small particle limit ($\alpha \to 4$) and goes to zero as the size increases. We will use such a simple approach in Part II.

### 3.5 Formal solution of the equation of transfer

We are now going to derive the formal solution of eq. (3.7) and look at its behaviour in some limiting cases. As the adjective formal suggests, writing this formal solution does not mean that we are done with solving the problem, even if we know all the air optical properties we need: in the general case (out of equilibrium or with scattering contribution) the source function and optical depth may be dependent on the specific intensity, so making the problem non-linear in nature. We rewrite here equation 3.7 for convenience:

$$n \cdot \nabla I_w(x, n) = \varepsilon_w(x, n) - \alpha_w(x, n) I_w(x, n)$$

The operator $n \cdot \nabla$ means that we are deriving the specific intensity along the ray path, so we could rewrite it as a derivative with respect to a path coordinate $s$. We can put the origin of the coordinate system at our observatory; doing so and omitting the direction $n$ among the functions arguments, we obtain:

$$\frac{d}{ds} I_w(-n s) = \varepsilon_w(-n s) - \alpha_w(-n s) I_w(-n s)$$

To solve the problem, we need to know the intensity at some point $x_0 = -n s_0$, that is a point along the past ray path at distance $s_0$ from us. The solution of the above equation is obtained solving first the homogeneous part, without the emission term, which depends on our boundary condition and gives simply a decaying exponential, and then adding the solution of the disomogeneous equation. We write here only the result of this operation, that can however be easily verified by substitution:

$$I_w(0) = I_w(-n s_0) e^{-\tau_w(0,s_0)} + \int_0^{s_0} \varepsilon_w(-n s) e^{-\tau_w(0,s)} ds$$  \hspace{1cm} (3.19)$$

Here $\tau_w(0,s) = \int_0^s \alpha_w(-n l) dl$ is the optical depth between a point $s$ along the ray path and the observer. The meaning of eq. 3.19 is clear: we have a first part which is the original intensity, attenuated by the exponential of the total optical depth of the atmospheric slab, and a second which is the radiation emitted at each point $s$ along the line of sight, attenuated by the absorption in the remaining path before reaching us. We rewrite eq. 3.19 in an equivalent form we will use later on, substituting for the source function and making all quantities depend on the optical depth:

$$I_w(0) = I_w(\tau_w^{\text{tot}}) e^{-\tau_w^{\text{tot}}} + \int_0^{\tau_w^{\text{tot}}} S_w(\tau_w) e^{-\tau_w} d\tau_w$$  \hspace{1cm} (3.20)$$
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Where $\tau_w^{\text{tot}}$ is the total optical depth of the slab. We can now study two interesting limiting cases of this equation.

Limiting cases

The two evident limits we could consider are the ones for $\tau_w^{\text{tot}} \ll 1$ and $\tau_w^{\text{tot}} \gg 1$, which are usually called the optically thin and optically thick limits. In the first case we obtain:

$$
\lim_{\tau_w^{\text{tot}} \to 0} I_w(0) \sim I_w(\tau_w^{\text{tot}}) + \tau_w^{\text{tot}} \cdot [S_w^* - I_w(\tau_w^{\text{tot}})]
$$

(3.21)

$S_w^*$ is an appropriate mean of the source function in the thin slab. In this case, we can see, the material along the ray path is almost transparent to the incoming radiation, with only a slight perturbation proportional to the total optical depth and to the difference between the source function and the original intensity. If we had not an incoming radiation, we would see a signal proportional only to the optical depth and to the source function.

The opposite situation is obtained setting the limit for large optical depth:

$$
\lim_{\tau_w^{\text{tot}} \to \infty} I_w(0) = \int_0^{\tau_w^{\text{thin}}} S_w(\tau_w) e^{-\tau_w} d\tau_w \sim S_w^*
$$

(3.22)

In this case we completely loose information about the original radiation, seeing only the photons emitted in the part of the atmospheric slab nearer to us: we indicated this with $\tau_w^{\text{thin}}$, but we have to be very careful because, in general, the source function may vary by orders of magnitude with position. If instead we are in presence of a reasonably homogeneous medium, what we see is the source function itself of the medium (as stated by the last equality in the equation above). Let us underline this point, making explicit the dependence of the optical depth from the number density of a certain gas. If we are in presence of a homogeneous medium (or not too far from) and in absence of an incoming radiation, the two limits will give these observed intensities:

$$
\lim_{\tau_w^{\text{tot}} \to 0} I_w(0) = n_g L_{\chi w} S_w^* \quad \lim_{\tau_w^{\text{tot}} \to \infty} I_w(0) = S_w^*
$$

(3.23)

As we can see, in the optically thin case the observed radiation is proportional to the number density $n_g$ of the emitters, whereas in the optically thick case it is not: if we double the gas concentration in the atmosphere, we see a doubly strong signal in the first case and exactly the same in the second. If there were two lines of the same emitter in the same spectral region, one in the thin regime and the other in the thick one, their relative weight would be strongly dependent on the gas concentration, because the intensity in the first line would change, whereas the second would not.

We are going to see a real example of this behaviour in section ?? of Part II, regarding the relative importance of CO fundamental and first hot band.

\[\text{Let us pretend we are observing at the characteristic frequency of a molecule, so that the only important contribution is its.}\]
Discretization of the radiative transfer equation

In order to conclude this section on the solution of the radiative transfer equation, it is useful to have a look at the fundamental equation in a discrete form. The reason for this is that radiative transfer problems are usually solved through numerical computations, as we will do in the second part of this work. The first step for the creation of a numerical model for an atmosphere is to discretize it, building a grid and numbering all the elements. Of course, the grid should be narrow enough to consider a single step as infinitesimal. If this condition holds, we do not make a relevant error in transforming the integrals into summations and, for a single step between \( x_i \) and \( x_{i+1} \) along a ray path, we have:

\[
\Upsilon_{i,i+1} \equiv e^{-\tau(x_i,x_{i+1})} \approx 1 - \tau(x_i,x_{i+1}) = 1 - \alpha_i \Delta x_{i,i+1}
\] (3.24)

Where we have defined a new quantity \( \Upsilon(x_i,x_{i+1}) \) as the exponential of the optical depth; we left implicit the wavenumber indexes. If we now consider the integral in eq. 3.20, we obtain:

\[
\int_0^{\tau_{\text{tot}}} S(\tau) e^{-\tau} d\tau \sim \sum_{i=0}^{n} S_i \alpha_i \Delta x_{i,i+1} \prod_{j=1}^{n} \Upsilon_{j,j+1}
\] (3.25)

Then, using approximation 3.24, we may rewrite equation 3.20 in its discrete form as:

\[
I_n = I_0 \prod_{i=0}^{n} \Upsilon_{i,i+1} + \sum_{i=0}^{n} (1 - \Upsilon_{i,i+1}) S_i \prod_{j=1}^{n} \Upsilon_{i,j+1}
\] (3.26)

The introduction of the new quantity \( \Upsilon \) and the approximation of infinitesimal grid spacing have allowed us to rewrite our fundamental equation in a simple form. The dependence of all quantities on the wavenumber is treated discretizing the wavenumber spectra and solving for each discrete component separately.

3.6 About thermodynamic equilibrium, LTE and non-LTE

Strict thermodynamic equilibrium means that we have a closed system at uniform temperature \( T \), with all distribution functions being those given by statistical physics; we may schematically write three conditions that characterize the perfect equilibrium state:

- the particles translational velocities follow the well-known maxwellian curve;
- the populations of all excited levels of molecules are given by Boltzmann distribution;
- the radiation is isotropic and its intensity is represented by the Planck function.

Of course, this would be a really convenient situation if we had to solve a radiative transfer problem (actually it is already solved in this case), but unfortunately we never find it in the real world. In nature, we always have temperature gradients and photons can escape, thus making the system not closed anymore.

Looking for black bodies

Although strict thermodynamic equilibrium never holds in nature, we still have very good approximations to it, the best examples around us being inside stellar interiors. In fact we get something very close to a black body, a system for which all the three conditions above hold, when photons are trapped into matter with an effectively fixed temperature: to determine more quantitatively this condition we should compare the typical scale of temperature variation, estimated by\(^{12} \) \( h_{\tau} = T / (\partial T / \partial s) \), with the characteristic length for thermalization of radiation

\(^{12}\)s being here the direction in which the temperature gradient is at its maximum.
with matter $L_w$, which we define more rigorously in the box in the next page; if $L_w \ll h_\tau$ at some frequency, the radiation will be close to $B_{w}(T)$ at that frequency. If this applies at each frequency, we are in what is said to be the diffusion limit: the specific intensity is well approximated everywhere by the Planck function, although we have to allow for a slight perturbation, as we still have a temperature gradient, even if a small one. Strict thermodynamic equilibrium - and a specific intensity exactly equal to the Planck one - would in fact mean that no net radiative flux can take place.

All the three conditions written at the beginning of the section hold to a quite good degree of accuracy in the diffusion limit. If, instead, we further weaken the assumptions of closed system and no temperature gradients, they will fall one after the other, depending on the typical times of restoration of equilibrium and on the forces that try to drive the system far from the equilibrium state. Clearly, if the condition for diffusive approximation does not hold, the first constraint to fall is the one regarding radiation: if we can define a local temperature, particles always ”communicate” through collisions with a thermal bath at fixed temperature, whereas a photon, having a typical thermalization length larger or comparable with the temperature scale height, comes into touch with regions far apart and at sensibly different temperature.

**Typical lengths at comparison**

The simplest characteristic length of radiation is the photon mean free path $\lambda_w$, that is the typical distance a photon travels freely before coming into touch with another particle and being absorbed or scattered. It simply equals the inverse of the total extinction coefficient $\lambda_w = 1/\alpha_w$. The type of interaction this length is linked to does not lead in general to an energy exchange between the radiation field and matter, thus it doesn’t tell much about the exchange process, that is fundamental to achieve thermodynamic equilibrium.

So, we might think that the true typical length for energy exchange between radiation and matter is the mean distance traveled by a photon before being absorbed, the photon destruction length $\lambda_w' = \lambda_w \sqrt{N_s} = \lambda_w \sqrt{\lambda_w/\lambda_w} = 1/\sqrt{\lambda_w \alpha_w}$, $N_s$ being the number of steps the photon does in its random walk before being absorbed. But still this is not the length we are looking for, because the fact that a photon is being absorbed does not mean its energy will be transferred to the thermal bath: if the excited molecule deexcited itself emitting back a photon of the same energy or of a smaller one, we would have no or only partial energy transfer.

In order to have a complete transfer to the thermal bath, the excited molecule has to be deexcited by a collisional process, thus transferring the excitation energy to translational energy or other thermal energy reservoirs. We will talk in detail about excitation energy transfer and the balance between collisional and radiative deexcitation in Chapters 4 and 5; yet let us define here, for a particular excited level, a generic probability for collisional deexcitation $C$ and compare it to the probability for radiative deexcitation $A$. We are now able to estimate the true thermalization length $L_w$ of radiation, the typical length a photon travels before being absorbed and having its energy transferred to the thermal bath*, as:

$$\text{Thermalization length } \sim L_w = \lambda_w \sqrt{\frac{\alpha_w}{C \chi_w/(A+C)}} = \lambda_w \sqrt{\frac{A+C}{C}}$$

In the limiting case of no collisions at all ($C \to 0$), we see that the thermalization length correctly goes to infinity: no thermalization is possible in this case.

---

*Here we mean that we keep following the reemitted photon in case of an event of absorption with reemission, till there is a complete transfer of the original photon energy to the thermal bath.
“Thermodynamic equilibrium” in a planetary atmosphere

A common characteristic of all atmospheres is the escape of photons to space and the anisotropy of the radiation field; therefore, we are quite far from the situation we described above and the third condition we wrote at the beginning of Section 3.6, the one regarding radiation, will not be valid here anymore.

Though the radiation is far from being at equilibrium, we still can have all matter degrees of freedom diligently following Boltzmann laws\textsuperscript{13}. When we have such a situation, that is when we can define a local temperature $T$ such that Boltzmann distribution functions at that temperature correctly describe all matter degrees of freedom, we say that matter is at Local Thermodynamic Equilibrium (LTE) at temperature $T$. Of course, not all matter degrees of freedom have the same characteristic time for re-establishing equilibrium, nor are they all equally sensible to the presence of a non-equilibrium radiation. For example, if photons that can excite a certain transition were much more than what they should be at the matter temperature, we can easily imagine that the excited level population would be raised by an absorption stronger than predicted, bringing that level out of equilibrium. This means that we could have some degrees of freedom out of equilibrium (or even only some particular level of one or another molecule), while all others are: in that case we say that only some degrees of freedom (or levels) are in LTE and some are in non-LTE. And what if none of them is? How could we define a temperature? Of course, in general such a situation can take place, but it is a a very uncommon situation for the atmospheric regions we will study\textsuperscript{14}, far from our interests: we will assume that at least translational degrees of freedom always follow a maxwellian distribution at some temperature $T$, allowing us to define, at each point, the matter temperature as the kinetic one.

Our great interest on the question of LTE is explained with the fact that, if we can assume it, the transfer problem is greatly simplified: the absorption and emission coefficients we defined in section 3.3 take in this case a very simple form, as the populations of all excited states are known and equal to their equilibrium values. Moreover, if we consider only molecular absorption and emission, an important relation is valid, known as the Kirchhoff-Planck relation, which states that the source function of matter equals the Planck function at the local temperature. If we were in strict thermodynamic equilibrium, this statement appears quite obvious if we look at it starting from the transfer equation 3.9: solving for an intensity identically equal to $B_w(T)$ in the whole space, we note at once that the difference between the intensity and the source function has to vanish in all points. Since we are now considering radiation out of equilibrium, we know it would tend to drive matter out of equilibrium as well, but if its influence is not too strong and LTE conditions are still satisfied with regards to all excited levels, we can prove that the Kirchhoff-Planck relation will be valid anyway.

Let us show this fact, starting from the expressions 3.14 and 3.16 for the molecular absorption and emission coefficients at equilibrium:

\textsuperscript{13}Actually this is the most common situation we live every day: in the air around us, all molecules excited levels and translational degrees of freedom are in equilibrium (apart from extraordinary situations), whereas the radiation clearly isn’t, for the only fact that we can see something.

\textsuperscript{14}A proof of the existence in the universe of populations of non-thermal particles are the so called cosmic rays, particles with extremely high translational energies that each day keep falling on our atmosphere. These are yet a minor component, completely negligible in most situations, but are of interest because their speed distribution follows a power law, instead of the exponential tail of a maxwellian. Closer to us, there is evidence for small deviations from the Maxwellian distribution only in the highest part of our atmosphere, where free electrons and photochemical processes become more important.
\[ S_w = \frac{n_w}{\chi_w} = \frac{2h^2c^3wAe^{-hcw/kT}}{hcw(1 - e^{-hcw/kT})} \sum_g \frac{n_g}{Z_g} \sum_u \sum_d g_{gd} e^{-E_d/kT} B_{du} \psi_{du}(w) = B_w(T) \] (3.27)

When some levels are out of LTE, no such simple relation is valid: the populations of those levels, to be used in formulas 3.13 and 3.15, have to be determined by a more complicated statistical study, involving collisions by other molecules and radiative processes. That is, the problem becomes non linear in nature, because the absorption and emission coefficients now depend on radiation itself. We are going to study this situation in depth in chapter 5.
Chapter 4

Collisional energy transfer between molecules

At the end of the previous chapter we stated that, if we cannot a priori assume LTE, we have to take explicitly into account the collisional processes between particles, analyzing the amount of energy exchanged and the degrees of freedom involved. The physics of collisions is in fact the key point in understanding how a state of LTE can be reached. We may imagine the thermalization process as a struggle between restoring forces, given by exchange of energy with a thermal reservoir, and forces that tend to drive the system out of equilibrium, given by interaction with a non-equilibrium radiation or by exchange of energy with some non-LTE part of the system. The stronger the restoring forces are and, therefore, the smaller is the typical relaxing time of the distribution function of a certain degree of freedom, the more probable is to find that distribution in its equilibrium form.

As we are primarily interested in molecular infrared emission, we will specialize our study to collisions between molecules, considering only translational, rotational and vibrational degrees of freedom. In the most general context, electronic excitation and chemical equilibrium of ionized species are certainly of interest, but we will not treat them here. In our treatment of non-LTE radiative transfer, we will assume that the distribution functions of translational and rotational degrees of freedom are always well represented by the Boltzmann ones, allowing only vibrational excited states to run away from their equilibrium population. With regards to translational degrees of freedom, we already assumed this fact in the previous chapter, when we said that we are always able to define a local temperature. As the translational part of the system is characterized by a continue of states, we can understand that it is more simple for it to maintain its equilibrium form: each collision will do the job of exchanging some energy between different states (the gap between them can be as small as we want), while the influence of non-thermal processes, like inelastic collisions that transfer energy from or to other degrees of freedom, is very weak, as we will see.

Considering, instead, rotational degrees of freedom, which present a discrete spectra, it is not that obvious that LTE always holds for them. Radiation might excite some particular transition, enhancing the population of some particular level, and the energy exchange between rotational degrees of freedom and translational ones (our sure thermal reservoir) might not be that efficient. In this sense, there is no conceptual difference between the case of rotational and that of vibrational levels: the reason why, for our purposes, the first ones can always be considered in LTE whereas the second ones cannot, is that the energy gap between two following rotational levels is considerably lower, allowing collisions to easily thermalize them. Some numbers may make this point more persuasive: if we consider a diatomic molecule like CO, we see from eq. 1.12 that the gap between a level with angular momentum $J$ and the
following one is given at first approximation by $2B_e (J + 1)$, which ranges in the CO molecule from $3.8 \text{ cm}^{-1}$ for the transition $J = 0 \rightarrow 1$, to $152 \text{ cm}^{-1}$ for $J = 40 \rightarrow 41$; these have to be compared with the energy gap between the first excited vibrational level and the ground which is about $2140 \text{ cm}^{-1}$. Even the highly excited rotational states have an energy gap with their closest levels which are more than ten times lower than the vibrational energy gap: the gap between the $J = 40$ and $J = 41$ states equals the mean translational energy of a gas at 150 K, so a mean collision at that temperature has the energy to excite that transition. Of course this is a really simplified way of looking at the problem, because also different types of collisions, involving more than one transition, are possible, but it still gives us a first argument.

Before studying in detail the vibrational case, let us first justify our last statements with a stronger, although still qualitative, analysis involving typical relaxation times.

4.1 Classical estimates of typical relaxation times

When dealing with translational degrees of freedom, we shall take into consideration the Boltzmann equation that determines the form of the one-particle distribution function.

$$\left( \frac{\partial}{\partial t} + v \cdot \nabla \right) f(x, v, t) = \frac{\partial f}{\partial t} \text{coll} \quad (4.1)$$

For our purposes, it is sufficient to assume that the collisional term at the right-hand side is the one derived by Boltzmann in the approximation of no correlation between particle positions, which can be written as:

$$\frac{\partial f}{\partial t} \text{coll} = \int \sigma(\Omega_2) v_{\text{rel}}(f(v') f(v_2) - f(v) f(v_2)) d^3v_2 \quad (4.2)$$

Where $v'$ and $v_2$ are the velocities after the collision of two particles with initial velocities $v$ and $v_2$. Let us imagine we have a non-equilibrium distribution funcion $f$, in completely homogeneous conditions without external forces, so that $\frac{\partial f}{\partial t} = \left( \frac{\partial f}{\partial t} \right) \text{coll}$. The typical time of relaxation $\tau$ may be estimated saying that $\frac{\partial f}{\partial t} \sim f / \tau_{\text{rel}}$, and then giving an estimation of the integral at the right-hand side:

$$\int \sigma(\Omega_2) v_{\text{rel}}(f(v') f(v_2) - f(v) f(v_2)) d^3v_2 \sim \sigma v_{\text{th}} f(v) \int f(v_2) d^3v_2 \quad (4.3)$$

Where we have assumed that the integral is of the same order of each of the two subtracting terms in its expression. Observing that the remaining integral is simply equal to the particle density, it follows that:

$$\tau_{\text{rel}} \approx \frac{1}{n \sigma v_{\text{th}}} \quad (4.4)$$

That is, this time is of the same order of magnitude of the mean time between two collisions for a particle.

Rotational case: collision of a rigid rotor

A simple estimate of the typical thermalization time of the rotational degrees of freedom can be obtained considering the following classical situation: a point particle of mass $m_A$ colliding with a rigid rotor of length $\ell$ composed by two particle of mass $m_B$, which represents a diatomic molecule. Since the rapidity of thermalization depends on the frequency of collisions and on the amount of energy exchanged in each of them, an estimate of the ratio between translational
and rotational typical relaxation times will be given, in the case we are considering, by the ratio between translational and rotational energy gained by our diatomic molecule in the collision. If we consider the most favourable situation of the point particle colliding at right angle at one extreme of the rotor, with the rotor initially at rest, we easily get from conservation of angular momentum with respect to the collision point that:

\[ J = 2m_B v_B \ell / 2 \leadsto \Delta E_{\text{rot}} = J^2 / 2I = m_B v_B^2 = \Delta E_{\text{tr}} \]

Where \( J \) is the angular momentum with respect to the center of mass and \( v_B \) is the velocity of the center of mass of the rotor after the collision. We see that in this particular case the amount of rotational energy gained is exactly equal to the translational one. We have to say, this is a very special situation and considering collisions over the whole solid angle and with different initial condition the ratio will be larger, with favour of the translational energy. But this argument still suggests that the typical relaxation time for the rotational levels shall not be too much lower than the typical translational time \( \tau_{\text{TT}} \), maybe of the same order of magnitude.

Of course, a satisfying treatment of this topic would require a complete consideration of the discrete quantum spectra of rotational energy levels and a realistic interaction between colliding particles, but we will not deal with it here and will from now on always consider the rotational energy levels at thermal equilibrium as well.

