# 9. Atomic and Molecular Spectroscopy

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9.1 Introduction

Spectroscopy is a general technique for analyzing the radiation emitted or absorbed by a plasma in order to measure certain properties of the medium. The aim is to obtain absolute measurements of species densities, their spatial variation, as well as their variation with control parameters of the plasma (gas mixture, pressure, power dissipated in the discharge...). Although some techniques are convenient for measuring relative variations, they are not able to easily provide absolute numbers. Some techniques are able to give chord-integrated measurements, while others give local measurements directly. Although emission spectroscopy is generally convenient, it is only in special cases when absolute measurements of the main species can be obtained. Thus other, complementary techniques have been developed.

In general, spectroscopy is a versatile and powerful diagnostic: it is non-perturbing in most cases, techniques are available for a broad range of wavelengths from the Infra-Red to the X-ray, and good spatial and spectral resolution is possible.

Several books and review articles are available describing the spectroscopy of plasmas: Griem [1], Hutchinson [2], Marr [3], McWhirter [4], Pecker-Wimpel [5], Thorne [8], Thorne, Litzen and Johansson [6]. These describe the physics of the excitation of atoms and atomic ions and the subsequent emission of radiation. The radiation is emitted when an atom (or ion or molecule) makes a downward transition from an upper level to a lower level. The energy (or the wavelength) of the emitted photons is given by the difference in energy between the atomic levels. The intensity of the radiation depends on the number of atoms in the upper excited level and on the transition probability (the Einstein coefficients) between the two levels.

Molecules generally have bound electronically-excited configurations, as well as vibrational and rotational energy levels corresponding to motions within these "potential wells" [7]. A molecular spectrum is thus much more complicated, but also much richer, than an atomic spectrum, allowing a range of wavelengths to be observed, from the UV (electronic transitions) through the IR (vibrational transitions) to the microwave (pure rotational transitions).

We looked at processes for producing plasma particles (electrons, ions, radicals) in chapter 2. We will here look in more detail at processes which can produce excited species, since we are often limited to observing the radiation from these excited states. There are many processes which can lead to the production (or destruction) of excited species, and which could thus play a role in determining the intensity of the radiation. These must be carefully considered when analysing the radiation emitted from the plasma. Generally, the population of the excited level is proportional to the density of the ground state of the given species, if pure “excitation” is dominant. The density of the ground state, and that of metastable states when they are present, depends on transport. In some cases, the density of the emitting species A* depends on another species B, and hence there is a less direct relation with the ground state of species A.
9.1.1 Excitation and deexcitation processes

In order for an atom or molecule to emit radiation and hence to be seen, it must be excited – promoted to an upper level from which it can make a transition to a lower level, with the emission of radiation. There are several mechanisms by which these excited atoms and molecules can be produced.

Collisional excitation and deexcitation

In this process, the impact of an electron excites the atom or molecule from the ground state up to an excited state:

\[ e + A \rightarrow e + A^* \]  \hspace{1cm} (9.1)

Here again, the energy of the incident electron must be greater than a certain threshold, \( E_i > h\nu_{ij} \), where \( h\nu_{ij} \) is the energy difference between levels \( j \) and \( i \) (generally assumed to be the ground state). The cross section for such excitation processes shows a typical form – threshold energy, with a rapid rise to a maximum at a few times the threshold energy, and a more gradual decrease at higher energies. Figure 9.1 shows the excitation of the 2p level of the hydrogen atom [98] by electron impact: the cross section as function of energy (dotted line) and the reaction rate as a function of temperature.

Figure 9.1 Excitation of level 2p in hydrogen by electron impact [98]
Again, in the case of atoms and molecules immersed in plasmas, where the electrons have a range of energies, we are generally more interested in the rate coefficient, which is calculated as above from the cross section (see Chapter 2). In some cases a relatively simple expression can be found for the cross section or the rate coefficient – much effort has been put into finding such expressions for use in numerical codes for describing Collisional-Radiative models for laboratory plasmas or for use in transport codes to simulate thermonuclear fusion experiments, but often these expressions are of limited accuracy at low temperatures. We can find such expressions in books [98] and reports [99, Lennon et al.). In some cases, though, we must also consider the excitation of a level from other excited levels. This is particularly important for atoms (such as He, Ne, Ar) which have metastable levels which can have relatively large populations compared to the other excited levels. We should note that although metastable levels are unable to radiatively decay too lower levels, they can be excited (or deexcited) by electron impact:

\[ e + A \leftrightarrow e + A^{m*} \]
\[ e + A^{m*} \rightarrow e + A^{**} \]
\[ A^{**} \rightarrow A + h\nu \]  