**Vibrational case: Landau-Teller formula**

The analogous of the previous simplified classical model for the vibrational case has had a great fortune historically, having been the only general result on vibrational energy transfer for many years. This first theoretical prediction is due to Landau and Teller, which - in a famous 1936 work [23] - gave a quite good qualitative interpretation of experimental data and of their trend with the change in temperature.

Their model system consists of a point particle linearly colliding with a classical oscillator (the diatomic molecule), with the assumption of an interaction potential of exponential form \( V = V_0 e^{-a r} \); the equation of motion is that of a forced oscillator and from there, integrating with respect to time, the mean energy exchanged in such a collision can be evaluated. Without deriving it here, the result of this calculation gives:

\[ \Delta E \propto \frac{\mu \omega^2}{a^2} e^{-3\mu v_{\text{max}}^2/2kT} \quad \text{with} \quad v_{\text{max}} = \left( \frac{2\pi kT \omega}{a \mu} \right)^{1/3} \]  

(4.5)

Where \( v_{\text{max}} \) is the velocity at which the energy transfer is maximum, \( \mu \) the reduced mass of particle and oscillator and \( \omega \) the characteristic angular frequency of the oscillator.

Now let us imagine that our gas originally has zero vibrational energy, and “restore” the quantum nature of our oscillator, focusing on the first vibrational level. The typical time for the equilibrium state to be reached can be estimated considering the total equilibrium energy density of molecules excited to the first level and dividing it by the rate of collisions times the mean energy exchanged in such a collision can be evaluated. Without deriving it here, the result of this calculation gives:

\[ \tau_{\text{VT}} = E_{\text{rot}} (1) \frac{dE}{dt} = \frac{n_{\text{mol}} h\omega e^{-h\omega/kT} / \sum_n n e^{-nh\omega/kT}}{n_{\text{mol}} f_{\text{coll}} \Delta E} \approx \tau_{\text{TT}} \frac{h\omega}{\Delta E e^{h\omega/kT}} \]  

(4.6)

Where we have recognised that the inverse of the collision frequency is equal to the typical time for translational relaxation we derived above, and neglected \( 1 \) with respect to \( e^{h\omega/kT} \), thus considering the case in which the vibrational energy gap is far larger than the average
thermal energy. Remembering the quantum nature of the oscillator, we shall write the mean exchanged energy as a probability $P_{01}$ for the transition from the ground to the first excited level to take place during the collision, times the quantum of vibrational energy $\hbar\omega$, so that $P_{01} = \Delta E / \hbar\omega$. Taking the expression above for $\Delta E$ we can derive the trend of the probability with the change in temperature; taking logarithms of both sides:

$$\text{Landau-Teller formula} \quad \ln P_{01} \sim -T^{-1/3}$$

(4.7)

This is the famous result of Landau and Teller, which, despite the too simple classical model, is in a quite good agreement with the real behaviour of experimental data, apart from the lowest temperatures.

From this simple analysis follows that the typical time of transfer of energy between vibrational and translational degrees of freedom has to be much longer than the translational time, justifying the assumption of LTE for translational and rotational degrees of freedom even when the vibrational distribution function is far from equilibrium.

### 4.2 Vibrational energy transfer

As we previously said, we are going to spend some more words on energy transfer involving vibrational excited states. Vibrational LTE cannot in fact be assumed in many situations, thus limiting ourselves to consider each single collisional process. If we have a molecule $X$ in a vibrationally excited state $\nu$, different things may happen during a collision with another molecule $M$: in the most common situation nothing happens to the vibrational state, which is another argument in saying that its thermalization is not that easy; otherwise molecule $X$ may de-excite from the original vibrational state to another one (let us call it $\nu'$), transferring the lost energy to other degrees of freedom of its own or belonging to molecule $M$. We can roughly distinguish between two types of de-excitation: we call vibrational-translational (V-T) energy transfer the one in which the whole energy difference between $\nu$ and $\nu'$ is completely transferred to translational degrees of freedom of the two molecules; the other possible situation is the vibrational-vibrational (V-V) transfer that refers to the case when the $\nu \rightarrow \nu'$ transition is not the only one taking place, but another transition happens, exciting molecule $M$ from the initial state $\alpha$ to a higher vibrational state $\beta$.

$$X_\nu + M_\alpha \rightarrow \left\{ \begin{array}{ll}
X_\nu' + M_\alpha & \text{elastic collision} \\
X_\nu' + M_\beta & \text{inelastic collision: V-T transfer} \\
X_\nu' + M_\beta & \text{inelastic collision: V-V transfer}
\end{array} \right.$$  

(4.8)

In a general situation, if the two simultaneous transitions are not exactly resonant ($E_\nu - E_\nu' \neq E_\beta - E_\alpha$), part of the energy will be transferred to the vibrational energy of molecule $M$ and part will go to the translational degrees of freedom: we speak of V-V transfer in this case as well. The different nature of V-T and V-V processes and the reason to distinguish between them will be clear in the next chapter, when we will need to consider them to study the statistical equilibrium of a system out of LTE. For now, let us define some quantities and explore the physical basis of the theory of molecular collisions.

When studying a particular collision, the quantity we are primarily interested in is the number $N$ of such collisions that take place per unit time and volume: if the collision involves

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1Of course a transfer to rotational degrees of freedom may happen as well and it should be considered in the exact treatment of the problem but, since we consider the rotational levels with equilibrium populations and thus part of the thermal bath, this will be equivalent to a transfer to the translational degrees of freedom.
two molecular species $M$ and $X$, we may make explicit the dependence on the number densities of the two species, which is a linear dependence in usual situations\(^2\). Let us focus on a particular collision between molecule $M$ in the vibrational state $\alpha$ and molecule $X$ in state $\nu$ which brings them in the final states $\beta$ and $\nu'$ respectively. We may write:

$$N^{M-X}_{\alpha,\nu;\beta,\nu'} = n_M f_\alpha n_X f_\nu k^{M-X}_{\alpha,\nu;\beta,\nu'}$$  \hspace{1cm} (4.9)$$

Where $N$ is the number of transitions per unit time and volume, $n_M$ and $n_X$ are the number density of the two species, $f_\alpha$ and $f_\nu$, the population fraction of the two levels $\alpha$ and $\nu$. The quantity carrying information on the specific process is $k$, known as \textit{the rate constant}, which has dimensions of $cm^3 s^{-1}$. This is the quantity we are looking for.

If all encounters took place at a fixed relative velocity $v$, the rate constant would be obtained by the product between $v$ and a characteristic cross section; in a more general case we will have to average on the thermal distributions of velocity, obtaining:

$$k^{M-X}_{\alpha,\nu;\beta,\nu'}(T) = \int_0^\infty \rho_{T,v}(v) \sigma^{M-X}_{\alpha,\nu;\beta,\nu'}(v) v \, dv$$  \hspace{1cm} (4.10)$$

In the above equation $v = |v_2 - v_1|$ is the relative velocity, in function of which we write the Maxwell-Boltzmann distribution $\rho_{T,v}(v) = (\mu/2\pi k_b T)^{3/2} 4\pi v^2 e^{-\mu v^2/2k_b T}$; we have already integrated with respect to the center of mass velocity and the solid angle.

The goal of molecular collision theory is to calculate the cross section $\sigma$ of specific processes. Many different approaches have been developed, ranging from simple classical models to semi-classical approaches or even full-quantum treatments. But before choosing the most adequate approach, we need to know the forces that rule collisions between molecules.

\section*{Intermolecular potentials}

The main problem in all theoretical attempts to predict the cross sections for various processes is the incomplete knowledge of molecular reciprocal interaction, which is still an open field of investigation. That interaction is in fact due to the full systems of electrons and nuclei, and trying to reduce it to the form of a simple potential is maybe already an over-simplifying assumption. Besides, the calculation of the residual field produced by a system composed by many particles, as is the case of all molecules, even the simplest ones, is a matter of complex and time-consuming numerical calculations (see [25],[26]); even determining these potentials experimentally is not a simple matter, since it is done through the analysis of transport coefficients of gases (see [27]). This is to say that the safest and most precise way to get the rate constants for different collisional processes is still, at the time being, to directly get them from experimental analysis, as we will briefly describe at the end of this chapter. But there are cases in which this is not possible (like the $N_2-N_2$ case, as we will discuss below) or simply it has not been done yet, so that a theoretical prediction becomes fundamental.

Intermolecular interaction can be divided mainly in two parts: a steep short-range repulsive core and a softer long-range attractive part. The first one, due to the quantum nature of the problem, is not actually reducible to a simple potential dependent on distance: however, effective hard-sphere potentials or other really sharp forms have been used to model the strong repulsion that molecules feel when they come too close to each other. The long-range part is instead due to residual forces of electromagnetic nature, known as \textit{van der Waals forces}: at the lowest order they are mainly of three types, depending on whether they involve two permanent

\footnote{If the correlation between the particles positions can be neglected, which is certainly a good approximation for non-charged gases at low densities.}
dipoles (orientation interaction), a dipole and an induced dipole (induction interaction) or two induced dipoles (London interaction). The curious point is that these three interactions all give a long-range dependence of $1/r^6$ on reciprocal distance and have an attractive nature (see [24]). This is one of the reason why, historically, one of the most used potential to model intermolecular forces has been the so called Lennard-Jones potential, which is written as follows:

$$W_{LJ}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]$$

Where $\varepsilon$ is the absolute value of potential minimum and $\sigma$ is the point in which the positive short-range barrier begins. As we can see, apart from the attractive interaction $\propto r^{-6}$, the repulsive barrier is modeled by a $\propto r^{-12}$ power law.

Another form widely used for the intermolecular potential is the Morse function we saw in chapter ??, which follows the characteristic repulsive-attractive shape.

$$W_{M}(r) = \varepsilon \left( e^{-a(R-R_c)} - 2e^{-a(R-R_c)} \right)$$

When studying strong collisions, such as the ones responsible for transitions with large energy gaps, the main contribution is given as we will see by the repulsive core of the potential: for this reason often only a simple repulsive exponential is used to model the molecular interaction, as is the case for example of SSH theory (see 4.2).

**Semiclassical approximation**

There are different ways in which we could calculate the cross section for the particular collision process we are interested in. The simplest approach, yet leading to quantitatively significant results, is the semiclassical one, which assumes that the two colliding molecules follow a classical path, whereas the transition probability during the collision is calculated regarding the mutual time-dependent potential as a perturbation to the molecular system. Since we can here define an impact parameter, we can write the following expression for the cross section and take into consideration a single collision at fixed $b$ and $v$:

$$\sigma^{M-X}_{\alpha,\beta;\alpha',\beta'}(v) = \int_{0}^{\infty} P^{M-X}_{\alpha,\beta;\alpha',\beta'}(b, v) 2\pi b db$$

If we write as $V(t, s_{X,i}, s_{M,j})$ the instantaneous potential at time $t$ depending on the internal variables of the two molecules, the transition probability $P$ is easily obtained, at the first order of perturbation theory:

$$P^{M-X}_{\alpha,\beta;\alpha',\beta'} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} \langle \psi_{X,i} \psi_{M,j} | e^{i\Delta E t/\hbar} dt \rangle^2 \right|^2$$

Where $\Delta E = E_{\alpha} + E_{\beta} - E_{\alpha'} - E_{\beta'}$ is the energy difference between initial and final states and the $\psi$ are the internal states of the two molecules; the quantity to be determined is so the expectation value of the instantaneous potential between the initial and final states. So we can see that what matters is the Fourier transform with respect to time of the potential matrix element between initial and final states: as we were expecting, the larger is the energy gap between them, the closer has to be the collision in order to make the transition take place; in other words, with large energy gaps we need fast variations in time of the potential.

\footnote{For the first kind of interaction, involving permanent dipoles of polar molecules, this is true only when mediating on the angles for freely rotating dipoles. In the long range case this is a good approximation, whereas for closest approaches the interaction becomes stronger (to be rigorous, here again the complete quantum problem and the rotational state of molecules shall be considered).}
which we can have only for the strongest collisions; this is the reason why transition with large energy gaps are less probable. Again thinking about rotational transitions, we can now easily understand why their collisional relaxation rates are far faster than the vibrational ones.

If we assume that the potential depends only on the distance between the two molecules (apart from the internal variables), the expression above can be rewritten as:

\[ P_{M-X} = \frac{2}{\hbar^2} \int_{d_{\text{min}}}^{\infty} \left( \langle \Psi_{X,v} | V(r,s_{X,i},s_{M,j}) | \Psi_{X,v'} \rangle \cos \left( \frac{r \Delta E}{\hbar v} \right) \right)^2 dr \]  

(4.15)

Where we have made explicit the dependence on \( r \) and on the instantaneous velocity \( v \); \( d_{\text{min}} \) is the distance of closest approach.

This semi-classical treatment is used by many authors in the study of rate constant for certain processes (see [30],[31]). Among them, we are particularly interested in the work by Shin [31] on the rate constants of V-T and V-V processes between \( \text{N}_2 \) and \( \text{CO} \). In that paper he assumes that the intermolecular potential can be written as the sum of four parts, representing the interaction of each couple of atoms, and then averages the total interaction over all possible relative orientations of the two molecules. We will speak further on about the results of his work, but let us remark its importance here, given that this is the only one (including experiments too) that analyzes the relative weight of V-T and V-V rates between these two molecular species.

In conclusion, the semi-classical approach can lead to important results, although it obviously has some limits, especially for strong collisions. The most evident is that the classical trajectory is calculated for the initial relative translational energy and cannot take into account the amount of energy possibly transferred in consequence of a vibrational de-excitation (usually greater than the mean thermal energy and certainly non-negligible). Let us briefly introduce a more complete quantum approach that is able to go beyond this difficulties.

**SSH theory**

The fundamental theoretical basis about vibrational energy transfer between molecules is known as **SSH theory**, from the names of Schwartz, Slawsky and Herzfeld that first developed it in 1952 (see [28],[29]). Making use of the theory of quantum scattering, they were able to derive, with some simplifying assumption on the interaction potential and without taking into account the possibility of molecular rotation, a general result about vibrational transition probability during molecular collisions.

Let us sketch their work, starting from the system hamiltonian:

\[ H = H_X(s_{X,i}) + H_M(s_{M,j}) - \frac{\hbar^2}{2\mu} \nabla^2_{r,\theta,\phi} + V(r, \theta, \phi, s_{X,i}, s_{M,j}) \]  

(4.16)

Here we have the sum of the two internal hamiltonians, a term representing the kinetic energy of relative motion and the interaction potential, dependent on both the relative and internal coordinates.

Following SSH, we expand the eigenfunctions \( \psi_E \) of \( H \) in terms of products of the unperturbed eigenfunctions \( \Psi_{X,\kappa} \), \( \Psi_{M,\lambda} \) of the internal hamiltonians and of the eigenstates of the relative motion \( \Phi_{E,\kappa,\lambda} \), so that:

\[ \psi_E = \sum_{\kappa,\lambda} \Phi_{E,\kappa,\lambda}(r, \theta, \phi) \Psi_{X,\kappa}(s_{X,i}) \Psi_{M,\lambda}(s_{M,j}) \]  

(4.17)
Where $\Phi_{E,\kappa,\lambda}(r, \theta, \phi)$ is the eigenfunction of the relative motion with kinetic energy equal to $E_{E,\kappa,\lambda} = E - E_\kappa - E_\lambda$; from now on we will omit the subscript E, but quantities will keep depending on the total energy $E$. Inserting this expansion in the eigenvalue equation $H\psi_E = E\psi_E$, multiplying each of the two sides for $\Psi^*_{X,\xi}(s_{X,i})\Psi_{M,\xi}(s_{M,j})$ and integrating on the internal variables, we obtain:

$$
\left(\nabla^2_{r,\theta,\phi} + k^2_{\xi,\xi}\right) \Phi_{\xi,\xi}(r, \theta, \phi) = \sum_{\nu,\beta} W_{\xi,\alpha,\lambda}(r, \theta, \phi) \Phi_{\alpha,\lambda}(r, \theta, \phi)
$$

(4.18)

where

$$
W_{\xi,\alpha,\lambda}(r, \theta, \phi) \equiv \int \Psi^*_{X,\xi}(s_{X,i})\Psi_{M,\xi}(s_{M,j}) V(r, \theta, \phi)\Psi_{X,\xi}(s_{X,i})\Psi_{M,\xi}(s_{M,j}) ds_{X,i} ds_{M,j}
$$

In the equation above $k_{\xi,\xi} \equiv \sqrt{2\mu E_{\xi,\xi}/\hbar^2}$. We now assume (as in SSH theory) the potential to be central and so independent on the angles $\theta$ and $\phi$, so that we can separate the equation corresponding to each value of the orbital angular momentum; in other words, we ignore the possibility of exchange of angular momentum between the internal and orbital degrees of freedom. Passing to the reduced radial function $R_{\xi,\lambda}^j(r)$, for each eigenvalue $j$ of the orbital angular momentum, we have the following set of coupled differential equations:

$$
\left(\frac{d^2}{dr^2} + k^2_{\xi,\xi}\right) R_{\xi,\lambda}^j(r) = \frac{2\mu}{\hbar^2} \sum_{\alpha,\lambda} \left( W_{\xi,\alpha,\lambda}(r, \theta, \phi) + \delta_{\xi,\alpha} \frac{j(j+1)\hbar^2}{2\mu r^2} \right) R_{\alpha,\lambda}^j(r)
$$

(4.19)

Let us now assume that the two molecule X and M are originally in the states $\nu$ and $\alpha$ respectively, and consider a plane wave along the $z$ axis $e^{ik_{\nu,\alpha}z}$ as the unperturbed state for the relative motion. Now adding the perturbation given by the interaction, the wave functions will change such as to satisfy the following limits:

$$
\lim_{r \to \infty} \sum_j R_{\nu,\alpha}^j(r) P_j(\cos \theta) \approx e^{ik_{\nu,\alpha}r} + e^{ik_{\nu,\alpha}r} f_{\nu,\alpha}(\theta)
$$

(4.20)

$$
\lim_{r \to \infty} \sum_j R_{\nu,\alpha}^j(r) P_j(\cos \theta) \approx \frac{e^{ik_{\nu,\alpha}r}}{r} f_{\nu,\alpha}(\theta)
$$

The first expression, in which the internal final state is still described by $(\nu, \alpha)$, represents elastic scattering and the relative motion at infinity is the sum of a plane wave and an outgoing spherical wave with amplitude given by $f_{\nu,\alpha}(\theta)$. The second one describes instead the inelastic processes, in which there is a transition from $(\nu, \alpha)$ to $(\nu', \beta)$, and the wave function of the relative motion is, at infinity, an outgoing spherical wave.

Therefore, the cross section for each inelastic process $(\nu, \alpha) \to (\nu', \beta)$, for initial velocity $v_0$, is given by:

$$
\sigma_{\nu,\alpha,\nu',\beta}(v_0) = \frac{v_f}{v_0} \int |f_{\nu,\alpha,\nu',\beta}(\theta)|^2 d\Omega
$$

(4.21)

Where the factor $v_f/v_0 = k_{\nu',\beta}/k_{\nu,\alpha}$ appears because of the ratio between the outgoing and the incoming flux.

Now comes the assumption on the potential: SSH assume a simple repulsive exponential interaction, such as to separate the potential as a product of parts depending on each single coordinate; doing so allows them to separately solve the orbital problem with a repulsive exponential potential, for which an analytic solution exists. So the potential can be written as:

$$
V(r, s_{X,i}, s_{M,j}) \equiv V e^{-ar} \prod_i V_{X,i}(s_{X,i}) \prod_j V_{M,j}(s_{M,j})
$$

(4.22)
4.2. VIBRATIONAL ENERGY TRANSFER

Where we have made explicit only the dependence on the relative distance $r$ and left the other potentials implicit because they will depend on the particular configuration chose for the collision.

The solution for the wave functions relative to the inelastic processes are obtained from eqs. 4.19 and may be written, in the limit 4.20, as:

$$\lim_{r \to \infty} \frac{R_{v',\beta}^{j}(r)}{r} P_j(\cos \theta) = \frac{2j + 1}{2k_{v,\alpha}} i^{j} e^{i\eta(u',\beta)} A_{v',\beta}^{j} e^{ik_{v',\beta}r} P_j(\cos \theta)$$  (4.23)

where $A_{v',\beta}^{j} = \frac{2}{k_{v',\beta}} V_{v \to v'}^{X} V_{\alpha \to \beta}^{M} \frac{2\mu V}{\hbar^2} \int_{0}^{\infty} F_{v,\alpha}^{j}(r)e^{-ar} F_{v',\beta}^{j}(r)dr$

The functions $F_{v,\alpha}^{j}(r)$ are the (known) solutions for the problem of a particle of mass $\mu$ in the potential $V e^{-ar}$, with energy $E_{\zeta,\xi} = \hbar^2 k_{\zeta,\xi}^2 / 2\mu$ and angular momentum $j$. The term $V_{\alpha \to \beta}^{M}$ is given by integration on the internal coordinates:

$$V_{\alpha \to \beta}^{M} = \prod_{j} \int \Psi_{M,\alpha}(s_{M}) \Psi_{M,\beta}(s_{M}) ds_{M}$$  (4.24)

And an analogous expression is valid for $V_{v \to v'}^{X}$. The cross section for a particular inelastic process is finally obtained from eq. 4.21, substituting the solutions given in 4.23 and summing on all $j$. The result is:

$$\sigma_{v,\alpha ; v',\beta}(v_0) = \frac{4\pi v_f}{v_0} \sum_{j} (2j + 1) \left( \frac{V_{v \to v'}^{X} V_{\alpha \to \beta}^{M} U_{v,\alpha;v',\beta}^{j}}{k_0 k_f} \right)^2$$  (4.25)

Where $U_{v,\alpha;v',\beta}^{j} = \frac{2\mu V}{\hbar^2} \int_{0}^{\infty} F_{v,\alpha}^{j}(r)e^{-ar} F_{v',\beta}^{j}(r)dr$. The great simplification introduced by the SSH formulation is due to the fact that an analytical expression for $U_{v,\alpha;v',\beta}^{j}$ in function of $j$, $k_0$, $k_f$ and $a$ exists, reducing the problem to the determination of the $V_{v \to v'}^{X}$ and $V_{\alpha \to \beta}^{M}$ terms.

Experimental determination of rate constants

As we said at the beginning of this section, the experimental measurement of rates constants for vibrational excitation/de-excitation remains, when available, the safest way to obtain them. The theoretical approach becomes necessary when too difficult experimental conditions or availability of only indirect probes make the measure less precise. We will briefly describe here the most used experimental method, the one used in determining most rates we will need in Part II of this work.

The typical way to determine collisional rates is known as laser fluorescence technique. It makes use of a fluorescence cell containing a mixture of the gases under study (usually two or three different species), into which a laser beam at the characteristic frequency of one of the molecules is directed. The function of the laser, which is turned on only for a short period of time (of the order of $\mu$s), is to raise the population of one or more excited levels of that molecule far above its equilibrium value, such as to enhance by many orders of magnitude the spontaneous emission from that level. Finally the emission of the whole gas mixture is analyzed, in a direction at right angle with the incoming laser beam, in order to minimize the scattered laser light (see for example [32]).
The amount of light emitted in function of time is linked to the populations of the excited levels and thus gives the time evolution of each of them. In order to get the values of the collisional rates, the set of equations of statistical equilibrium for the system is analyzed\(^4\); as many authors point out (see again [32]), here comes the first problem, because there is the possibility for propagation of errors due to an ill-determination of some known rates needed in the analysis. Moreover, only the total de-excitation rate of the levels under study is determined, because their initial population is above the equilibrium value and the evolution in time will follow some exponential decay (in general, the sum of more exponential decays): this means that in most cases we do not know to which particular level the energy is being transferred, but only that it is.

\(^4\)We will derive these equations in the next chapter and study them in a specific case in Part II.
Chapter 5
The radiative transfer problem in non-LTE

We ended chapter 3 with the need to determine, in order to solve the problem of radiative transfer, the population of the (vibrational) excited levels for which LTE might not hold. In the previous chapter we instead studied the microphysics of collisions, that is the key point in understanding how a state of thermal equilibrium can be established. What is still missing is the link between the microscopic world and the macroscopic one: this link is provided by the so called statistical equilibrium equation, which we are now going to derive, on the basis of what we have studied so far.

5.1 The equation of statistical equilibrium

Let us focus on a particular excited vibrational level \( v \) of some molecule \( X \), which we will indicate as \( X(v) \). That level can relax to lower ones through spontaneous emission of a photon (induced emission, as usual, is taken into account as negative absorption) or through a collisional process, which could be mainly of two kinds, as we said in the previous chapter, a V-V or a V-T process\(^1\). With regards to the process of excitation, it can happen as well through a collisional process (V-V or V-T) or through absorption of a photon; this point is central, because the coupling between the statistical equilibrium equations and the equation of radiative transfer appears here: we need to know the mean intensity to find the actual population of the excited level; this, in turn, determines absorption and spontaneous emission and so the radiation intensity, which we started from. The radiative processes, both absorption and spontaneous emission, play a primary role in bringing vibrational levels out of LTE: absorption of a strong incoming radiative field can significantly raise the excited level population, whereas spontaneous emission in the absence of an intense radiative field and of fast enough collisions can lower it compared to LTE.

We should reflect a bit more on the nature of the various collisional processes, as there is a fundamental difference between V-T and V-V ones: whereas the first ones directly couple the populations of the excited vibrational levels with the thermal reservoir and so contribute to restore LTE, a V-V process couples the population of our vibrational level \( v \) to the one of another vibrational level of the same or of another molecule; if the latter is out of LTE, level \( v \) will feel an inclination to leave LTE too and in this meaning a V-V coupling can represent

\(^1\)As we said before, we will regard the transfer from vibrational to rotational levels as a V-T process as well, because we always assume the rotational degrees of freedom to be in LTE.
an additional way out from LTE, instead that a contribution to thermalization. Besides, chemical production or destruction of a molecule in a specific vibrational state may happen: this processes would deserve a wider discussion but, since they usually play an important role only where an intense radiation field and low densities allow a significant photodissociation of molecules, that is in the highest atmospheric layers (higher than the ones we are going to study), we will always neglect these contributions and avoid going deeper in their study here.

Thus, neglecting chemical production and losses, we can write the statistical equation that rules the evolution of the number density of molecule $X$ in the $v$ level (indicated as $[X_{(v)}]$), just converting in symbols what we said in words:

$$\frac{d[X_{(v)}]}{dt} = - \sum_{v'} [X_{(v')}][R_{v,v'}] + \sum_{v'} [X_{(v')}][R_{v',v}] - [X_{(v)}] \sum_{M,\alpha} k_{\alpha,v,v}^{M-X} [M_{(\alpha)}] + \sum_{M,\alpha,\beta} k_{\beta,\alpha,\alpha',v}^{M-X} [M_{(\beta)}] [X_{(v')}]

(5.1)$$

where $R_{v,\lambda} = \begin{cases} \mathcal{A}_v \lambda & \text{if } \kappa > \lambda \\ \int (\nu_{v,\lambda}) B_{v,\lambda} \left(1 - \frac{g_{\kappa}}{g_{\lambda}} \frac{[X_{(\lambda)}]}{[X_{(v)}]} \right) & \text{if } \kappa < \lambda \end{cases}$

The meaning of the different part of the above equation is as follows:

$\sum_{v'} [X_{(v')}][R_{v,v'}]$ Losses due to absorption of a photon and radiative excitation to a higher level $(v' > v)$ or spontaneous emission and relaxation to a lower one $(v' < v)$. The total Einstein coefficients between vibrational bands and the mean band intensity $\int (\nu_{v,\lambda}) B_{v,\lambda}$ will be defined below.

$\sum_{v'} [X_{(v')}][R_{v',v}]$ Production of $X$ molecules in the $(v)$ state due to radiative excitation/relaxation from other excited states or from the ground.

$\sum_{M,\alpha} k_{\alpha,v,v}^{M-X} [M_{(\alpha)}]$ Overall losses due to collisional relaxation of the $X_{(v)}$ level: the energy lost in the process can excite a vibrational transition in the colliding partner ($M_{\alpha} \rightarrow M_{\beta}$, V-V process) or go directly to translational degrees of freedom, without any further excitation (V-T process). Losses can as well occur after collisional excitation from our level. Here $k_{\alpha,v,v}^{M-X}$ is the total rate for all these processes between molecules $M$ and $X$.

$\sum_{M,\alpha,\beta} k_{\beta,\alpha,\alpha',v}^{M-X} [M_{(\beta)}] [X_{(v')}]$ In the case of production of $X$ molecules in the $(v)$ state, we need to consider all V-V and V-T processes that could have that as final state. $k_{\beta,\alpha,\alpha',v}^{M-X}$ is the characteristic rate: we will speak of a V-V process if $\beta \neq \alpha$ and of a V-T one if they are equal.
5.1. THE EQUATION OF STATISTICAL EQUILIBRIUM

As we will always deal with atmospheres in stationary conditions\(^2\), our interest will be focused on the stationary state of equation above, where concentrations do not change in time; the time-varying version of the equation of statistical equilibrium is instead fundamental in the experimental determination of rate constants, which we briefly described at the end of Chapter 4.

From lines to bands

In equation 5.1 we need to know the rate \( R_{\kappa,\lambda} \) of radiative excitation between two vibrational levels \( \kappa \) and \( \lambda \). The problem is that we only defined the Einstein coefficients for single transitions between two levels with defined rotational and vibrational excitation described by the whole set of vibrational and rotational quantum numbers; yet we want here a sort of total Einstein coefficient between all levels in the vibrational state \( \kappa \) and those in state \( \lambda \). So, we need to sum on the contributions of all rotational sub-levels\(^3\). Besides, a vibrational band is usually some hundreds wavenumbers wide, so that we need to define a proper average in wavenumbers of the mean intensity to be used in eq. 5.1, in place of what we called \( J(w_{\kappa,\lambda}) \).

Indicating as \( \kappa \) and \( \lambda \) the two vibrational states and as \( j \) and \( j' \) the rotational excitations, we define the new quantities so that:

\[
\sum_j \sum_{j'} n_{\kappa,j} f_{j}^{\kappa} \tilde{J}(\nu_{\kappa,j'} - \nu_{\kappa,j}) B_{\kappa,j \rightarrow \lambda,j'} \left( 1 - \frac{g_{\kappa,j} n_{\lambda,j'}}{g_{\lambda,j'} n_{\kappa,j}} \right) \equiv n_{\kappa} \tilde{J}(w_{\kappa} - w_{\lambda}) B_{\kappa \rightarrow \lambda} \left( 1 - \frac{g_{\kappa} n_{\lambda}}{g_{\lambda} n_{\kappa}} \right) \tag{5.2}
\]

Where \( \tilde{J}(w_{\kappa,j'} - w_{\kappa,j}) = \int J(w) \Psi_{\kappa,j \rightarrow \lambda,j'}(w) dw \), \( \Psi \) being the line profile, \( n_{\kappa} \) is the number density of molecules in the vibrational state \( \kappa \) and \( f_{j}^{\kappa} \) is the fraction of the population of the vibrational state \( \kappa \) which is in the rotational state \( j \). If we assume rotational LTE we have:

\[
f_{j}^{\kappa} = \frac{g_{j} e^{-(E_{\kappa,j} - E_{\kappa,j=0})/kT}}{\sum_{j'} g_{j'} e^{-(E_{\kappa,j'} - E_{\kappa,j=0})/kT}}
\]

From eq. 5.2, we then can define the new band quantities:

\[
B_{\kappa \rightarrow \lambda} \equiv \sum_j \sum_{j'} f_{j}^{\kappa} B_{\kappa,j \rightarrow \lambda,j'} \left( 1 - \frac{g_{\kappa,j} n_{\lambda,j'}}{g_{\lambda,j'} n_{\kappa,j}} \right) \left( 1 - \frac{g_{\kappa} n_{\lambda}}{g_{\lambda} n_{\kappa}} \right) \tag{5.3}
\]

\[
\tilde{J}(\nu_{\kappa} - \nu_{\lambda}) \equiv \sum_j \sum_{j'} f_{j}^{\kappa} \tilde{J}(\nu_{\kappa,j'} - \nu_{\kappa,j}) B_{\kappa,j \rightarrow \lambda,j'} \frac{B_{\kappa,j \rightarrow \lambda,j'}}{B_{\kappa \rightarrow \lambda} \left( 1 - \frac{g_{\kappa} n_{\lambda}}{g_{\lambda} n_{\kappa}} \right)} \tag{5.4}
\]

Analogously, for the band coefficient of spontaneous emission, the following relation holds:

\[
A_{\kappa \rightarrow \lambda} \equiv \sum_j \sum_{j'} f_{j}^{\kappa} A_{\kappa,j \rightarrow \lambda,j'} \tag{5.5}
\]

\(^2\)Also for time-varying atmosphere, it suffices to assume that the time required to reach a stationary state is far smaller than the characteristic time of variation of atmospheric conditions.

\(^3\)By sub-levels we mean here all rotational excited levels with the same vibrational excitation; we should not think about them as slightly spaced levels about the same energy, because for the highest excited rotational states the gap with the fundamental \( J = 0 \) level may be very large (even larger than the vibrational gap).
Vibrational temperatures

When an excited state $v$ is out of LTE, its population differs from the equilibrium one at the local kinetic temperature $T$, given by $g_v e^{-E_v/kT} Z_{\text{vib}}^{\text{eq}}$, but we still may want to write it in a similar way. This is usually done defining a fictitious temperature, called the vibrational temperature $T_v$, different for each excited state, that is the temperature at which the considered level would have an equilibrium population equal to the effective one it has now (out of LTE). Thus we are allowed to write:

$$n_v = n_{\text{tot}} g_v e^{-E_v/kT_v} + \sum_{\lambda} g_{\lambda} e^{-E_{\lambda}/kT_{\lambda}}$$

In the equation above we also defined the non-LTE partition function $Z_{\text{vib}}$ of the vibrational levels, which in general differs from the equilibrium one; $n_{\text{tot}}$ is the total number density of the molecule under consideration. Considering the population of the ground level, the vibrational temperature can thus be defined as:

$$n_0 = n_{\text{tot}} g_0 e^{-E_0/kT_0} \rightarrow T_v = -\frac{E_v}{k \log\left(\frac{n_0}{n_v}\right)}$$

Another quantity often used is the ratio $r_v = n_v/g_v^{\text{eq}}$ of the effective population of a vibrational state to its equilibrium value; from the relations above, we obtain:

$$r_v = \frac{Z_{\text{vib}}^{\text{eq}}}{Z_{\text{vib}}} e^{-E_v/k(T_0 - T_v)}$$

On the principle of detailed balance

One key point in understanding the collisional thermalization processes is the principle of detailed balance, which we already used in section 2.1 when following Einstein’s derivation of the spontaneous emission coefficient. The principle of detailed balance states that, at thermal equilibrium, each process is perfectly balanced by its inverse; if we apply it to a single collisional process between $X(a)$ and $M(b)$ that brings them in the states $X(0)$ and $M(0)$, we have that, at thermal equilibrium:

$$k_{M-X}^a(0) \left[ M(0) \right] \left[ X(a) \right] = k_{M-X}^b(0) \left[ M(0) \right] \left[ X(b) \right]$$

So that, writing the equilibrium populations:

$$k_{M-X}^a(0) = k_{M-X}^b(0) \frac{g_a g_{0a}}{g_b g_{0b}} e^{-\left(E_a + E_0 - E_{0a} - E_{0b}\right)/kT}$$

For a generic process (Reagents → Products + $\Delta E$), the inverse rate constant is then given by $k' = k \left( \prod_{i} g_{\text{react}} / \prod_{j} g_{\text{prod}} \right) e^{-\Delta E/kT}$. This relation between the direct and inverse rate constants acts such as to restore the equilibrium ratio between the populations of two different levels; but a true thermalization can only be reached due to the coupling with the ground states.

5.2 Resolution of the non-LTE radiative transfer problem

Taking into account all relevant vibrational levels of each molecule potentially out of LTE (let us say these are $n_v$ vibrational levels), we obtain a system of $n_v$ (in general coupled) equations in the $n_v$ unknowns of the level populations, for each fixed position $x$ in the atmosphere. The
point is that, as we saw in the previous section, these \( n \) equations contain an additional term proportional to the local mean radiance, which in turn depend on the \( n \) unknown populations at all points along all the lines of sight reaching \( x \). So we have to consider, simultaneously with our \( n \) statistical equations, \( m \) equations of radiative transfer, one for each vibrational band involved (in general \( n \neq m \)). The resulting problem is quite complicated: it is non-local, because the level populations at some place in the atmosphere depend on the ones at other positions in the atmosphere, and moreover it is in general non-linear too. Non-linearities in the statistical equations arise when we consider collisions between two species whose populations are among the unknowns of our problem: strictly speaking this is always the case, because when we do not know the population of some level in a molecule we do not know the populations of the other levels as well, but usually we can neglect the non-linear terms without making relevant errors. Another non-linearity might arise in the radiative excitation term: if there is a strong dependence of the absorption coefficient (Eq. 5.3) on the upper level unknown population (that is, if induced emission is important) or if the population of the lower level is itself influenced by the fact that the upper one is out of LTE, because the partition function changes, this term becomes non-linear too.

Linearization of the problem

What is usually done is trying to make the problem linear, neglecting the non-linear terms. So, when writing the statistical equations, it is really important to make a first qualitative analysis on the order of magnitude of the different terms. What it is usually find is that the only relevant collisions are those involving ground states, and the same holds for the radiative excitation terms, that is only excitation from the ground states needs to be considered. The system so obtained still has some non-linear terms: the ground state population depends on the excited states out of LTE, since \( n_0 = n_{\text{tot}} / Z_{\text{vib}} \), and we still have the induced emission term. In the most common situations, we can neglect this minor effects, taking \( Z_{\text{vib}} = Z_{\text{eq}} \) and without considering the induced emission, thus linearizing the equations. Some numbers may clarify this point.

The value obtained for the population ratio of a certain excited level to the ground \( n_e / n_0 \) takes a value of \( \sim 7.5 \cdot 10^{-4} \) for \( E_v = 1000 \text{ cm}^{-1} \), \( T_v = 200 \text{ K} \) and unity degeneracy. More often the energy difference between the levels under study and the ground is larger and this ratio is even smaller: in the case of the first excited state of CO, whose energy is 2143 cm\(^{-1}\), it is of the order of \( 10^{-8} \), at the same vibrational temperature. So we see that considering fixed the ground state population or neglecting the induced emission term does not lead in most cases to significant errors. We yet cannot exclude that this rate could be of some importance in the case of levels with low energy and higher vibrational temperature, and so this will be something to check on a case-by-case basis.

Resolution of the linear problem in the two-level case

Certainly, a jungle of \( n + m \) coupled equations would not encourage to look for a solution of our system, nor would it allow a comprehension of the basic concepts. It is useful then to limit ourselves to a simple two-level system, with a single unknown population and a single radiative transfer band, and try to solve our problem in this case.

Let us consider a molecule in its ground \( X_0 \) and first excited vibrational state \( X_1 \), with unit degeneracy. For the sake of simplicity\(^4\), let us assume that there is only one important

\[^4\text{The generalization here is trivial if we consider only V-T collisional processes or V-V processes with molecules of which we know the excited states populations.}\]
collisonal process of excitation/de-excitation of our molecule in the first level, due to collision with molecule \( M_{(0)} \), that is:

\[
X_{(1)} + M_{(0)} \rightleftharpoons X_{(0)} + M_{(0)} + \Delta E
\]  

(5.10)

In the stationary state and for a point \( x \) in the atmosphere, the statistical equation for \( X_{(1)} \) is then given by:

\[
B_{0 \rightarrow 1} J_{01}[X_{(0)}] + k[X_{(0)}][M_{(0)}] - \mathcal{A}_{1 \rightarrow 0}[X_{(1)}] - k'[M_{(0)}][X_{(1)}] = 0
\]  

(5.11)

Where \( k \) is the rate constant for the collisional process 5.10 (\( k' \) is the inverse rate), and \( \mathcal{A}_{1 \rightarrow 0}, B_{0 \rightarrow 1} \) and \( J_{01} \) are the total Einstein coefficients and the mean intensity of the vibrational band considered; we have left implicit the dependence of all quantities on the position \( x \).

From the equation above, we obtain the ratio of the first vibrational level population to the equilibrium one:

\[
\frac{[X_{(1)}]}{[X_{(1)}]^{(0)}}(x) = \frac{B_{0 \rightarrow 1} J_{01}(x) + k(x)[M_{(0)}](x)}{\mathcal{A}_{1 \rightarrow 0} + k'(x)[M_{(0)}](x)} e^{E_1/kT(x)} \equiv \gamma(x) J_{01}(x) + \beta(x)
\]  

(5.12)

Where we have defined the two quantities \( \gamma \) and \( \beta \) for future use, dividing the expression at the left hand side in a part proportional to the intensity and a part independent on it. We still have an unknown in eq. 5.12, that is the mean band intensity \( J_{01}(x) \) and so we need to consider the equation of radiative transfer. First of all, from the definition 5.4, if we neglect the induced emission term such as to linearize the system, we have:

\[
J_{01} \equiv \int \left[ \sum_{j=1}^{n_{\text{ang}}} \sum_{j'=1}^{n_{\text{ang}}} J_j^0 J(w) \Psi_{0,j \rightarrow j',j}(w) B_{0,j \rightarrow j',j} \right] dw \equiv \int J_{0 \rightarrow 1}(w) J(w) dw
\]  

(5.13)

Here we again left implicit the dependence on position. Now, let us assume that all quantities only depend on altitude and let us discretize our atmosphere so that we have \( n_{\text{alt}} \) altitudes \( (z_1 \ldots z_k \ldots z_{n_{\text{alt}}}) \). If we are looking for the mean intensity \( J(w) \) at point \( z_k \), we should integrate the equation of radiative transfer on solid angle, considering all light rays reaching point \( k \): we discretize this dependence too and say we have \( n_{\text{ang}} \) possible directions at \( (\theta_1 \ldots \theta_m \ldots \theta_{n_{\text{ang}}}) \). For each single wavenumber component \( J(w) \) we may now write the discretized radiative transfer equation, integrating eq. 3.26 over solid angle and omitting the wavenumber dependence:

\[
J_k = \sum_{m=1}^{n_{\text{ang}}} \Omega_m \left[ \prod_{i=1}^{n_{\text{step}}} \Gamma_{i,i+1}^{km} + \sum_{\ell=1}^{n_{\text{step}} \ell \rightarrow 1} \left( 1 - \Gamma_{\ell,\ell+1}^{km} \right) \prod_{j=\ell}^{n_{\text{step}}} \Gamma_{j,j+1}^{km} \right]
\]  

(5.14)

In the equation above, index \( k \) refers to the altitude \( z_k \) at which we want to know the mean intensity \( J \), and index \( m \) indicates the direction: so \( k \) and \( m \) identify a particular line of sight, whereas \( \ell, i, j \) represent the steps made along each line. \( \Omega_m \) is a factor indicating the portion of solid angle corresponding to the discrete direction \( m \); \( \Gamma_{i,i+1}^{km} \) is the original intensity along the considered ray path: if the line of sight intersects the ground, this should be equal to the surface thermal emission, if instead the ray comes from the outer space, \( \Gamma_{i,i+1}^{km} \) should be zero apart from the direction of solar radiation:

\[
\Gamma_{\text{ground}}^{km} = B(T_{\text{ground}}) \quad \Gamma_{\text{space}}^{km} = \frac{\delta_{m,\text{sol}}}{\Omega_m} \frac{\pi R_{\text{sol}}^2}{d^2} B(T_{\text{sol}})
\]
5.2. RESOLUTION OF THE NON-LTE RADIATIVE TRANSFER PROBLEM