(9.2)

Here, \( A^{m*} \) represents an atom in the excited metastable level and \( A^{**} \) represents another (non-metastable) excited atom. Atoms created in such long-lived metastable states will generally remain in these levels until they are transferred to other excited levels by electron impact, collide with other atoms or molecules or with the wall of the reactor (hence the importance of transport processes for these species). We should note that the general form for the cross section for excitation of metastable levels, although similar to that for “allowed” levels, rises more sharply above threshold, and decreases more rapidly above the maximum (compare Figure 9.2 for the excitation of the 2s level in hydrogen, which is metastable, to that of Figure 9.1). The resulting rate coefficient is about a factor 10 lower than that for exciting an allowed transition.
Although the level 2s is formally a metastable level, it is coupled very strongly to the 2p level, which can make a radiative transition to the ground level. The cross section and the rate coefficient for the 2s-2p transition is shown rate coefficient very large even at low temperatures (see Figure 9.3, from [98]). A ground level hydrogen atom immersed in a plasma with an electron temperature of 5 eV and a density of $10^{17}$ m$^{-3}$ would be excited to the 2s level in about 10 ms, from which it would be transferred to the 2p level in about 4 μs (and from there to the ground level by a radiative transition).
Figure 9.3 Excitation transfer from level 2s to level 2p in hydrogen by electron impact [98]

The rate of transfer from an upper level $j$ to a lower level $i$ via electron collisions is given by:

$$\frac{dn_j}{dt} = -n_e n_j X_{ji}(T_e)$$

(9.3)

Here, we have written $X_{ji}$ as a function of temperature – the electron temperature, and we have thus assumed that the electron distribution function is Maxwellian. This is not always the case, and there is a significant effort to calculate the electron distribution function in laboratory plasmas. In this case, the reaction rates must be determined by evaluating the cross section as function of the electron energy, and then integrating over the distribution function (Chapter 2). For inclusion in numerical calculations of the intensities of spectral lines, we want to use simple, yet sufficiently accurate, expressions for the excitation rate coefficients. These have been provided for hydrogen and helium by Janev et al. [98] and for argon by several authors, notably Vlcek [100]. Broadly applicable, approximate expressions for $X_{ij}(T_e)$ have also been derived by several authors – one of the standard simple representations is due to Seaton [4]:

\[ \text{Figure 9.3 Excitation transfer from level 2s to level 2p in hydrogen by electron impact [98]} \]
\[
X_{ji}(T_e) = \frac{6.5 \times 10^{-4}}{\chi_{ji} T_e^{1/2}} f_{ji} \exp\left(-\frac{e \chi_{ji}}{k T_e}\right)
\]  

(9.4)

Note that this expression is for the excitation rate coefficient in cm\(^3\)s\(^{-1}\). \(\chi_{ji}\) is the excitation potential in eV, \(f_{ji}\) is the absorption oscillator strength, and the electron temperature \(T_e\) is in K.

The inverse deexcitation process has also to be taken into account, particularly in high density plasmas where the electron collision rate is comparable to the radiative decay rate. The rate for collisional deexcitation can be calculated from that for excitation by the principle of detailed balance (see section 9.1.2).

In the case of molecules, electron impact can efficiently excite higher electronic and vibrational levels, but heavy particle impact is more important for the excitation of rotational levels.

**Excitation transfer**

Excitation can be transferred from one chemical species to another in a discharge via a "Penning" excitation process. This process is generally only important if one of the species has excited metastable levels that can develop substantial populations:

\[
A + B^{m^*} \rightarrow A^* + B
\]

\[
A^* \rightarrow A + h\nu
\]

(9.5)

If the excited level in the colliding species A can radiatively decay, the result can be a sequence of radiation events, with the emission of spectral lines characteristic of the species A. This process is of practical use in the HeNe laser. Metastable He atoms are