Going back to eq. 5.14, all the $\gamma$’s are known from the atmospheric structure and composition (absorption does not depend, at first approximation, on the population of the excited level), and we have $\gamma_{\ell,\ell+1}^{\ell m} = e^{-\alpha(z_{\ell}^{\ell m})\Delta z_{\ell,\ell+1}}$, where $z_{\ell}^{\ell m}$ is the altitude of point $\ell$ along the $(k, m)$ line of sight. So, the unknown quantity in equation above is the source function $S(z_{\ell}^{\ell m})$, which may be written as:

$$S(z_{\ell}^{\ell m}) = \frac{\varepsilon_{\text{other}} + \varepsilon_{10}^\text{eq}[X_{1(1)}]}{\alpha_{\text{tot}}} \frac{[X_{1(1)}]}{[X_{1(1)}]}$$

(5.15)

Where $\alpha_{\text{tot}}$ is the total absorption coefficient, $\varepsilon_{\text{other}}$ is the emissivity due to all contributions but the 1-0 band of molecule $X$ and $\varepsilon_{10}^\text{eq}$ is the emissivity of the 1-0 band with equilibrium population of the excited level. Making use of equation 5.12, we are now able to write the source function $S$ in function of the mean band intensity $J_{01}$. We obtain:

$$S(z_{\ell}^{\ell m}) = \frac{\varepsilon_{\text{other}} + \varepsilon_{10}^\text{eq} \beta}{\alpha_{\text{tot}}} + \frac{\varepsilon_{10}^\text{eq} \gamma_{\ell} J_{01}(z_{\ell}^{\ell m})}{\alpha_{\text{tot}}} = \gamma_{\ell} J_{01}(z_{\ell}^{\ell m}) + \beta_{\ell}$$

(5.16)

Here again we have divided our expression in a part proportional to the mean band intensity and another independent on it, re-defining the two coefficients. Now it is the time to write this expression for the source function back in equation 5.14, so as to obtain a closed equation for the unknown intensities. Since in eq. 5.16 we have the band integrated intensity $\tilde{J}_{01}$, it is convenient here to integrate eq. 5.14 (which is referred to a single wavenumber component) on wavenumbers, following the definition 5.13 of the band intensity. Doing so, the unknown of our problem are the $n_{\text{alt}}$ band intensities $\tilde{J}_{01}(z_{\ell}^{\ell m})$ at each altitude of our grid, and for each one we have a wavenumber-integrated equation of the type 5.14. Thus, we obtain a linear system of $n_{\text{alt}}$ coupled equations:

$$\mathbf{F}_{k\ell} J_{01}(z_{\ell}^{\ell m}) = \mathbf{G}_{k}$$

(5.17)

where,

$$\mathbf{F}_{k\ell} = -\delta_{k\ell} + \sum_{m=1}^{n_{\text{ang}}} \Omega_m \left[ (1 - \gamma_{\ell,\ell+1}^{\ell m}) \gamma_{\ell}^{\ell m} \prod_{j=\ell}^{n_{\text{step}}} \gamma_{j+1}^{\ell m} \right]$$

$$\mathbf{G}_{k} = -\sum_{m=1}^{n_{\text{ang}}} \Omega_m \left[ \gamma_{1}^{\ell m} \prod_{i=1}^{n_{\text{step}}} \gamma_{i+1}^{\ell m} + \sum_{\ell=1}^{n_{\text{step}}} (1 - \gamma_{\ell,\ell+1}^{\ell m}) \beta_{\ell}^{\ell m} \prod_{j=\ell}^{n_{\text{step}}} \gamma_{j+1}^{\ell m} \right]$$

Solving the linear system we finally obtain the mean band intensities at each altitude of our grid and, through equation 5.12, the profile of the unknown excited state population.

We have been dealing here with the simplest possible situation for a radiative transfer problem in non-LTE conditions. Of course, it is possible to generalize it to more general situations, in which we have more excited states and radiative bands. In the most complicated cases or if nonlinear effects are important, an iterative approach can be used instead of the inversion of a matrix but, for our purposes, the approach treated here will be sufficient.
Chapter 6

Retrieval problem

In chapter 3 we were interested in deriving the radiation emitted by an atmospheric slab of which we knew thermodynamic state and concentration of different molecular species. When studying a planetary atmosphere, we usually face the opposite situation, that is we measure a radianc and we want to derive the concentration of a particular molecule or the temperature profile. This is known as the inverse or retrieval problem. Let us focus here on the retrieval of some molecular concentration from a set of limb radianc measurements of the atmosphere. These are observations made from the outer space, with the instrument looking at the atmosphere in a direction that does not intersect the planetary surface\(^1\). The minimal distance from the planet surface and the instrument line of sight is called tangent altitude of the limb measurement. A limb scan is a sequence of radianc measurements acquired with changing tangent altitudes. Here we want to derive from the observations a set of parameters, that is the concentration of our molecule \(M\) at a number of fixed altitudes. If \(y\) is the vector containing the observed spectra in a limb scan and \(x\) is the vector containing our parameters, we can write:

\[
y = f(x) + e
\]

Where \(f : \mathbb{R}^n \to \mathbb{R}^m\) is the function that assigns to a given atmospheric composition (determined through the set of \(n\) parameters) the value of the expected emission at each of the \(m\) limb observations, that is the solution of the direct problem we studied in Chapter 3; \(e\) is the measurement error. Therefore, the difficult point in the inversion is that each limb observation only gives an overall information, dependent on many of our parameters (if not all of them), because our line of sight crosses different atmospheric layers. The problem thus generally does not have a unique solution, because of the unavoidable correlation between the different parameters: the inversion is said to be ill-conditioned. The conditioning can be improved by decreasing the measurement noise through averaging a great number of limb scannings acquired in the same atmospheric conditions. What is usually done is taking the most probable configuration, on the basis of observations only or adding an additional \textit{a priori} information on the value of the parameters, with a suitable error. This approach is known as the maximum likelihood method; we are going to discuss its basis below.

6.1 Maximum likelihood method

Our problem is then to determine, on the basis of a set of measurements \(y\) and of an \textit{a priori} expectation \(x_a\) on the set of parameters (for example, given by other independent measurements), which is the set of parameters \(x\) that maximizes the joint conditional probability

\(^1\)Of course, the same problem can be set for \textit{nadir} observations, looking at the ground, or for observations made from the surface.
\( P(y, x_a | x) \). Since we have assumed as completely independent the set of measurements and the a priori information, we can write:

\[
P(y, x_a | x) = P(y | x) \cdot P(x_a | x)
\]  

(6.2)

We now assume that both our measurement and a priori parameters set follow gaussian distributions about their actual values with known variance-covariance matrices; saying this we exclude the possibility of systematic errors and regard \( y \) and \( x_a \) as random variables. We will call \( \hat{C}_y = E(ee^T) \) the variance-covariance matrix of the set of measurements (\( e \) is the measurement noise, as in eq. 6.1), and \( \hat{C}_a \) that of the a priori information. We are now able to write \( P(y, x_a | x) \), ignoring normalization constants:

\[
P(y, x_a | x) = e^{-\frac{(x_a - x)^T \hat{C}_a^{-1} (x_a - x)}{2}} e^{-\frac{(y - f(x))^T \hat{C}_y^{-1} (y - f(x))}{2}}
\]  

(6.3)

In order to maximize the conditional probability, we have to minimize the \( \chi^2 \) function in the exponent, given by:

\[
\chi^2 = (x_a - x)^T \hat{C}_a^{-1} (x_a - x) + (y - f(x))^T \hat{C}_y^{-1} (y - f(x))
\]  

(6.4)

Our solution to the problem is the value of \( x \) for which the \( \chi^2 \) function is at a minimum. We then have to look for the points\(^2\) in which \( \nabla_x \chi^2 = 0 \) that is:

\[
g(x) = \nabla_x \chi^2 = -2 \hat{J}^T \hat{C}_y^{-1} (y - f(x)) - 2 \hat{C}_a^{-1} (x_a - x) = 0
\]  

(6.5)

Where \( \hat{J} \) is the jacobian matrix of the function \( f \), our direct model, with respect to each of the parameters; that is \( \hat{J}_{ij} = \frac{\partial f_i}{\partial x_j} \). Equation 6.5 does not have an analytic solution in the great majority of cases, depending on the complexity of the function \( f \); in our case, in which \( f \) is the result of integration of the radiative transfer equation along our line of sights, there is no alternative to considering a numerical approach in its resolution.

### 6.2 Numerical inversion procedures

The equation \( g(x) = \nabla_x \chi^2 = 0 \) can be solved numerically with an iterative procedure. The success of such iteration will depend on the degree of non-linearity of function \( f \), so that a procedure that is successful in one case may not be equally adequate for a different situation. Let us begin with one of the methods most used, first derived by Newton and then modified by Gauss.

**Gauss-Newton method**

If we have a scalar function \( g(x) \) of which we want to find the closest zero to our starting point \( x_1 \), one possible way to do this is to follow the tangent till it intersect the \( x \) axis and starting again from there (let us call this point \( x_2 \), calculating the new tangent at \( x_2 \) and repeating the procedure. Generalized to the many variables case where \( g \) is a vectorial quantity depending on the vector \( x \), this iterative procedure can be written:

\[
x_{i+1} = x_i - (\nabla_x g(x_i))^{-1} g(x_i)
\]  

(6.6)

\(^2\)In this way we look for the stationary points. It has then to be checked that the point found is actually the absolute minimum.
6.2. NUMERICAL INVERSION PROCEDURES

The quantity in squared parenthesis is the Hessian of the \( \chi^2 \) function and we can write it explicitly starting from equation 6.5, obtaining:

\[
\nabla_y g(x) = 2 \tilde{J}^\top \tilde{C}_y^{-1} \tilde{J} - 2 [\nabla_y \tilde{J}] \tilde{C}_y^{-1} (y - f(x)) + 2 \tilde{C}_s^{-1}
\]

(6.7)

The method involving the full expression 6.7 for the Hessian is known as the Newton method. The second term in this expression, however, is quite complicated (it is a third-rank tensor) and is related to the second derivatives of the function \( f \). The calculation of this term requires a significant effort in terms of computational time. For this reason, an approximation is often made, first proposed by Gauss: the dependence on \( x \) of the Jacobian of our direct model is neglected and so is the second term in expression 6.7. The result is the well-known Gauss-Newton method. Making all quantities explicit (from eqs. 6.5, 6.6 and 6.7):

\[
x_{i+1} = x_i + (\tilde{J}^\top \tilde{C}_y^{-1} \tilde{J} + \tilde{C}_s^{-1})^{-1} \left[ \tilde{J}^\top \tilde{C}_y^{-1} (y - f(x)) + \tilde{C}_s^{-1} (x_a - x) \right]
\]

(6.8)

We see here that an additional effect of adding the \textit{a priori} estimate \( x_a \) is to assure the invertibility of matrix \( \tilde{J}^\top \tilde{C}_y^{-1} \tilde{J} + \tilde{C}_s^{-1} \), which would not otherwise be guaranteed. It is important to give a reasonable value to the error of \( x_a \): in case we set a too small error, the term \( \tilde{C}_s^{-1} \) would dominate with respect to the other, with the result that our iteration will converge to the \textit{a priori} estimate. The opposite case corresponds to an inversion based on the measurements only and we might find some problems in this case. The iteration can be stopped with some convergence criterion, that is usually the requirement that the computed \( \chi^2 \) and that of the previous iteration have a relative difference smaller than some fixed value. The error on the retrieved parameters \( x \) can be related to those on the measurements and on the \textit{a priori} estimate. Using the relation 6.8 above, we obtain, for the variance-covariance matrix \( \tilde{C}_x \):

\[
\tilde{C}_x = (\tilde{J}^\top \tilde{C}_y^{-1} \tilde{J} + \tilde{C}_s^{-1})^{-1}
\]

(6.9)

The Gauss-Newton method is quite powerful, but may fail in case of strongly non-linear problems, in which the step might be too large and project the state vector \( x_{i+1} \) out of the forward model linearity region. Of course there is a huge amount of works on the convergence of numerical methods and we will not go in depth in this matter. Yet we will only briefly explore an optimization to the Gauss-Newton method, due to the works of Levenberg and Marquardt.

Levenberg-Marquardt method

The Levenberg-Marquardt procedure is also known as the \textit{damped least squares method}. The main problem with the Gauss-Newton method is that it may fail convergence due to too large steps: thinking about the one-dimensional case, we can understand that, if we are in a relatively flat region, following the tangent may project us too far, probably passing the actual zero. The idea is then to reduce the single steps, assuring that the \( \chi^2 \) function is still decreasing. This result is obtained by adding a new term to equation 6.8, so that:

\[
x_{i+1} = x_i + (\tilde{J}^\top \tilde{C}_y^{-1} \tilde{J} + \tilde{C}_s^{-1} + \lambda_{\text{lm}} \tilde{D})^{-1} \left[ \tilde{J}^\top \tilde{C}_y^{-1} (y - f(x)) + \tilde{C}_s^{-1} (x_a - x) \right]
\]

(6.10)

Where \( \tilde{D} \) is a diagonal matrix that can be taken equal to the diagonal elements of \( \tilde{J}^\top \tilde{C}_y^{-1} \tilde{J} + \tilde{C}_s^{-1} \); \( \lambda_{\text{lm}} \) is a positive scalar parameter. The original idea of Levenberg was to determine \( \lambda_{\text{lm}} \) so as to minimize the \( \chi^2 \) function at each iterate. Although this approach would certainly lead to the right step, the computational time needed for this operation is quite
large. A more efficient approach was later introduce by Marquardt. It consists in choosing $\lambda_{LM}$ at the first iteration so that the $\chi^2$ decreases, and then move to the next iteration. The best strategy is to start from a small $\lambda_{LM}$ value, so as to maximize the step size (in the limit $\lambda_{LM} \to 0$ we are in the Gauss-Newton case), then eventually raise it if the $\chi^2$ increases.

The Levenberg-Marquardt method is the one adopted in the inversion program used later in Part II for the data analysis, in Chapter 8.
Part II

Case study: CO emission in Titan’s atmosphere
Chapter 7
Non-LTE processes in Titan’s atmosphere

Titan is the largest satellite of Saturn, orbiting at a mean distance of about $1.2 \times 10^6$ km around it, and was discovered in 1655 by Huygens. With a mean radius of about 2575 km, it is the second largest satellite of the solar system after Ganymede and is slightly bigger than planet Mercury. But the most interesting aspect regarding Titan is its dense atmosphere, with a surface pressure about 1.5 times the Earth’s one and a molecular number density at the surface about 5 times larger. No other satellite in the Solar system shows such an important atmosphere. Due to the large distance from the Sun, which varies with that of Saturn between 9.0 and 10.1 AU, the solar flux is approximately one percent that on Earth and thus the mean surface temperature is around 90 K.

Our knowledge of Titan’s atmosphere has greatly improved in the last 20 years thanks to the Voyager mission, launched in 1977 and passed right close to Titan in 1980, and to the Cassini one, which has been orbiting Saturn since 2004 and made many Titan’s flybys since then. The Cassini mission is still operating, carrying on board many different instruments for the analysis of atmospheres; among them, CIRS (Composite InfraRed Spectrometer) which works in the mid- and far-infrared (at wavelengths larger than 6.5 $\mu$m) and VIMS (Visual and Infrared Mapping Spectrometer) measuring from 300 nm to 5.1 $\mu$m. Besides, the Huygens probe, detaching from Cassini spacecraft, descended in Titan’s atmosphere and landed on its surface, giving the first direct determination of atmospheric structure and composition.

Temperature and pressure profiles

Despite the new data that have come in the latest years, our knowledge of Titan’s atmosphere still presents many unknown aspects, among which the thermal structure. The profile used in most works on atmospheric emission was determined by Yelle et al. [38] on the basis of measurements made by the Voyager 1 spacecraft, with instruments working in three different spectral regions (radio (RSS), infrared (IRIS) and ultraviolet (UVS)). Yelle and collaborators fitted the temperature and mass density profile from this measurements, adding the constraint of hydrostatic equilibrium and making use of further information derived by the first theoretical models of the atmospheric structure. The best-fit result is shown in Figure 7.1.

We can see that this model atmospheric structure presents similarities with the Earth’s one, showing a first temperature inversion at 40 km, with a minimum value of 70 K, a second one at 270 km, with a maximum of 185 K, and a third one at about 500 km: the atmosphere can thus be divided in troposphere, stratosphere, mesosphere and thermosphere. In January 2005 an in situ measurement of the temperature profile was taken by the Huygens probe, during...
Figure 7.1: Yelle recommended profiles for temperature and pressure. Data taken from [38].
its descent in Titan’s atmosphere; the landing point was situated at a latitude of 20° S (see Fulchignoni et al. [39]). The direct measurement of temperature and pressure was possible only below 150 km, whereas in the upper atmosphere the density profile was determined from data on the deceleration of the probe. The result (see Figure 7.2) is in quite good agreement with the Yelle one below about 500 km, whereas in the upper part 20 K fluctuations around a mean temperature of 170 K are visible, probably due to gravity waves.

More recently, new data on the temperature profile on Titan and a first evaluation of the latitude and seasonal variations came from analysis of the CIRS data (see Flasar et al. [40], Achterberg et al. [41],[42]). The temperature profile (retrieved only below 400 km in [40] and below 500 km in [41],[42]) not too far from the equator is in quite good agreement with the previous ones, giving almost the same altitudes for the main temperature inversions. As Achterberg et al. have determined, the temperature structure for different latitudes can differ in a significant way from the nominal profile and show an important seasonal dependence. The upper panel in Figure 7.3 shows mean temperatures determined with data collected between 2004 and 2006, during the second part of northern winter. As we can see the structure is significantly different between the northern regions and the southern ones. The lower panel shows latitude dependence of the temperature profile for the southern hemisphere in 2007; the upper stratospheric inversion takes place at higher altitudes and the general trend is a lower temperature below that level and higher above, with stronger differences for latitudes near the pole. These conclusions are in general agreement with those by Teanby et al. [60], which as well determine the southern thermal structure in year 2007 to be significantly different form the Yelle one, especially at large latitudes.

We will comment further on the influence of the different profiles in the data analysis.

**Atmospheric composition**

Measurements of atmospheric emission from Earth or made by the instruments on board Voyager 1 and Cassini, have allowed the detection of many species, among which CH₄, HCN, CO, CH₃CN and several hydrocarbons of the type CₙHₙ. Direct detection of the atmospheric constituents has then been possible during the descent of the Huygens probe, with the aid of a mass spectrometer: the presence of many constituents was confirmed, as well as that of the main component since then only theorized, N₂, which cannot be seen in the infrared spectra. We now know that Titan’s atmosphere is made almost completely of N₂ and CH₄, the latter

Figure 7.2: Comparison between the HASI and Yelle temperature profiles (after Fulchignoni et al. [39]).
Figure 7.3: Upper panel: Titan’s mean temperatures between 2004 and 2006. We can see the strong differences between northern (winter) and southern (summer) region. After Achterberg et al. (2008) [41]. Lower panel: temperature profiles in year 2007 at different latitudes in the Southern hemisphere, Achterberg et al. (2011) [42]. Courtesy of R. Achterberg.
reaching 5% at the surface and approximately 1-2% in the upper regions. The concentration of the traces constituents is still object of analysis on the basis of observational data and has been studied thoroughly with atmospheric photochemical models, which give constraints to their abundance. Among these, two of the most complete are the works by Lara et al. [43] and Wilson & Atreya [44]: they both solve the steady state continuity equation 7.1 simultaneously for many particle species, including all photochemical ways of production and destruction and the effect of molecular and eddy diffusion.

$$P_X - \left[ X \right] L_X = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \Phi_X \right)$$ (7.1)

Where $P_X$ and $L_X$ are the production and loss terms, $\Phi_X$ is the vertical flux of $X$ molecules. Critical points in these analyses are the rate constants for the involved reactions, not always well known at the temperatures of Titan’s atmosphere, and the ingoing fluxes at the boundaries, that is from the ground (outgassing from the interior) or from outer space (deposition by meteorites).

Lara et al. and Wilson & Atreya both single out two major chemical cycles, the first involving CH$_4$ and the hydrocarbons family, initiated by the photolysis of methane to produce CH$_3$, and the second regarding N$_2$ and nitriles (like HCN).

Oxygen chemistry and the CO mystery

Oxigen compounds play a secondary role in Titan’s atmospheric chemistry, due to the poor abundance of oxygen. To date only three molecules carrying oxygen have been detected in the atmosphere: CO$_2$, CO and H$_2$O. Among them CO is by far the most abundant, compared with a mean concentration of about $1.5 \times 10^{-9}$ for CO$_2$ and $4 \times 10^{-10}$ for H$_2$O.

CO observations

Observations made up to now generally agree that the total concentration of CO in the atmosphere is of the order of $10^{-5}$ but do not agree at all on more quantitative estimates nor on the distribution of CO mixing ratio with altitude. Observations from Earth have lead to contrasted results up to now: Noll et al. ([45], 1996), observed the signal in the 4.7 $\mu$m region, showing absorption in the CO 1-0 vibrational band of solar reflected radiation and concluded that the tropospheric abundance of CO was about 10 ppmv if radiation was reflected at the surface, although a larger concentration would have been compatible with an higher position of the reflecting layer; Hidayat et al. ([46], 1998), observing rotational transitions at different millimeter wavelengths, found an higher concentration (27 ppmv) in the lower stratosphere, decreasing to 5 ppmv in the higher part (300 km). Gurwell & Muhleman ([47], 2000), on the basis of interferometric observations of the CO 2-1 pure rotational line concluded that the observed spectrum was best fitted by a uniform 50 ppmv distribution, but pointed out that there was not enough sensitivity to distinguish it from a non uniform profile raising from 48 ppmv in the lower stratosphere to 60 ppmv in the upper stratosphere at 300 km. More recently, absorption of the reflected solar light in the 4.7 $\mu$m region has again been analyzed by Lellouch et al. ([48], 2003) and Lopez-Valverde et al. ([49], 2005), leading to a tropospheric abundance of (32±10) ppmv; in the latter a non-LTE model of CO excited states was developed and the result suggested a larger abundance in the stratosphere, about 60 ppmv, even if the authors pointed out that the fit was not satisfying in any case and did not allow a strong argument in determining CO concentration, due to possible problems in the CO collisional model. The last observation that has been analyzed up to now is the first based on VIMS data (see section below) in the 4.7 $\mu$m region: Baines et al. ([50], 2006) focused on spectra observed on the night
side of the planet, in order to avoid the complications of non-LTE and scattered solar light and agreed with the 32 ppmv concentration determined by Lellouch et al. and Lopez-Valverde et al. for the stratosphere up to 300 km.

**Photochemical models of CO abundance**

According to Lara et al., the oxygen cycle begins with the photolysis of CH₄ to produce CH₃ and CH₂ and of H₂O to produce OH; these compounds then combine to produce CO:

\[
OH + CH_3 \rightarrow CO + 2H_2 \quad OH + CH_2 \rightarrow CO + H_2 + H \quad (7.2)
\]

Carbon monoxide can then itself react with OH to produce CO₂ (CO+OH→CO₂+H), but is produced again through photolysis of CO₂ and further reaction of the produced atomic oxygen with C₂H₂; the total effect of the last two processes is an effective recycling of CO through the photochemical route:

\[
H_2O + CO \rightarrow CO_2 + 2H \quad \rightarrow \quad 2CO_2 + C_2H_2 \rightarrow 4CO + 2H \quad (7.3)
\]

The combined effect of the two reactions above is that CO chemical lifetime in Titan’s atmosphere is very high, about \(7.8 \times 10^{11}\) s (at 300 km, as given by Wilson & Atreya, [44]). This leads to the fact that CO has to be well-mixed in whole Titan’s atmosphere, following a uniform concentration profile if no external production exists. It turns out that for a CO concentration of \(5 \times 10^{-5}\), a further external production of \(4 \times 10^{-6} \text{ cm}^{-2} \text{ s}^{-1}\) is needed for a steady state to be maintained. Given that the quantity deposited in the typical time-scale for atmospheric diffusion is far lower than the overall CO atmospheric content, a uniform distribution profile is expected.

It should be pointed out that this conclusion is based on theoretical models of atmospheric diffusion and photochemical processes on Titan, that still have to be tested; one critical point of all this works is the coefficient for eddy diffusion, which is estimated on the basis of the concentration of tracer gases (that is gases with a reasonably large chemical lifetime, so as to be sensible mostly on diffusion) and is matter of discussion. In any case, a mystery remains about which the external sources of oxygen on Titan’s atmosphere might be, if the CO mixing ratio is actually as high as determined by the latest observations and if the CO is in steady state. Lara et al. hypothized that such continuous source of CO in Titan’s atmosphere might be due to deposition of water by micrometeorites (like those constituting Titan’s rings) in the highest part of the atmosphere, then dissociated to produce OH (which in turn produces CO through the processes 7.2). But Wilson & Atreya point out that processes 7.2 have never been observed in laboratory to produce CO and their rates may be far too small to explain the CO external source in this way. According to them, the most likely source of CO might be outgassing from the interior of the planet, although there are not models that can give a meaningful estimate of this process. The possibility of CO not being in a steady state has also been explored; this would mean that CO was up to 14 times more abundant in the atmosphere during Titan’s earlier life, being constantly deposited on the ground.

An accurate retrieval of the actual CO profile up to 600 km could be a test for the photochemical models and at the same time give constraints to which may be the origin of oxygen in Titan’s atmosphere.

**Aerosols and haze**

The evidence of an important presence of aerosols in Titan’s atmosphere was clear since the very first observations by Voyager I. The images acquired in the visible showed in fact a dark
reddish haze layer covering the whole planet, which prevented from seeing the planetary surface. The nature and origin of particles constituting this haze layer has been object of discussion for many years and, as the real nature was unknown, the name tholins was coined to refer to them. In year 1984, Khare & Sagan ([61], [62]) performed an Urey-Miller like experiment for a gas mixture similar to the upper part of Titan’s atmosphere (10% CH$_4$ and 90% N$_2$), using electrical discharges to simulate the effect of UV radiation and cosmic rays. The result, after 4 months, was a dark red solid composed by tens of different organic polymers, many of which of biological importance. Then they analyzed the optical properties of this solid and found them to be in good accordance with the observed albedo in the visible. The tholin refractive index, measured on a thin film of the solid obtained, is shown in Figure 7.4. The imaginary part of the refractive index shows a strong dependence on frequency, whereas the real part has a smoother dependence and, in the infrared region between 4 and 5 $\mu$m, there only small variations about a value of 1.6.

Figure 7.4: Real (top) and imaginary (bottom) parts of the tholins refractive index, measured on a laboratory simulated compound (after Khane & Sagan, [61]).

More recently, theoretical models have tried to predict the actual size and distribution of aerosol particles in Titan’s atmosphere. Lavvas et al. (see [64] and [65], 2008) developed a coupled photochemical and microphysical model. They computed the production profile of several polymers starting from the known concentration of different key molecules ($C_nH_m$, HCN, $C_3N_2$, HC$_3$N..); from there, the rate of formation of agglomerates of these polymers can be calculated, giving the characteristic size and abundance of particles for different altitudes. Finally, using Mie theory and the results by Khare & Sagan on the refractive index, they derived the effective aerosol column opacity, as a function of wavelength, that is shown in Figure 7.5. We see two curves, one for total extinction and the other for absorption only, the first one peaking at a value of 2 in the visible part of the spectrum: this means that almost 90% of incoming visible photons are absorbed or scattered before reaching the surface, and thus we actually observe the atmosphere, instead that the surface, when looking at Titan in the visible. In the region between 4 and 5 $\mu$m absorption dominates and shows a particular dependence
on frequency, that peaks about 4.7 \( \mu \text{m} \), with a total column extinction of \( 2 \times 10^{-2} \) at the maximum. For the estimation of the scattering part, given by the difference of the two curves, we must pay attention, as the graph is in logarithmic scale; actually, the scattering column opacity turns out to be only weakly dependent on frequency, being approximately \( 3 \times 10^{-3} \) at 4 \( \mu \text{m} \) and \( 2 \times 10^{-5} \) at 5 \( \mu \text{m} \). Let us have a look at the region around 2.3 \( \mu \text{m} \), typical of the first CO overtone band. The effect here is slightly larger, giving a total column extinction of \( 5 \times 10^{-2} \), mainly due to scattering.

![Figure 7.5: Haze total column opacity in the model by Lavvas et al.](image)

7.1 VIMS measurements of Titan’s atmosphere

The Visual and Infrared Mapping Spectrometer (VIMS) is an imaging spectrometer which acts in a wide spectral region ranging from 0.3 to 5.1 \( \mu \text{m} \). It has been thought to work in sinergy with other imaging and spectrometric instruments on board the Cassini spacecraft and it is the result of an optimization between the requirement of high spectral and spatial resolution. The spectral resolution in the infrared region is of\(^1\) 16.6 nm, and does not allow the identification of single spectral lines, making the data more difficult to analyze. On the other hand VIMS has enough spatial resolution so as to allow a study of its atmosphere with the change in altitude: in order to collect enough signal from each spatial point, the instrument is equipped with a Ritchey-Chrétien telescope (23 cm in diameter). VIMS takes an image of Titan and its atmosphere with 64 \( \times \) 64 pixels (each with a field of view 0.5 \( \times \) 0.5 mrad), and for each pixel there are 256 spectral points.

Each spectral point corresponds to the signal generated at one of the 256 Indium Antimonide (InSb) photodiodes that constitute the detector array; these are kept at a temperature of 60 K, in order to reduce the noise given by thermal excitation (as it was designed to measure the faint signal of the cold Titan’s atmosphere). The upper spectral limit of the instrument is

\(^1\)The spectral resolution is higher in the visible, about 7.3 nm.
explained with the characteristic band gap of InSb, which is at approximately $0.24 \mu m$ ($5.2 \mu m$) at the working temperature.

The typical image is like that in Figure 7.6, here shown with latitude and altitude grids, and for two different wavelengths: the left one at $4.7 \mu m$ shows the emission right in the middle of CO vibrational band, whereas the other has been taken at $5 \mu m$, where there is no important contribution from molecular emission. Just looking at these images, one could guess the presence of CO in Titan’s atmosphere.

![Figure 7.6: Images taken by VIMS in 2007 (cube 9485) at 4.7 \mu m and 5 \mu m. Courtesy of M. L. Moriconi (ISAC - Roma).](image)

We will not deal here with the calibration in wavelength and intensity of the raw data, done by the VIMS team, and we will focus instead on the study and simulation of already calibrated data. Thus, we will consider only the limb measurements, those which do not look at the planet surface but only through the atmosphere, as they allow a higher altitude resolution.

**Data of the CO emission**

As we said, we will focus in the following on the study of emission. A limb spectrum taken by VIMS, in the full spectral range, appears like that in Figure 7.7. We can distinguish the strong CH$_4$ peak at $3.3 \mu m$ and the HCN one at $3.0 \mu m$; these two emissions have already been analyzed from VIMS data and have allowed the determination of the concentration of this two species in the highest part of the atmosphere (see [51] and [52]). The characteristic feature of CO can be distinguished at the right side of this image. In that figure we also plotted a Planck function at Sun’s temperature, adequately normalized to fit the data: given that this spectrum is taken at day-time at 300 km, there is a continuous signal due to scattering of solar light, which will be a considerable complication to data analysis. The scattering signal is however very weak in observations above 400 - 500 km, depending on the wavelength.

As we said, we will focus here on the $4.7 \mu m$ region of the spectra, where there is the strongest detectable contribution due to CO (the overtone band at $2.3 \mu m$ is far too weak for VIMS to detect it). Before analyzing the data, it is worth having a first look at some VIMS spectra at these wavelengths. To make this first qualitative study, we averaged around one hundred of VIMS data spectra, in order to enhance the signal to noise ratio. As we wanted to point out the dependence of CO emission on altitude and solar zenith angle, we averaged the
CHAPTER 7. NON-LTE PROCESSES IN TITAN’S ATMOSPHERE

measurements in bins of 50 km with respect to the tangent altitude\(^2\) and in four solar zenith angle intervals\(^3\): below 40°, between 40° and 70°, between 70° and 90°; night indicates here a sza larger than 4 90°. The results of this average for some altitudes are in Figures 7.8 and 7.9.

As we can see, the resulting spectra is strongly dependent on the solar zenith angle. We clearly distinguish the P and R bands of CO and another peak at smaller wavelengths, which is the Q band of CH\(_3\)D. The first thing to note is how the CO emission during night almost disappears, even at the 250 km: it would be impossible to make a retrieval of CO above this altitude using the data taken on the night side of the planet. If we focus on the spectra at 250 km (Fig.7.9, right panel), we see how the CO signal raises for lower solar zenith angles: this is a first hint to the non-LTE behaviour of the CO emission, which appears to be stronger for a stronger solar flux, but it still is not very clear from this image, given that the whole spectral region appears to have an enhanced emission with the sun higher with respect to the horizon. This is due to the strong continuum contribution produced by scattering of solar light; this is clearer if we look at a greater portion of the spectra, like Figure 7.7 above. Now let us look at Figure 7.8: if we focus on the relative intensity of the CH\(_3\)D and CO peaks, we see that this changes dramatically with different solar positions, and the same can be seen in Figure 7.9; this effect can only be produced by a run-away of CO excited states from their equilibrium populations. This manifests the necessity for a thorough study of the collisional and radiative processes responsible for enhancing the CO excited states populations. In the next section we

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\(^2\)That is, the minimum distance between our line of sight and the planet’s surface.

\(^3\)The solar zenith angle is meant here referred to the vertical of the tangent point.

\(^4\)Strictly speaking, whether it is night or not at solar zenith angles between 90° and 100° depends on the altitude; however, for this preliminary study we put all measurements with sza larger than 90° in the same solar zenith angle interval, as the CO signal is always very weak for them.
Figure 7.8: Average of VIMS data between 2004 and 2009, for four different ranges of solar zenith angles. Here the average spectra around a tangent altitude of 350 km.

Figure 7.9: Average of VIMS data between 2004 and 2009, for four different ranges of solar zenith angles. Here the average spectra for tangent altitudes around 500 km (left panel) and 250 km (right panel).
will develop a model for these phenomena in Titan’s atmosphere.

### 7.2 CO collisional model

As we have seen from the VIMS measurements in the preceding section, in order to analyze CO day-time atmospheric emission a non-LTE treatment is needed, determining the populations of its excited states with the approach developed in Chapter 5. Here we are developing a model that rules the excited states populations, based on the knowledge of the collisional rates for excitation and de-excitation and on the relative abundance of the species in Titan’s atmosphere. The estimations are difficult when the rates for some collisions are not well known, particularly at the unusual low temperatures of Titan.

A previous work on this topic has been done by Lopez-Valverde et al. [49]. The collisional model we are describing here presents many points in common with that one, but with two important differences that we will comment further on. As we made at the end of Chapter 5, we will consider the population of the ground state as fixed: the error made is completely negligible, given that the relative population of the first excited state will never be larger than $10^{-7}$, even in a strong non-LTE regime. Looking for the key collisional partners in exciting and de-exciting CO, we shall at first look at the most abundant species in Titan’s atmosphere. In fact, the most important processes in determining the CO (1) and CO (2) populations turn out to be the collisions of CO with CH$_4$ and N$_2$, apart from the radiative processes of absorption and spontaneous emission. We will focus mainly on the population of the first excited state, then taking into account and commenting the case of the second excited state. One of the fastest process in the de-excitation of CO(1) is the vibrational energy transfer towards the first excited state of N$_2$, due to the quite large rate ($1.4 \times 10^{-15}$ cm$^3$s$^{-1}$ at 170 K, [53]) and to the large abundance of N$_2$. The point is that the energy gap between the two first excited states of CO (2143 cm$^{-1}$) and N$_2$ (2330 cm$^{-1}$) is very small, coupling their populations in a strong way. Therefore, we need to consider the statistical equilibrium equation for the first excited state of N$_2$, monitoring its population too. We list here the fundamental processes at work, commenting below their relative importance and the difficulties of this model.

#### Vibrational - Vibrational (V-V) processes

1a. $CO(1) + N_2 \rightleftharpoons CO + N_2(1) + \Delta E$ \hspace{1cm} $\Delta E = -188$ cm$^{-1}$

2a. $CO(1) + CH_4 \rightleftharpoons CO + CH_4(\nu_2) + \Delta E$ \hspace{1cm} $\Delta E = 610$ cm$^{-1}$

2b. $CO(1) + CH_4 \rightleftharpoons CO + CH_4(\nu_4) + \Delta E$ \hspace{1cm} $\Delta E = 832$ cm$^{-1}$

2c. $CO(1) + CH_4 \rightleftharpoons CO + CH_4(2\nu_4) + \Delta E$ \hspace{1cm} $\Delta E = -453$ cm$^{-1}$

3a. $N_2(1) + CH_4 \rightleftharpoons N_2 + CH_4(\nu_2) + \Delta E$ \hspace{1cm} $\Delta E = 797$ cm$^{-1}$

3b. $N_2(1) + CH_4 \rightleftharpoons N_2 + CH_4(\nu_4) + \Delta E$ \hspace{1cm} $\Delta E = 1019$ cm$^{-1}$

3c. $N_2(1) + CH_4 \rightleftharpoons N_2 + CH_4(2\nu_4) + \Delta E$ \hspace{1cm} $\Delta E = -266$ cm$^{-1}$

(7.4)

#### Vibrational - Translational (V-T) processes

4. $CO(1) + N_2 \rightleftharpoons CO + N_2 + \Delta E$ \hspace{1cm} $\Delta E = 2143$ cm$^{-1}$

2d. $CO(1) + CH_4 \rightleftharpoons CO + CH_4 + \Delta E$ \hspace{1cm} $\Delta E = 2143$ cm$^{-1}$ (7.5)

3d. $N_2(1) + CH_4 \rightleftharpoons N_2 + CH_4 + \Delta E$ \hspace{1cm} $\Delta E = 2330$ cm$^{-1}$

5. $N_2(1) + N_2 \rightleftharpoons N_2 + N_2 + \Delta E$ \hspace{1cm} $\Delta E = 2330$ cm$^{-1}$
7.2. CO COLLISIONAL MODEL

The rates for the V-T processes 4 and 5, lacking experimental values, are taken from the theoretical calculations by Shin (see [31], [54]): the de-excitation of N_2(1) through N_2 is calculated to have a value of \(1 \times 10^{-23}\), much lower than the other rates involved. For the CO(1) V-T de-excitation through N_2, his calculations do not reach our low temperatures, but we can at least place a higher threshold: at 300 K the ratio of the rates of processes 1. and 4. is of \(10^{-6}\) and it is going to increase with lower temperature values. In fact, if we assume that the ratio \(k_1/k_4\) follows the classical Landau-Teller behaviour \(k_1/k_4 \propto e^{-(\alpha_1-\alpha_4)(T^{-1/3} - T_0^{-1/3})}\), see Chapter 4, with \(\alpha_1\) and \(\alpha_4\) being characteristic constants for the two processes \((\alpha_1 < \alpha_4)\), according to Shin) at lower temperatures \((T < T_0)\) it is expected to be even smaller. However, the actual dependence of transition probabilities is somewhat weaker than \(\log P \sim -T^{-1/3}\), as Shin himself points out, so that we will keep the value of \(10^{-23}\) in our model. The rate constants for the overall processes 2 and 3 are taken from Gregory et al. [32], who studied these relaxation processes in a large temperature range, from 300 K to below 100 K. In that work, using the laser fluorescence technique, they excited with a laser impulse the CO(1) population in a mixture of N_2, CO and CH_4 and then analyzed the evolution of the system by monitoring the emission in the CO 1-0 band. The N_2(1) state was pumped in the excited level through collisions with CO (process 1 in the table above). In this way, they were able to derive an accurate measurement for the de-excitation rates of processes 2 and 3. However, the experiment did not clearly distinguish between the different de-excitation channels, as this needed the analysis of the emission from CH_4 excited states. Due to the large energy gap between CO(1) and the ground, the more likely pathways for the de-excitation process of CO(1) and N_2(1) are the V-V transfers to the CH_4 levels closest in energy, which are:

\[
\begin{align*}
CH_4(\nu_2) &\rightarrow E = 1533 \text{ cm}^{-1} \quad (g = 2) \\
CH_4(\nu_4) &\rightarrow E = 1311 \text{ cm}^{-1} \quad (g = 3) \\
CH_4(2\nu_4) &\rightarrow E = 2596 \text{ cm}^{-1} \quad (g = 6)
\end{align*}
\]

The V-T routes (2d and 3d) are expected to be negligible given the much larger energy gap. Gregory et al. regarded as negligible the inverse processes 2c and 3c in the excitation of CO(1) and assumed that the final result of processes 2 and 3 was a transfer of energy to the CH_4(\nu_4) level, because of the fast internal relaxation among the excited states of CH_4. This conclusion was meaningful because of the absence of other excitation mechanisms for the CH_4 levels, which is not our case: Garcia-Comas et al. (2011) analyzed the non-LTE emission of CH_4 in the highest part of the atmosphere of Titan (from 450 to 1050 km), determining the populations of these exited states. In Figure 7.10, taken from that work, we can see the population of the excited states of CH_4 for daytime conditions: \(\nu_2\) and \(\nu_4\) are below their LTE population above 400 km, whereas the \(2\nu_4\) level shows an enhancement. Above 400 km, transfer from \(\nu_2\) and \(\nu_3\) states to CO(1) and N_2(1), unfavoured by being in endothermic direction with a quite large energy gap, will be less important than transfer from \(2\nu_4\), due to the low energy gap in exothermic direction and to its enhanced population. Though we are not discussing them here, transfer from higher excited states of CH_4 may not be negligible: the levels around 3000 cm\(^{-1}\) \((\nu_1, \nu_3, 2\nu_2, \ldots)\), despite their populations are never larger than that of \(2\nu_4\), may have larger rate constants for transfer of energy to N_2(1) and CO(1). We therefore leave this point to future investigation.

So, below 400 km, where levels \(\nu_2, \nu_4\) and \(2\nu_4\) are in LTE to a good approximation, it is equivalent to consider processes 2 and 3 as V-T (following routes 2d and 3d), but above 400 km the additional production given by \(2\nu_4\) level may be of some importance. The problem is that we do not know the relative importance of the four processes \((a, b, c, d)\) and we can only make some estimates for the actual rate of each of them. Rates 2c and 3c are the most interesting as may lead to an important additional production of CO(1) and N_2(1) in the
highest part of the atmosphere. We expect process 3c to dominate with respect to 2c, due to the much larger concentration of N\textsubscript{2} and the fast transfer from N\textsubscript{2}(1) to CO(1). In a search for estimating the importance of these processes, we look for the highest possible estimate (in the following referred to as \textit{estim.2}) and a more reasonable one (\textit{estim.1}) of these collisional rates.

**First estimate of the CO(1) $\rightleftharpoons$ CH\textsubscript{4}(2\nu\textsubscript{4}) and N\textsubscript{2}(1) $\rightleftharpoons$ CH\textsubscript{4}(2\nu\textsubscript{4}) rates**

We take as a reasonable value for the inverse rate $k_{3c}'$ that for de-excitation of a $\nu_4$ excited level of CH\textsubscript{4} through encounters with N\textsubscript{2}, so a value of about $3.7 \cdot 10^{-16}$ cm\textsuperscript{3}s\textsuperscript{-1} at T=170 K (as determined by Siddles \textit{et al.} [55]) for N\textsubscript{2}; this assumption is not completely justifiable as that rate refers to a de-excitation from the first excited $\nu_4$ level to the ground, whereas we are here considering a double quantum jump ($2\nu_4 \rightarrow 0$), but the quasi-resonance condition due to the much lower energy gap between CH\textsubscript{4}(2$\nu_4$) and N\textsubscript{2}(1) than that between the first excited $\nu_4$ level and the ground may favour this transition. For the rate of de-excitation of 2$\nu_4$ level through collisions with CO, lacking of experimental values, we take that for N\textsubscript{2}, because, as a general rule, the CO rates are always comparable with the N\textsubscript{2} ones (or often larger). We refer to these estimates as \textit{estim. 1} in the table below.

**Maximum estimate of the CO(1) $\rightleftharpoons$ CH\textsubscript{4}(2$\nu_4$) and N\textsubscript{2}(1) $\rightleftharpoons$ CH\textsubscript{4}(2$\nu_4$) rates**

On the other hand, as the highest threshold we take the inverses of the total 2 and 3 rates, as if the only process in deactivating N\textsubscript{2}(1) and CO(1) was the coupling with CH\textsubscript{4}(2$\nu_4$). Because of the endothermic nature of processes 2c and 3c, with $\Delta E = -266$ cm\textsuperscript{-1} for N\textsubscript{2} and $\Delta E = -453$ cm\textsuperscript{-1} for CO, this assumption is not realistic but will work as highest estimate and can give hints for the need of a precise determination of these rates\textsuperscript{5}. We refer to these

\textsuperscript{5}That is, if even with the highest estimate these processes appear to be negligible with respect to others,
estimates as *estim. 2* in the table below.

In both cases, the estimated value of the rate constants for processes (2a,2b,2c) and (3a,3b,3c) has to be chosen so that the sum of the three rate constant (a,b,c) equals the total rate constant as obtained by Gregory *et al.*, such as to assure thermalization where only collisions matter. For simplicity we will assume that the transfer to the ν4 level is negligible compared to the ν2 level, because of the lower energy gap with N2(1) and CO(1), so taking into account only pathways a and c. Besides, according to García-Comas *et al.*, the vibrational temperature for states ν4 and ν2 differs only slightly below 800 km, so that considering one or the other process is effectively equivalent.

In Table 7.1 we summarize the rate constants we need.

**Table 7.1:** Rate constants for the involved collisional processes. The second column indicates the rate for the process in the forward direction, whereas the third column shows the reference from which it has been taken (or inferred in the case of estimates). The rates for the processes in the reverse direction are obtained through the principle of detailed balance, that is

\[ k_{0} = k_{i \rightarrow g} = \frac{\Pi_{i} g_{\text{react}}}{\Pi_{j} g_{\text{prod}}} e^{-\Delta E/kT}. \]

<table>
<thead>
<tr>
<th>Process</th>
<th>( k ) (cm(^3)s(^{-1})) at 170 K</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( 1.4 \times 10^{-15} )</td>
<td>Allen &amp; Simpson [53]</td>
</tr>
<tr>
<td>2. (total)</td>
<td>( 3.0 \times 10^{-15} )</td>
<td>Gregory <em>et al.</em> [32]</td>
</tr>
<tr>
<td>3. (total)</td>
<td>( 8.6 \times 10^{-16} )</td>
<td>Gregory <em>et al.</em> [32]</td>
</tr>
<tr>
<td>2c. (estim. 1)</td>
<td>( 4.8 \times 10^{-17} )</td>
<td>Siddles <em>et al.</em> [55]</td>
</tr>
<tr>
<td>2a. (estim. 1)</td>
<td>( 2.95 \times 10^{-15} )</td>
<td></td>
</tr>
<tr>
<td>3c. (estim. 1)</td>
<td>( 2.3 \times 10^{-16} )</td>
<td>Siddles <em>et al.</em> [55]</td>
</tr>
<tr>
<td>3a. (estim. 1)</td>
<td>( 6.3 \times 10^{-16} )</td>
<td></td>
</tr>
<tr>
<td>2c. (estim. 2)</td>
<td>( 3.0 \times 10^{-16} )</td>
<td>Gregory <em>et al.</em> [32]</td>
</tr>
<tr>
<td>2a. (estim. 2)</td>
<td>( 0 )</td>
<td></td>
</tr>
<tr>
<td>3c. (estim. 2)</td>
<td>( 8.6 \times 10^{-16} )</td>
<td>Gregory <em>et al.</em> [32]</td>
</tr>
<tr>
<td>3a. (estim. 2)</td>
<td>( 0 )</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>( 1 \times 10^{-21} )</td>
<td>Shin [31]</td>
</tr>
<tr>
<td>5.</td>
<td>( 1 \times 10^{-23} )</td>
<td>Shin [54]</td>
</tr>
</tbody>
</table>

In the following, we will assume fixed the populations of CH\(_4\) excited states, as given by García-Comas *et al.*. In that work, the coupling between N\(_2\)(1) and CH\(_4\)(2ν4) was assumed as negligible for the excitation of the 2ν4 level: with any realistic possible estimation of \( k_{3c} \), the rate constant for the equilibrating process \( CH_{4}(2\nu_{4}) + CH_{4} \rightleftharpoons 2 \; CH_{4}(1\nu_{4}) \) is always by far faster with a value of \( 4 \times 10^{-11} \text{ cm}^{3}\text{s}^{-1} \) [51]. The rate constant \( k_{3c} \) should be close to \( 6 \sim 1.8/\alpha \times 10^{-14} \text{ cm}^{3}\text{s}^{-1} \) for this process to be important in determining the CH\(_4\)(2ν4) population, which seems really improbable.

Let us now write the statistical equilibrium equations for both N\(_2\)(1) and CO (1). Slightly changing the notation of Chapter 5, we indicate as \( \chi^{(v)} \) the number density of molecule X in the ν state. The N\(_2\)(1) statistical equation is:

\[ \text{there is no need for their precise determination, at least for the purposes we have here.} \]

\( ^{6} \text{Here } \alpha \text{ is the ratio of the actual non-LTE population of } N_{2}(1) \text{ and its LTE value.} \)
losses were much lower, the coupling with CO deexcitation is very different from a V-T one: if the losses of obtain:

\[ \frac{d[N_2^{(1)}]}{dt} = [N_2] \left( k_1 [CO^{(1)}] + k_{3a}' [CH_4^{(2v4)}] + k_{3a} [CH_4^{(v3)}] + k_4' [N_2] \right) - [N_2^{(1)}] \left( k'_1 [CO] + k_3 [CH_4] + k_4 [N_2] \right) \] (7.6)

Considering a stationary state, we obtain an expression which depends on \([CO^{(1)}]::\)

\[ [N_2^{(1)}] = \frac{k_1 [CO^{(1)}] + k_{3c} [CH_4^{(2v4)}] + k_{3a} [CH_4^{(v3)}] + k_4' [N_2]}{k'_1 [CO] + k_3 [CH_4] + k_4 [N_2]} = \frac{\alpha [CO^{(1)}] + \beta}{L_{N_2}} \] (7.7)

Apart from the dependence on CO(1) abundance, in the last expression all terms are known, thanks to the fact that N_2 does not absorb infrared radiation, letting us to avoid the calculation of the photoabsorption rate. In the last step we separated the terms proportional to and independent from \([CO^{(1)}], \) for future convenience. Let us now have a look at the statistical equation for CO (1), which instead contains the production and losses due to the absorption of radiation and spontaneous emission. Already assuming a stationary state, we obtain:

\[ \frac{[CO^{(1)}]}{[CO]} = \frac{P_{rad} + k_1 [N_2^{(1)}] + k_{1b} [N_2] + k_{2c} [CH_4^{(2v4)}] + k_{2a} [CH_4^{(v2)}]}{L_{rad} + k_1 [N_2] + k_2 [CH_4] + k_4 [N_2]} \] (7.8)

Here \( P_{rad} = B_{\nu \rightarrow \nu} \tilde{J}_{\nu \nu} \) is the number of photons absorbed per CO molecule and per unit time, so that, multiplying it by the CO number density, we obtain the number of CO molecules that are excited to the first level from the ground due to the absorption of a photon. With regards to the radiation losses, \( L_{rad} [CO^{(1)}] \) is the number of CO molecules that de-excite spontaneously to the ground level with the emission of photons; \( L_{rad} \) is equal to the Einstein coefficient \( A_{\nu \rightarrow \nu}. \) Before substituting for \( [N_2^{(1)}] \) we should note that in the expression for \( [N_2^{(1)}] \) (eq. 7.7) there is a term proportional to \([CO^{(1)}] \) and another one which instead is independent from it. Being a supplemental way of \( CO (1) \) production, the latter represents, in a certain sense, “the failure” of the de-excitation of \( CO (1) \) through the \( N_2 \) route. Let us regard as Prod the production term, that is the part of the numerator in eq. 7.8 not dependent on \([CO^{(1)}] \) (including herein the similar term in the expression of \([N_2^{(1)}]\)), Loss all the losses (the denominator of eq. 7.8), so that:

\[ Prod = P_{rad} + k_1' \beta / L_{N_2} + k_{2c} [CH_4^{(2v4)}] + k_{2a} [CH_4^{(v2)}] + k_{1b} [N_2] \]

\[ Loss = L_{rad} + k_1 [N_2] + k_2 [CH_4] \]

\[ \frac{[CO^{(1)}]}{[CO]} = \frac{Prod}{Loss \cdot \left( 1 - \frac{k_1' \alpha [CO]}{L_{N_2} Loss} \right)} = \frac{Prod}{Loss - k_1' \alpha [CO] / L_{N_2}} \] (7.9)

Here we can clearly see the role of the processes that de-excite \( N_2 (1) \) and why a V-V deexcitation is very different from a V-T one: if the losses of \( N_2 (1) \) were very large, then the transfer of energy between \( CO (1) \) and \( N_2 (1) \) would go only in one direction, from \( CO \) to \( N_2 \), and the system would be equivalent to one with a strong V-T de-excitation. If instead these losses were much lower, the coupling with \( N_2 (1) \) would serve to \( CO (1) \) as an energy reservoir.
7.2. CO COLLISIONAL MODEL

that could prevent the system from loosing energy via spontaneous emission and increment the population of the excited state.

Let us now write the final expression explicitly, already neglecting the V-T terms that we will find out to be negligible with respect to the other terms:

\[
\frac{[CO(1)]}{[CO]} = \frac{\mathcal{P}_{\text{rad}} + \left( k'_{2e} + k'_1 k'_{3e} \frac{[N_2]}{L_{N_2}} \right) [CH_4^{2\nu_4}] + \left( k'_{2a} + k'_1 k'_{3a} \frac{[N_2]}{L_{N_2}} \right) [CH_4^{\nu_2}]}{\mathcal{L}_{\text{rad}} + k_1 [N_2] + k_2 [CH_4] - k'_1 k'_1' [CO] \frac{[N_2]}{L_{N_2}}}.
\]

Now it is interesting to see which processes dominate in the determination of the CO(1) population. In Figure 7.12 we see a comparison of the two choices estim. 1 and estim. 2 for the V-V rates involving CH$_4$ excited states with an assumption of complete V-T deactivation in the collision with methane (routes 2d and 3d). As we can see, below 400 km the effect is the same\(^7\), whereas above that altitude a strong coupling with CH$_4$($2\nu_4$) may enhance the CO(1) production. Between processes 2 and 3, the latter is stronger: energy follows preferably the route $CH_4(2\nu_4) \rightarrow N_2(1) \rightarrow CO(1)$ instead that the direct transfer $CH_4(2\nu_4) \rightarrow CO(1)$.

This two terms turn both out to be far stronger than the V-T terms of de-excitation of CO(1) and N$_2$(1) through N$_2$, that do not go beyond $10^{-10}$ s$^{-1}$. We show in Figure 7.11 the relative importance of all losses; we can see that at about 220 km the spontaneous emission term becomes more important than the collisional ones. Below that altitude the main contribution to the losses is due to V-V transfer with N$_2$(1), only slightly attenuated by the negative term in the denominator of eq. 7.10: CO(1) can actually transfer energy to N$_2$(1), since thermalization of N$_2$(1) is very efficient.

The case of the second excited level CO(2) has an additional complication with respect to the one just studied, namely the coupling with the CO(1) level both by collisions and by radiative processes. Besides, ther is an increased difficulty in the determination of the collisional

\(^7\)The slight difference that we see here is due to the fact that the two levels are not exactly in LTE below 400 km.

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Figure 7.11: Collisional and radiative losses of CO(1) population, appearing in the denominator of eq. 7.10.
rates, due to the complete lack of experimental data. The theory of vibrational energy transfer, restricted to the case of harmonic oscillators, predicts that the probability of transition from an excited state to the lower one ($\Delta n = -1$) increases linearly with the number of the excited level. In our case this means that the processes listed in Table 7.1 are the same, but for transitions between CO(2) and CO(1) (instead that between CO(1) and CO) the value of the rate constants is the double. Of course, this is an approximation and the actual value of these rates may differ from that calculated in this way. The scheme of the main collisions is thus:

1. $\text{CO} (2) + N_2 \rightleftharpoons \text{CO} (1) + N_2 (1) + \Delta E \quad \Delta E = -204 \text{ cm}^{-1}$
2. $\text{CO} (2) + CO \rightleftharpoons \text{CO} (1) + CO (1) + \Delta E \quad \Delta E = -26 \text{ cm}^{-1}$
3. $\text{CO} (2) + CH_4 \rightleftharpoons \text{CO} (1) + CH_4 (x) + \Delta E$

(7.11)

Due to the resonance condition the rate of process 3 is really fast ($2 \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$, as reported by Harding & Wilson [56] at 170 K) and makes this process compete with those involving $N_2$ and $CH_4$ even if the abundance of CO molecule is far smaller.

The radiative excitation rate is the key for the run-away of CO(1) (and of $N_2 (1)$ as well) from equilibrium population during day-time: the absorption of the incoming solar flux and of emission from other atmospheric regions in the $4.7 \mu m$ band is the main responsible for pumping molecules in the excited state and dominates in the higher parts of the atmosphere, as we will see in the next section. With regards to the CO(2) state, the more important spectral region is the one at $2.3 \mu m$, corresponding to a direct absorption from the ground state and so to a double quantum jump ($0 \rightarrow 2$); this is a forbidden transition, according to what we studied in Chapter 2, but even though the Einstein absorption coefficient is far lower there, the absorption in this band still dominates with respect to that in the 2-1 band (first hot band). The reason for this is that the abundance of particle in the ground state is still far larger than the one of CO(1) (the maximum value reached for the ratio is $10^{-7}$) and the incoming solar flux at $4270 \text{ cm}^{-1}$ (central wavenumber of the 2-0 band) is almost 3 times larger than the one at $2127 \text{ cm}^{-1}$ (central wavenumber of 2-1 band).

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*We are not going to justify here this result and we refer to [21] and the references therein.*
Figure 7.12: Top panel: effect of the two estimates for process 2, in terms of the production relative to the ground state. Bottom panel: the same for process 3, but the quantities indicated in the label box are multiplied by $k_1 \left[ N_2 \right] / L_{N_2}$ as in equation 7.10.
Resolution of the non-LTE problem

The calculations of the populations of CO excited states have been performed with the aid of GRANADA (Generic radiative transfer and non-LTE population algorithm) developed by the group of atmospheric physics at the IAA of Granada, Spain. The code, extensively presented in [34], makes use of the direct radiative transfer simulations performed by KOPRA (Karlsruhe optimized and precise radiative transfer algorithm, presented in Stiller et al. [57]). It can work with an arbitrary number of vibrational bands and vibrational excited levels, and an hierarchy of the levels can be defined, solving first the equations for the states more populated and only then those depending on them. Given the non-linear nature of the problem, GRANADA adopts a Lambda iteration scheme, which can optionally be coupled to an algebraical resolution of the linearized system of equation (modified Curtis-Matrix method9), in order to make the convergence faster. Lambda iteration is the method most used in the resolution of radiative transfer problems in stellar atmospheres: it is based on a two step calculation, solving first the statistical equilibrium equations and then determining the effective mean10 radiance at each point with the new populations so obtained; this scheme is then iterated with back-substitution of the new mean radiances in the statistical equations. The ordinary Lambda iteration method can be considerably optimized with more complex iteration strategies (for an introduction, see [58]), but a thorough study of the efficiency of the algorithm is beyond our purposes in this work and we will not go deeper into the details of the numerical resolution.

Let us now describe the results obtained for the two CO excited levels populations in Titan’s atmosphere through the calculation with GRANADA. The model atmosphere assumed is the one by Yelle we described at the beginning of this chapter. This assumption works well for the simulation near to Titan’s equator, but may lead to some problems at different latitudes due to significant differences in the temperature-pressure profile (and then to a different actual density). We will come back to this point further on. The incoming solar flux was calculated for year 2007, when Titan was at an average distance of approximately 9.2 AU from the Sun, and for a solar zenith angle of 60°. Given that we are not able to properly estimate the particular rates for the V-V transfers from CH4 excited levels, in this first calculation we assumed that the de-excitation to CH4 follows entirely the V-T route. As we saw in Figure 7.12, the resulting CO(1) production profile is the same below 400 km, but may differ from the actual one if a different scheme for CH4 deactivation is closer to reality (like estim.1 or estim.2 above). We will come back on this point in the discussion at the end of Chapter 8.

For the computation of the radiative fluxes in the fundamental, first hot and first overtone bands, overlapping of the different bands as well as absorption by other molecular species (mainly CH4) has been taken into account, and has some effects in the lowest atmospheric regions. On the other hand, extinction due to aerosols has not been considered: since this effect may give a contribution in the atmosphere below 250 km, we should keep in mind this fact during the analysis of data in the next Chapter. In Figure 7.13 the rates of absorption of the solar flux in the three bands are shown, all normalized to the CO number density. As we can see, the flux in the fundamental band becomes to be significantly absorbed below 600 km, whereas that in the overtone bands is almost unmodified above 300 km. We note that the latter is very sensible to atmospheric extinction between 150 and 250 km, and a slight modification in the extinction coefficient can significantly vary the actual flux there. Whereas the radiative excitation in the overtone band (thus for level 2) is almost completely given by the incoming

9 The Curtis-Matrix method is similar to the one developed at the end of Chapter 5, generalized for an arbitrary number of vibrational bands and levels.
10 The mean radiance here is intended as defined in Chapter 5.
solar flux, for the fundamental band the situation is very different, as we can realize looking at Figure 7.14. The contribution of the atmospheric emission is at least comparable with the solar one even in the highest part of the atmosphere and contributes to significantly enhance CO(1) population. Here we can clearly see the non-local nature of the non-LTE problem: the CO(1) population at a point depends strongly by that in other atmospheric regions.

Figure 7.13: Rates of solar flux absorption in the three bands considered: CO fundamental, first hot and first overtone bands, as calculated with GRANADA.

The resulting profiles for the vibrational temperature of the two levels are shown in Figure 7.15. As we can see, the populations of both levels are strongly enhanced in the highest part of the atmosphere, being governed exclusively by radiation processes above ~ 300 km for both CO(1) and CO(2). The CO(1) state then relaxes to its equilibrium population, whereas CO(2) keeps being in strong non-equilibrium in the whole atmosphere.

In Figure 7.16 we show the actual population ratios of the two levels with respect to the ground state. We also indicated there the ratio between non-LTE CO(2) and CO(1) population (multiplied by 10^{-10} in order to fit in the graph). As we can see, despite the far higher vibrational temperature of the second level, its population is never higher than 1% that of CO(1). Comparing the non-LTE populations with their equilibrium value we can see how this effect is determinant: CO(1) population is enhanced by up to 2 orders of magnitude (and so its emissivity) and that of CO(2) up to almost 8 orders of magnitude!

It is worth here looking at the relative importance of the collisional and radiative production terms in the case of CO(1). In Figure 7.17 we see a comparison between the total collisional excitation due to CH₄, considering the contributions of the routes CH₄ → CO(1) and CH₄ → N₂(1) → CO(1) together, and the total photoabsorption rate in the fundamental band. As we can see, above 400 km, the radiative production is at least two order of magnitude more important, even in the case in which the maximum estimate for the V-V coupling of N₂(1) with CH₄(2ν₄) is assumed. We thus exclude that such V-V processes may play a role in exciting CO(1).
Figure 7.14: Total photoabsorption rate in the fundamental band, as calculated with GRANADA. Three different contributions are shown: the solar flux and the atmospheric downwelling and upwelling fluxes.

In the next chapter we will see the effect of these vibrational temperature profiles in the actual emission of CO in Titan’s atmosphere, analyzing some VIMS measurements. We will come back later in Chapter 8 to the possible effect of changes in the non-LTE model described.
7.2. CO COLLISIONAL MODEL

Figure 7.15: Vibrational temperatures for CO(1) and CO(2) at different altitudes, as calculated with GRANADA for the model described above, assuming V-T CH$_4$ deactivation and daytime conditions (SZA=60°). We can see here the vibrational temperatures for the first excited states of the two main isotopologues too, calculated with a model analogous to the previous one.

Figure 7.16: Non-LTE populations compared to their equilibrium values. CO(1) level is enhanced up to 2 orders of magnitude, CO(2) up to 8 orders. Ratio$_{21}$ is the non-LTE ratio $[\text{CO(2)}]/[\text{CO(1)}]$, multiplied by $10^{-10}$ to fit in the graph.
Figure 7.17: Comparison between the collisional and radiative production terms for CO(1). The V-V coupling with the excited levels of CH\textsubscript{4} is shown for the two estimations we made above.
Comparison with other results

We can compare the nominal result for the CO(1) and CO(2) vibrational temperatures with that obtained by López-Valverde et al. [49]. Their model shows two main differences with that described here. For the V-T processes 4 (CO(1) + N\textsubscript{2} ⇌ CO + N\textsubscript{2}) and 5 (N\textsubscript{2}(1) + N\textsubscript{2} ⇌ N\textsubscript{2} + N\textsubscript{2}), different rate constants were used. Process 4 was estimated to be 1000 times less efficient than its V-V counterpart (process 1), whereas we use here a value almost 10\textsuperscript{5} times lower than this, according to the theoretical calculations by Shin [31]; in this way the V-T route turns out to be completely negligible with respect to other specific losses. Process 5 was estimated by López-Valverde et al. taking the measured value at higher temperatures and extended with the aid of predictions from SSH theory (see section 4.2), giving a value of about 3 \times 10^{-25} \text{cm}^3\text{s}^{-1}. This value is about 60 times lower than the one assumed here, again according to theoretical calculations by Shin [54]. But both these thermalization routes turned out to be negligible in our model compared to process 3, which was not considered in [49]. The coupling of N\textsubscript{2} with the CH\textsubscript{4} excited levels gives a strong additional thermalization contribution below 400 km, where the CH\textsubscript{4} levels are in LTE according to García-Comas et al. [51]. The thermalization in the route CO(1) ⇌ N\textsubscript{2}(1) ⇌ CH\textsubscript{4}(x), as we have seen in Figure 7.12, is almost 2 order of magnitudes stronger than process 2.

Figure 7.18: Vibrational temperatures with a different model for the CO excited states, after López-Valverde et al. [49].

Due to these modification to the collisional model, the nominal vibrational temperature of CO(1) differs substantially from that obtained by López-Valverde et al., shown in Figure 7.18. We see that the CO(1) vibrational temperature is significantly detached from the kinetic temperature even below 300 km, because the specific losses are here less efficient than in our case by at least one order of magnitude. The most important differences are seen below 400 km and can lead to significant differences in the emerging atmospheric emission. The vibrational temperature of the second excited state is instead perfectly equivalent to the one obtained here, given that its non-LTE behaviour is almost exclusively driven by radiation.
CHAPTER 7. NON-LTE PROCESSES IN TITAN’S ATMOSPHERE
Chapter 8

Data analysis

The observations we analyze here have been acquired by VIMS during year 2007 and correspond to the three data series (called cubes) 4168, 4658 and 5149. In Figure 8.1 below we show part of the VIMS images, for cubes 4168 and 4658, at two wavelengths (4.7 \( \mu \)m and 5 \( \mu \)m). We have focused on the less noisy data, so that to allow a better retrieval of CO. Even so, the noise is quite large, particularly at the highest altitudes, as we will comment later on.

Figure 8.1: Images acquired by VIMS at two different wavelengths (left \( \rightarrow \) 4.7 \( \mu \)m, right \( \rightarrow \) 5 \( \mu \)m) for cubes 4168 (top) and 4658 (bottom). Altitude and latitude grids are shown.

Nevertheless we preferred to retrieve the CO profile from single sets\(^1\) of spectra and only

\(^{1}\)With set of spectra we mean the spectra obtained from each pixel on a single vertical in images above, corresponding to different tangent altitudes.
then average the results, instead of retrieving it from an averaged set. Considering an averaged spectrum at a certain tangent altitude would certainly allow to reduce the noise, but would also introduce possible systematic errors. From the inspection of Figures ?? and 8.1, we see that the vertical sampling of these data is roughly 100 km in altitude, depending on the distance from the planet and on the orientation of the pixels with respect to the vertical. The central altitudes of two adjacent pixels can differ by up to about 20-30 km, due to the curvature of the planet, and the result of averaging cannot be treated in a simple way.

The five limb series we analyze in this work are plotted in Figure 8.2. For all of them the solar zenith angle is $60^\circ \pm 5^\circ$ and the latitude is $70^\circ \pm S$.

**Data recalibration and noise estimation**

The limb spectra are very noisy, especially at high tangent altitudes. Besides, it was evident a systematic shift below the zero level in the spectral region closer to 5 $\mu$m. We hypotized this could be due to an ill calibration of the zero level in this region, which appears plausible. In order to recalibrate the zero level and to give a more rigorous estimate of the measurement error, we considered a large number of limb observations at tangent altitudes higher than 800 km, in the 4 to 5 $\mu$m region. The only relevant emission in this spectral region should be due to CO, but it completely disappears below the instrumental noise above 700 km, so the signal we get can be regarded as pure noise. For each spectral point we averaged around 150 measurements, using two different prescriptions: 1) considering all measurements for each spectral point; excluding the pixels for which $|I_w(\text{pixel}) - \bar{I}_w| > 8 \times 10^{-8}$ W/(m$^2$ nm sr). The threshold for these “bad” pixels, which are clearly visible even in the full images shown in Figures ?? and 8.1, has been taken as to be significantly larger than the noise. This has to be verified at the end of the procedure.

The result for the latter prescription is shown in Figure 8.3. The systematic error in the determination of the zero level is clearly visible here and reaches a value of $3 \times 10^{-8}$ W/(m$^2$ nm sr) at 5 $\mu$m, which can be important with low signals. The offset has been obtained by using a least squares third-order polynomial fit (see Figure 8.3). We then used this result to recalibrate the spectra. Figure 8.4 shows the difference before and after the re-calibration for spectra A at 322 km and 523 km. As we can see, the recalibration produces a strong variation in the latter, because of its low signal.

The noise was estimated from the same procedure, calculating the standard deviations referred to a single value. No systematic trend in the error at different wavelengths was evident, so that it has been averaged over the full spectral region. The value obtained for the noise is $3.6 \times 10^{-8}$ W/(m$^2$ nm sr) with the first prescription above (i.e. considering bad pixels too), and $1.9 \times 10^{-8}$ W/(m$^2$ nm sr) with the second one. Given that a few bad pixels can significantly raise the mean error value, we took the latter as the characteristic noise and ignored bad pixels in the analysis, assigning artificially a far larger error bar ($1 \times 10^{-6}$ W/(m$^2$ nm sr)) to each of them.

### 8.1 Retrieval code

The code used in the simulations of the atmospheric emission and in the retrieval of CO concentration is the Geofit Broad Band (see [59],[52]), initially developed for the Earth’s atmosphere and then adapted to Titan and VIMS. Schematically speaking, the code is made of two main parts. The first one is the forward model, which, given the population of each molecule (and in case of non-LTE, the vibrational temperatures of each single excited level)
Figure 8.2: The five limb series analyzed, all corresponding to latitude (70°±5°) S and solar zenith angle (60°±5°). The central tangent altitude of each spectrum is indicated in the label box.
Figure 8.3: Average radiance for different spectral points in data without signal; we can note the systematic offset of the zero level for larger wavelengths. The error bars show the standard deviation referred to the mean value. The dashed line is a 3rd degree polynomial fit.

Figure 8.4: Recalibration of two spectra according to the offset obtained through the procedure described in the text.
and the thermal structure of the atmosphere, computes the atmospheric emission.

The atmosphere is first divided in boxes through an altitude and latitude grid; for each line of sight of the observations, corresponding to different tangent altitudes, the ray path across these boxes is defined, assigning to each step along the ray appropriate values of temperature, pressure and number density of each molecule, calculated on the basis of a Curtis-Gordon average. Then a line-by-line scheme is adopted, that is, each roto-vibrational transition is considered separately and, for each line, the profile produced by pressure and thermal broadening is calculated. The spectroscopic data are taken from the HITRAN database and the wavenumber grid used in our simulations has a 0.0005 cm\(^{-1}\) step. The forward model does not include scattering of radiation; we will discuss below about a modification in the code made during this work to account for this effect at least to a first approximation.

After calculating the absorption and emission coefficients (and then of the source function) for each step, the discretized radiative transfer equation (see section 3.5) is used to compute the emerging emission. The resulting spectra have to be convolved with the field of view, which is quite large for VIMS; this is done by interpolating the spectra obtained for adjacent tangent altitudes and integrating over the altitude width of the field of view. At this point we still have an high resolution spectrum, which allows the single transitions to be identified. The last step of the forward model is to convolve this spectrum with the VIMS spectral response function, that is a gaussian about 15.5 nm wide (corresponding to 6 to 10 cm\(^{-1}\) at our wavelengths).

The second part of the code solves the retrieval problem. The scheme used is the maximum likelyhood method (see Chapter 6). The iteration procedure follows a Levenberg-Marquardt method, described in Chapter 6 as well. It is important to stress here that this is not equivalent to solve the inverse problem on the basis of observations alone, because we use an additional constraint based on our a priori expectation.

8.2 First data simulations

With the forward model described above and the non-LTE populations of CO excited states described in Chapter 7, we tried first a simulation of the spectra labeled with letter A in Figure 8.2, assuming a uniform concentration\(^2\) of 32 ppmv in the whole atmosphere. This is our first guess according to the latest results in the lower stratosphere (see Lopez-Valverde et al. [49], Baines et al. [50] and section 7). The results are shown in Figure 8.5. At first sight, this CO concentration appears inadequate both at high and low altitudes.

It is interesting to look at the contributions from different bands, also shown in the same figure. Apart from the CO emission in the fundamental (1-0) band of the main and other two isotopologues and the first hot band (2-1) for the main isotopologue, we can single out the emission from the strong Q branch of CH\(_3\)D at 4550 nm and a weak emission from C\(_2\)H\(_2\) at the lowest tangent altitude. As we can see, the relative importance of the various bands changes with altitude. The hot band dominates below 350 km but it actually disappears above 500 km, where only the fundamental band of the main isotopologue is significant. We will comment further this behaviour below. It is important to note that the fundamental and first hot bands show a different spectral shape, centered respectively at about 4670 and 4720 nm.

The "valley" we see in the observed spectrum is effectively at 4720 nm for the lowest altitudes, whereas for the higher ones no evident valley is seen. It is instructive to compare this first simulation with the result we obtain for the same CO concentration but assuming all states in LTE, shown in Figure 8.6. As we can see, the emission from the hot band completely disappears and the fundamental band is far weaker, completely disappearing at 400 km.

\(^2\)Here and in the following we will always speak of concentrations in terms of Volume Mixing Ratios (VMR = \(n_y/\pi_{TOT}\)).
It is worth having a look at the high-resolution spectra, plotted in Figure 8.7, simulated with the forward model before the instrumental convolution. Here we can distinguish the thin CO lines for the four bands considered\(^3\) and those of CH\(_3\)D. We can note see clearly here the significant contribution of the Q branch intensity as compared with the convolved spectra in Figure 8.5. This is due to the fact that lines in the Q branch are very close, compared to the R and P branches, and integrating over the spectral windows the total contribution of the Q branch is concentrated in a single bin that assumes a larger value.

We then tried a first fit of the observed spectra by varying the CO concentration in the atmosphere (see Figure 8.8). The result of this second simulation (Figure 8.9), especially at low altitudes, is not satisfactory. Considering that the standard deviation of data is about $2 \times 10^{-8} \text{W/(m}^2 \text{nm sr)}$, at least for spectra at 166, 266 and 322 km, our simulation is systematically below the observed spectrum in the “wings” and in the central valley of the CO profile, far beyond the error bars. Our first impression is proved by the very large reduced $\chi^2$ for this fit, which is 19.45.

As we pointed out in section 7.1, this effect is due to the scattering of solar radiation by the particles that constitute Titan’s haze. The concentration we find in the highest part of the atmosphere is far greater than the one we would expect, but we will come back later to this point.

It is worth to discuss at this point the change of intensity of the single bands with the change in CO concentration. Comparing Figures 8.5 and 8.9, the major change in the total signal is due to the hot band 2-1 emission, which almost doubles its intensity at the lowest altitudes. We pointed out the possibility of such a behaviour in section 3.5, when we spoke of the optically thin limit. The hot band is optically thin in the whole atmosphere and so its intensity is almost proportional to the CO(2) concentration. On the other hand, the fundamental band hardly changes its intensity with the change in CO concentration, even at the highest altitudes. Whereas radiation in the fundamental band is absorbed by molecules in the fundamental state, the hot band only is absorbed by CO(1), that has an abundance at least $10^{-7}$ times lower. Of course this is correct only if there is no significant overlapping between the two bands, which is quite a good approximation for CO in Titan’s atmosphere, due to the small thermal broadening of lines. The isotopic bands show somewhat an intermediate behaviour, seeming optically thick at low altitudes and optically thin at the highest ones: the second main isotopologue has an abundance of about one hundred times lower than the first one, which seems to be the responsible for the different optical regimes of the two isotopologues. One consequence of this fact is that, because the emission at 500 km is mainly due to the fundamental band, it is only weakly dependent on the CO concentration, making the uncertainty of the inversion larger.

\(^3\)Again, the two minor isotopologues are plotted together.
8.2. FIRST DATA SIMULATIONS

### Simulated Spectra for CO Concentration of 32 ppmv

The contribution of different bands is indicated in Figure 8.5.

![Simulated Spectra](image)

Figure 8.5: Simulated spectra for a uniform CO concentration of 32 ppmv, compared to spectra A. The contribution of different bands is indicated.
Figure 8.6: Simulated spectra for a uniform CO concentration of 32 ppmv, assuming LTE for all states. Only contribution from the fundamental band is visible.
Figure 8.7: High resolution simulated spectra for a uniform CO concentration of 32 ppmv. The contribution of different bands is indicated.

Figure 8.8: CO Volume Mixing Ratio for the two simulations.
Figure 8.9: Simulated spectra for a "step" CO concentration profile, raising from 55 ppmv in the lower atmosphere to 170 ppmv above 400 km, compared to spectra A. The contribution of different bands is indicated.
8.3 Improvements to the forward model

Due to the importance of the scattered solar radiation at altitudes below 400 km, we included in the code a first order approximation of this effect. To introduce a rigorous treatment of scattering in the forward model would mean a global change in the GBB code, which is beyond the purposes of this work. This problem to be solved is in fact analogous to that of non-LTE we considered at the end of Chapter 5: the local source function depends on the mean intensity, which in turn depends on the source function in the whole atmosphere. Therefore, an iterative procedure or an inversion of a matrix would be needed. But such a work would be meaningless without a preliminary study on Titan’s aerosol optical properties (see section 7), at different altitudes, which are not completely known, and is not our primary interest here. For this reason we include this effect in an approximate way: we only considered an additional emissivity proportional to the solar flux at each point in the atmosphere, but without including an additional contribution to the opacity. Considering, for simplicity, isotropic scattering, the equation of radiative transfer can be written as:

\[
\frac{dI_w(n)}{ds} = \eta_w - \chi_w I_w(n) + \sigma_w I_{w}^{\text{sol}} + \sigma_w \left( J_{w}^{\text{atm}} - I_w(n) \right) \quad (8.1)
\]

Where all quantities depend on the position \( x \) in the atmosphere and we have separated the mean intensity \( J_w \) in the two contributions \( I_{w}^{\text{sol}}, \) the solar incoming radiation, and \( J_{w}^{\text{atm}}, \) the mean radiance coming from all other directions, emitted by other atmospheric regions. The problematic term in this equation is that containing \( J_{w}^{\text{atm}}, \) because it couples the radiative field along our line of sight with all others lines of sight. But if the solar term is far larger than the difference between the intensity along our line of sight and the mean atmospheric radiance, we could neglect the latter, to a first approximation. We will then assume:

\[
J_{w}^{\text{atm}} - I_w(n) \ll I_{w}^{\text{sol}} \quad (8.2)
\]

The solar flux at the top of Titan’s atmospheres, for the range of wavenumbers under consideration, is about \( 0.13 \text{ erg} / (\text{s cm}^{-1} \text{ cm}^2) \) whereas the wavenumber-averaged atmospheric emission is never larger than \( 10^{-3} \text{ erg} / (\text{s cm}^{-1} \text{ cm}^2) \) above 200 km. This approximation might fail only at too low altitudes, where the solar flux is significantly absorbed, but should work for the altitudes of our interest.

In order to include this new term in the forward model, we need to know the solar flux at each point in the atmosphere and to characterize \( \sigma_w \) and its dependence on wavenumber. The solar flux at each altitude is the result of absorption along the solar ray path due to all molecules. A new module has been added to the code, which computes the actual ray path in the direction of the sun and calculates the column density of absorbers and the optical depth \( \tau_w. \) This has been done for each altitude on a fixed grid and the result at some of them can be seen in Figure 8.10. Then a contribution to the emissivity is added in all points along VIMS’ line of sight, proportional to the computed solar intensity at that point.

A proper consideration of the effect of scattering by aerosols would need the evaluation of their concentration and optical properties and may lead to a response even strongly variable with frequency. However, according to the result by Lavvas et al. [65] (see section 7), the dependence of the scattering coefficient on wavelength should be quite smooth. Keeping in mind the possibility of errors produced by ignoring complex spectral features and leaving the complete matter to a future study, we yet limited ourselves to assume a simple dependence of \( \sigma_w \) on wavenumber (see section 3.4):

\[
\sigma_w(x) = \sigma(x) \left( \frac{w}{w_0} \right)^{\alpha(x)-2} \quad (8.3)
\]
We retrieved the scatterers efficiency \( \sigma(x) \) as well as the typical Ångström parameter \( \alpha(x) \) from the observations, in a region without molecular emission, as we will explain below. In order to allow the code to perform the inversion of this two quantities, we added them as two additional gas species. The analytical derivatives needed in the retrieval problem are easily derived from the relations above and from the discretized radiative transfer equation 3.26, that we rewrite here for convenience, for the case of limb view \( (I_0 = 0) \) and adding our new term to the source function:

\[
I_n = \sum_{i=0}^{n} (1 - \tau_{ij+1}) \left[ S_i^{\text{gas}} + \frac{\sigma_i}{k_i} \left( \frac{w}{w_0} \right)^{\alpha_i - 2} \right] \prod_{j=i}^{n} \tau_{ij+1} \quad (8.4)
\]

From this we get the derivatives of the final intensity \( I_n \) with respect to the aerosol scattering efficiency and to the exponent \( \alpha \) at each point \( x_i \) in the atmosphere:

\[
\frac{\partial I_n}{\partial \sigma(x_i)} = \sum_{i=0}^{n} \Delta x_{i+1} I_i^{\text{est}} \left( \frac{w}{w_0} \right)^{\alpha_i - 2} \frac{\partial \sigma_i}{\partial \sigma(x_i)} \prod_{j=i}^{n} \tau_{ij+1} \quad (8.5)
\]

\[
\frac{\partial I_n}{\partial \alpha(x_i)} = \sum_{i=0}^{n} \Delta x_{i+1} I_i^{\text{est}} \left( \frac{w}{w_0} \right)^{\alpha_i - 2} \log \left( \frac{w}{w_0} \right) \frac{\partial \alpha_i}{\partial \alpha(x_i)} \prod_{j=i}^{n} \tau_{ij+1} \quad (8.6)
\]
Figure 8.10: Solar flux at three different altitudes. We can note the absorption in the CO fundamental band in the CO isotopic bands and in the CH$_3$D band.
8.4 Retrieval of the CO concentration

In order to properly fit the solar scattering contribution, we considered a larger region of the spectra, from 4150 to 5120 nm, slightly larger than that in Figure 8.2. For the simultaneous retrieval of the scatterers concentration and of the Ångström parameter, we focused on the spectral points between 4150 and 4380 nm, at shorter wavelengths than the CO band, and between 4990 and 5120 nm, at longer wavelengths, that are not influenced by the CO emission. No other molecular species emits in these spectral ranges, apart from a very faint CO$_2$ band near 4250 nm, which is however completely undetectable in the observed spectra, due to the very low concentration of CO$_2$. In order to get values reasonably close to the actual ones, we assigned to the a priori estimation a large relative error, close to unity. We repeated the same procedure for all the five data series considered. In the left column of Table 8.1 we list the values of the reduced $\chi^2$ obtained for each spectra, limited to the spectral regions 4150-4380 nm and 4990-5120 nm. The values are quite small, due to the high degree of freedom of the fit (we are optimizing both the scattering efficiency and the dependence on frequency).

We then focused on the central part of the spectra, from 4380 to 4990 nm and made the program look for the optimal CO concentration. We assumed an a priori uniform concentration of 50 ppmv in the whole atmosphere, following the results by Gurwell & Muhleman [47] in the lower stratosphere and is the value assumed by many photochemical models (see Wilson & Atreya [44]). We assumed a large relative error of 70% on the a priori assumption, given that the spread of the retrieved concentration since now is quite important (see section 7) and we cannot be sure of our assumption beyond this error.

\[
\begin{array}{|c|c|c|}
\hline
\text{Spectra} & \chi^2/n & \chi^2_2/n \\
\hline
\text{A} & 0.35 & 1.08 \\
\text{B} & 0.65 & 0.79 \\
\text{C} & 0.40 & 0.65 \\
\text{D} & 0.40 & 2.54 \\
\text{E} & 0.30 & 2.09 \\
\hline
\end{array}
\]

Table 8.1: Values of the $\chi^2$ obtained for each spectra, for the first inversion (scattering efficiency) and the second (CO concentration).

The reduced $\chi^2$ obtained for each of the inversions are in the third column of table 8.1 and in Figures 8.11 to 8.15 we can see the simulations compared to the measurements for each one of the five observations. The fit is quite satisfying between 200 and 500 km, correctly reproducing the observed intensity and its shape, inside the error bars. Below 200 km (see Figures 8.11 and 8.14), the effect of scattering becomes stronger and we may note that there is a systematic over-estimation of the CO signal for the shortest wavelengths, whereas it is under-estimated for longer wavelengths. It seems plausible that this effect could be given by a more complex wavelength dependence of the scattering efficiency (and aerosol absorption) or by an overestimation of the CH$_3$-D emission, whose Q branch is almost invisible here. With regards to altitudes above 500 km, the analysis is complicated because of the noisy signal. Moreover, the signal here is weakly dependent on the CO concentration, because the main contribution is due to the fundamental band, which is still optically thick at these altitudes (see Figure 8.9 and the comment there). Since the noise can strongly alter the results in case of such a low sensibility, this is another reason for which the maximum likelihood method with an a priori assumption is more adequate than a simple inversion.

At altitudes above 400 km we note that the simulations are sistematically below the measurements, although inside the error bars. We will comment further this point later on.
8.4. RETRIEVAL OF THE CO CONCENTRATION

Figure 8.11: Spectra A
Figure 8.12: Spectra B
8.4. RETRIEVAL OF THE CO CONCENTRATION

Figure 8.13: Spectra C
Figure 8.14: Spectra D
Figure 8.15: Spectra E
8.5 Results and discussion

8.5.1 Scattering efficiency

The retrieved scattering efficiency $\sigma(x)$ is plotted in Figure 8.16, for each one of the 8 altitudes of the retrieval grid. The largest values are found for the lowest altitudes, but there is evidence of a new increase at about 500 km.

![Figure 8.16: Retrieved scattering efficiency $\sigma(x)$, average of the 5 retrievals.](image)

Our simple treatment of scattering does not claim to retrieve quantitatively the scattering efficiency in the infrared, however there are a few hints that suggest that this retrieval has some sense. The first is a qualitative argument, based on the known concentration of haze particles in Titan’s atmosphere. It is known in fact that Titan’s aerosols are mostly abundant below 200 km, but show another significant increase higher in the atmosphere peaking at 520 km. This second haze layer is known as detached haze layer and was first discovered by Voyager I. In Figure 8.17 the observed aerosol extinction in the UV region is shown, according to the results by Lavvas et al. [67] and Porco et al. [68], at 187 nm and 338 nm respectively. The values are much larger than those in Figure 8.16 because in the UV region the aerosol extinction if much more efficient, as we pointed out in section 7. But the profiles are in good agreement with the one retrieved here, reaching a minimum value at $\sim 490$ km (at 178 nm) and $\sim 470$ km (at 338 nm), and increasing again after that. This is in very good agreement with our 450 km minimum, moreover if we consider that a slight variation of this altitude with wavelength cannot be excluded.

The second argument is the total column opacity for scattering ($\int \sigma(z) dz$), which can be compared with the results of the model by Lavvas et al. [65] which gives about $2 \times 10^{-5}$ at 5 $\mu$m (see section 7). We can make an estimate of the value we get with the retrieved $\sigma(x)$ but, lacking of data below 250 km, to do this we have to assume some behaviour of $\sigma(x)$ below 250 km. Again according to Lavvas et al. [65], the value of the aerosol extinction coefficient close to the surface should be about ten times\(^4\) greater than that at 250 km. Assuming a linear

\(^4\)Their simulations gave this result for wavelengths ranging from 500 nm to 900 nm. We are here assuming that this holds for infrared radiation as well. This appears plausible because the aerosol composition
8.5. RESULTS AND DISCUSSION

Figure 8.17: Aerosol extinction efficiency measured in the UV region, according to Lavvas et al. [67] (187 nm) and Porco et al. [68] (338 nm). After [67].

dependence of $\sigma$ with altitude we can make a simple estimate for the total column opacity due to aerosol scattering:

Column opacity $\approx (\sigma_{0\text{km}} - \sigma_{250\text{km}}) \Delta \ell/2 \approx 10^{-10} \text{cm}^{-1} \cdot 2.5 \times 10^7 \text{cm} \approx 2 \times 10^{-3}$

Which is of the correct order of magnitude and in good agreement with the value obtained with the model by Lavvas et al. A complete treatment of the scattering problem is necessary for a more quantitative analysis, but we can conclude that our simple approach in the solar-scattering approximation appears able to correctly model at least the main effects produced by aerosols.

8.5.2 CO concentration

The inversion of the observations allowed to retrieve the distribution of the CO concentration. We show in Figure 8.18 the retrieved CO concentration for each one of the observed spectra and in Figure 8.19 the least squares fit of the five retrievals. In Table 8.2 we summarize the results with their errors.

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>VMR (ppmv)</th>
<th>Noise error (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600.0</td>
<td>86</td>
<td>± 15</td>
</tr>
<tr>
<td>550.0</td>
<td>78</td>
<td>± 15</td>
</tr>
<tr>
<td>500.0</td>
<td>87</td>
<td>± 15</td>
</tr>
<tr>
<td>450.0</td>
<td>125</td>
<td>± 12</td>
</tr>
<tr>
<td>400.0</td>
<td>119</td>
<td>± 9</td>
</tr>
<tr>
<td>350.0</td>
<td>79.5</td>
<td>± 7.0</td>
</tr>
<tr>
<td>300.0</td>
<td>57.8</td>
<td>± 3.7</td>
</tr>
<tr>
<td>250.0</td>
<td>17.3</td>
<td>± 3.9</td>
</tr>
</tbody>
</table>

Table 8.2: Results of the inversion for CO VMR, with an a priori assumption of 50 ppmv.

As we can see, our retrieved VMR profile, far from being uniform, is instead strongly dependent on altitude. The retrieved abundance at 400 km appears in fact to be at least three should be quite uniform in the last 200 km.
times larger than the one at lower altitudes. The retrieved concentration at 300 km is in general agreement with that obtained by Gurwell & Muhlerman in [47] through the analysis of the CO 2-1 rotational transition (see section 7): their best fit was given by a uniform concentration of 50 ppmv at the lowest altitudes, but was compatible with a concentration of 60 ppmv at 300 km as well. Also López-Valverde et al. [49] pointed out that a stratospheric concentration of 60 ppmv would have been in agreement with their measurements. The slightly larger value we obtain at 350 ppmv is actually to be considered in good agreement with the 50 ppmv concentration: in fact we see that the emission at 400 km is generally under-estimated and so a larger concentration at 350 km is required. In fact, given the low number of independent limb scannings, VMRs retrieved at adjacent altitudes on the retrieval grid are strongly correlated. Our result substantially differs from that obtained by Hidayat et al. [46], who suggested that the concentration of CO in the stratosphere falls to 5 ppmv. The value obtained at 250 km is almost three times lower than the one retrieved above: this value is slightly lower than that of (32±10) ppmv obtained by López-Valverde et al. [49] in the lower stratosphere and by Baines et al. [50] from VIMS observations on the night side below 300 km. This slight disagreement might be given by extinction due to aerosols, which becomes important at these altitudes. Besides, extinction by aerosols can have an important effect on the population of the second excited level at these altitudes, that is still strongly pumped by solar radiation. An additional extinction would decrease the solar flux reaching these regions and hence decreasing the population of CO(2).

Up to now, above 300 km there are no measurements constraining the CO concentration. Thus we cannot compare our values with other experiments. But, as we pointed out in section 7, all photochemical models of Titan’s atmosphere predict that CO should be uniformly mixed in the whole atmosphere. An observable evidence for a disuniform profile would mean that some new photochemical process is at work in producing/destroying CO, otherwise very stable and thus uniformly mixed. Coustenis et al. [70] suggest that the vertical distribution of CO might be altered by aerosols, which might absorb CO and transort it in other atmospheric regions. However, there is no evidence for this to happen. Due to most of the theoretical
8.5. RESULTS AND DISCUSSION

predictions, we strongly suspect that the actual VMR of CO above 350 km might differ from that obtained in this work and we explored some possible reasons for this.

Omitting scattering correction

The scattering correction has an important effect on the retrieved quantities, mainly at lower altitudes. Therefore, we performed an inversion without considering it and compared the results obtained. Given the strong continuum signal, we made the inversion considering only the peaks of the CO band, where CO signal is stronger compared to the background. The results, assuming an a priori uniform 50 ppmv concentration, are shown in Figure 8.20, compared to those we obtained above.

As we can see, the retrieved VMR is almost everywhere about 20 ppmv larger, apart from the highest altitudes. The profile, however, is still in disagreement with a uniform concentration, being almost only shifted at larger VMRs. The scattering correction has no role in the unexpected behaviour we obtained.

Different thermal structure

The spectra we analyzed were acquired by VIMS during 2007, at latitude 70°S, that is during summer conditions. Therefore, it is possible that the actual temperature-pressure profile is different from that of Yelle model, which is only a global average profile. As we discussed in section 7, in a recent work [42], the latitudinal variation of the temperature structure was first retrieved. This allows us to consider the actual temperature profile at 70°S in 2007. measured exactly during Cassini’s T32 flyby of Titan, the same as our observations.

The temperature and pressure profile was retrieved by Achterberg et al. from CIRS measurements\(^5\) of the CH\(_4\) emission below 550 km. Above that altitude we extended the temperature profile using the method of Yelle et al.. Thus, we extrapolated the temperature profile

\(^5\)For the profile we are going to use, the data were collected during Cassini’s T32 flyby of Titan, the same of our observations.
from 550 km to the mesospheric inversion, \( \sim 600 \) km, and specularly reflected it above, finally reaching a temperature close to 175 K. Though this is a rather crude approach, the temperature profile above 600 km is not of much importance for this work and will not influence our conclusions. For the extension of the pressure profile above 550 km, we relied on our extended temperature and integrated the hydrostatic equilibrium equation \( \frac{dP(z)}{dz} = -\rho(z)g(z) \) starting from the given values of temperature and pressure at 550 km.

A different thermal structure can influence the actual emission in two ways. First of all, the effect of all collisional processes have to be evaluated again and the vibrational temperatures may be modified. On the other hand, the volume mixing ratios have to be scaled for the new density. The first effect will be important were the kinetic and vibrational temperature profiles differ only slightly, that is below \( \sim 300 \) km. Therefore, this effect should be of secondary importance for us and we did not recalculate the vibrational temperature profiles, though we intend to do it in the future to quantify this effect. On the other hand, the new number density profile shows non-negligible differences with the Yelle one (as in Figure 8.21) and the re-scaling of volume mixing ratios is significant above 450 km, as we can note in Figure 8.22.

With this re-scaling, the new concentration is significantly smaller than that obtained before, although it is still too large in the highest part of the atmosphere. Thus, the nominal thermal structure is not the only responsible for the unexpected behaviour.

Different vibrational temperatures

The other aspect to be investigated is the possibility that the computed vibrational temperatures differ from the actual ones at least above 400 km. If the vibrational temperatures for the CO excited levels were significantly larger at high altitudes, we could give explain the observed emission with a smaller volume mixing ratio than the one retrieved. Above 400 km the populations of the first and second excited states are mainly controlled by absorption of radiation and no simple changes to the collisional model (like using different collisional rates) can explain such an over-excitation. At high altitudes (above 500 km), we saw that the role of
Figure 8.21: Comparison between densities obtained assuming Yelle thermal structure or the one by Achterberg et al.

Figure 8.22: Comparison between VMR for CO obtained assuming the temperature-pressure profile by Yelle et al. [38] and by Achterberg et al. [42].
CO(2) is of secondary importance (see Figures 8.11 to 8.15). Thus we need almost a factor of two larger CO(1) population at these altitudes to explain the observations with a uniform concentration of CO, at the value of 60 ppmv we retrieved at 300 km. An over-excitation of the CO(2) state may play some role only at 400 km, where its contribution is still important. In the following we discuss some possible further excitation mechanisms.

Further radiative excitation

In the calculation of the photoabsorption rates of the CO fundamental, first hot and first overtone bands, the contribution of scattering and absorption by aerosols has been neglected, as well as the radiation reflected at the surface. The first can give a contribution in two ways: radiation scattered back from lower atmospheric levels might contribute to enhance the absorption rate above and at the same time we have a further mechanism for extinction of radiation particularly at the lower levels. Neglecting the latter is thought to cause an over-estimation of CO(2) level population below 250 km, as we pointed out above. With regards to back-scattered radiation, neglecting it can be a probable source of under-estimation of the level populations. However, the most probable scenario is that this radiation is all absorbed in the lower atmospheric layers and can hardly reach the higher part of the atmosphere, where we are looking for further excitation mechanisms. But let us assume that the whole reflected/scattered radiation reaches the altitudes above 400 km; this case would be equivalent to one with an enhanced solar flux.

A maximum estimate of this effect is given by the planetary albedo near the CO fundamental and overtone bands. With regards to the fundamental at 4.7 μm, we refer to Lellouch et al. [48], who measured Titan’s albedo in the region from 4.7 μm and 5 μm: the value just outside the CO band is about 0.06. The authors point out that inside the CO band there is a residual flux probably due to scattering by stratospheric hazes, which amounts to 0.01 of the incoming solar flux. Therefore, even over-estimating the part of the back-scattered radiation that reaches 400 km we would have only a difference of 6% in the actual solar radiation. Therefore, we can exclude that this process is the one we are looking for, as we need something comparable to radiative excitation.

For the overtone band at 2.3 μm, the situation is a bit different, but not much. In the 2.3 μm window there is an important absorption by CH₄, so that the actual planetary albedo cannot be estimated clearly from observations (see Negrao et al., [69]). If we rely on the model assumed by Lavvas et al. [?] for the surface reflection, the albedo at 2.3 μm should be about 0.15. Again, this radiation is most suitably being absorbed in the lower atmospheric levels and only a minimum part would reach the regions above 400 km. In any case, we are assured that the absorption of back-scattered radiation cannot modify the nominal CO(2) population by more than a few percents.

Therefore, we can exclude back-scattered radiation as the main source of an enhanced non-LTE population for CO excited levels.

Further collisional excitation

Another possible reason for the disagreement between our retrieved CO concentration and the expected one is the presence of other excitation mechanisms than those considered in the nominal model. Vibrational energy transfer from other levels out of LTE can in principle be a significant source of excitation. The most interesting processes in this case were those we explored in section 7.2, that is the vibrational energy transfer from the excited levels of CH₄; in particular, 2ν₄ state, the last one, showing a strong non-LTE behaviour above 400 km due
to the absorption of solar radiation, and being quite close to CO(1) and N\textsubscript{2}(1) levels, was our first candidate. However, we saw at the end of section 7.2 that these processes are less important than the radiative excitation by almost two orders of magnitude and thus cannot give a significant contribution to the overpopulation of the CO(1) level.

In order to see which other collisional processes might be important for CO(1) over-excitation, we can follow the following procedure. Let us consider the V-V processes:

1. \text{CO}(1) + M =\text{CO} + M(x)

2. \text{N\textsubscript{2}}(1) + M =\text{N\textsubscript{2}} + M(x)

With M(x) indicating a molecule M in the state x. For these processes to be important in CO(1) over-population, they have to be of the order of radiative excitation. For process 1, if the rate constant in the forward direction (that is, for CO(1) de-excitation) is \(k_1\), the reverse process will be significant if \(k_0 [M(x)] = P_{01}\), \(P_{01}\) being the total photoabsorption rate. Substituting the expression for the inverse rate and writing \([M(x)]\) as the product of the non-LTE ratio \(r_x\) and its equilibrium population, we obtain:

\[
\frac{k_1 e^{(E_{M(x)} - E_{\text{CO}(1)})/kT}}{g_x} \{M\} n r_x g_x e^{-E_{M(x)}/kT} \sim P_{01}
\]

And then:

\[
k_1 r_x \{M\} \sim \frac{P_{01} e^{E_{\text{CO}(1)}/kT}}{n}
\]

Where \(\{M\}\) is the volume mixing ratio of molecule M, and \(n\) is the total number density. For process 2, the estimation is analogous, but we have to rescale by a factor \(k_0' [N_2]/L_{N_2}\) to account for the energy transferred from M(x) to N\textsubscript{2}(1) and from there to CO(1) (see section 7.2).

\[
k_2 r_x \{M\} \sim \frac{P_{01} e^{E_{\text{N\textsubscript{2}}(1)}/kT} L_{N_2}}{n k_0' [N_2]}
\]

Figure 8.23 shows the required value for the product \(k r_x \{M\}\) for a process to be important against radiative excitation. As we already saw in section 7.2, the excitation mediated by N\textsubscript{2}(1) is more efficient than the direct route. The requirement for the collisional rate becomes very strong above 400 km, and it seems difficult that some process can satisfy it, moreover because we have already considered processes that involve the abundant CH\textsubscript{4} and other molecules have very small concentrations. Up to now, we found no process satisfying this requirement and it seems unlikely that some exist.

With regards to the CO(2) level, it seems unlikely that it can be further excited by collisional processes. If we consider for example the possibility of V-V quasi-resonant transfer of energy from the CH\textsubscript{4} excited levels with energies about 4300 cm\textsuperscript{-1}, the rate constant for the process CH\textsubscript{4}(4300) + CO = CH\textsubscript{4} + CO(2) has to be of the order\textsuperscript{6} of \(10^{-8}\) cm\textsuperscript{3} s\textsuperscript{-1} for it to be as important as the radiative excitation, which is absolutely too large, given that it involves two double-gap transitions and the resonant processes between CH\textsubscript{4} levels have rates only of the order of \(10^{-11}\) cm\textsuperscript{3} s\textsuperscript{-1}.

\textsuperscript{6}We made this estimate assuming the vibrational temperatures for these levels as given by García-Comas \textit{et al.} [51], at an altitude of 500 km.
CHAPTER 8. DATA ANALYSIS

Other excitation mechanisms?

Other excitation of CO(1) may in principle be due to cascade processes from higher excited levels. However, this is not the case in Titan’s atmosphere. The third excited level (that we did not consider till now) is excited by solar radiation in the 1.5 $\mu$m band, where the solar flux is less than the double of that at 2.3 $\mu$m. However, the Einstein coefficient for the transition $0 \rightarrow 3$ is 100 hundred times smaller than that for $0 \rightarrow 2$ and 10000 times smaller than the one in the fundamental. The spontaneous decay of CO(3) to CO(2) should then have an effect of less than 2% on the CO(2) population. The same holds for higher excited levels and we can exclude that a cascade production from more excited vibrational levels may be important.

Further radiative pumping occurs in the UV region, exciting CO to higher electronic levels (or photodissociating it). There might be some decay from there to the ground electronic state but with higher vibrational excitation. However, this process is completely negligible. The population of the electronic excited levels, assuming that the only loss process from there is spontaneous emission, is equal to:

$$\frac{[\text{CO}(\alpha)]}{[\text{CO}]} \approx \frac{P_{0,\alpha}}{A_\alpha}$$

Where $P_{0,\alpha}$ is the total photoabsorption rate in the UV region and $A_\alpha$ the spontaneous emission coefficient. If we assume that all de-excitation from level $\alpha$ leads to the first vibrational state of the ground electronic level (that is, to CO(1)), the over-production for CO(1) would be equal to $A_\alpha [\text{CO}(\alpha)]/[\text{CO}]$, then to the total photoabsorption rate in the UV. The latter should be of the order of the photodissociation rate for N$_2$, which has a strong bond similar to CO; Wilson & Atreya [44] give a value of $10^{-8}$ s$^{-1}$ for this, in the upper part of the atmosphere. Assuming this value, we see that the contribution due to cascade processes from electronically excited levels is negligible, even with our unrealistic assumptions, with respect to others (direct...
8.5. RESULTS AND DISCUSSION

Radiative excitation is everywhere larger than $10^{-6}$.

Collisions with ions and with energetic particles coming from the outer space appear both to be negligible as well. Free electrons have a number density of the order of $10^{-5}$ cm$^{-3}$ at 800 km (see [44]), that corresponds to a VMR of less than $10^{-8}$, and this is steeply decreasing at lower altitudes. Looking at Figure 8.23, with VMR=$10^{-8}$ (which is a maximum estimate) we need a rate constant (multiplied by the non-LTE factor $r_x$) larger than $10^{-5}$, which appears too much even for collisions with charged particles. Excitation due to cosmic rays should show a variation depending on the position of the planet with respect to Saturn’s magnetosphere, that shields Titan from the incoming flux. Titan stays for 95% of its time inside it and only 5% outside (see [71]). However, no systematic trend in the observed emission at 500 km is seen considering measurements at different times and thus we are led to exclude this effect.
Conclusions

The study of non-LTE processes and of their influence on atmospheric molecular emission has allowed the analysis of CO concentration in Titan’s atmosphere, which is particularly interesting for many aspects. The analysis of the processes controlling the population of the first two vibrational excited states of CO have led to the inclusion of new collisional pathways for their excitation and de-excitation with respect to previous models. The solution of the non-LTE problem with the aid of GRANADA (Generic radiative transfer and non-LTE populations algorithm), on the basis of this new collisional scheme, allowed the determination of CO(1) and CO(2) populations in Titan’s atmosphere during daytime; the profile obtained differs substantially in the region around 300 km from previous ones. The possibility of further pathways for CO(1) excitation, due to vibrational energy transfer from the excited states of CH$_4$ (mainly from CH$_4$(2$\nu_4$), through the route CH$_4$(2$\nu_4$) → N$_2$(1) → CO(1)), is explored, but appears to be negligible if compared to the radiative excitation.

The retrieval of CO concentration from VIMS (Visual and Infrared Mapping Spectrometer, on board Cassini) observations is performed with the aid of the Geofit Broad Band (radiative transfer and retrieval code), on the basis of the non-LTE population profiles for CO(1) and CO(2) calculated in this work. Due to the presence of a continuum signal given by scattering of solar radiation by aerosols, quite important below 300 km, our radiative transfer code has been improved to take into account a first approximation of this effect, based on simple assumptions on the phase function and frequency dependence of the scattering coefficient. The retrieved scattering efficiency correctly reproduces the mesospheric detached haze layer and the resulting total column extinction is consistent with the model by Lavvas et al.

For CO, the result obtained at 300 km, where we mostly rely on our non-LTE populations, is in good agreement with the 50 ppmv concentration obtained by Gurwell & Muhleman (2000). However, the obtained CO concentration above that altitude seems to be significantly enhanced and is in disagreement with predictions based on photochemical models which give evidences for a uniform CO distribution in the whole atmosphere. Possible explanations of the observed emission at altitudes above 400 km without the need of a large CO concentration are explored. The assumption of a different thermal structure from the nominal one gives a first contribution above 450 km, lowering the CO concentration by almost 25%. This effect is however not enough to explain the disagreement between predictions and observations. It is noted that an enhanced CO(1) population by a factor of 2 in the region above 400 km would explain the observed behaviour and, then, possible changes to the nominal collisional model are explored. The possibility of an enhanced radiative excitation due to back-scattered radiation seems to be only of secondary importance. Otherwise, the effect of energy transfer from the excited states of other molecules may be significant if the rate constant for these processes is sufficiently strong. However, the required value of the rate constant for a process to compete with radiative excitation at 400 - 500 km is very large and it seems unlikely that some process can satisfy this requirement.
Further studies are needed at least in two directions. The effect of extinction by aerosols has an important effect on the population of CO(2) below 250 km, and scattered radiation is a significant additional difficulty in the data analysis at low altitudes. Our semi-empirical treatment of the scattered solar radiation, though explaining quite well the observations, is certainly not adequate for a most quantitative study and a further investigation on the actual aerosol optical properties is needed. On the other hand, we are still in search of further excitation mechanisms of CO(1) above 400 km. If no process satisfying our requirements will be found, the analyzed measurements indicate that the CO volume mixing ratio is effectively varying with altitude, in disagreement with the predictions of the photochemical models by Lara et al. and Wilson & Atreya.
Bibliography


Chapter 2


Chapter 4


Chapter 5


Chapter 6:


Chapter 7 & 8:


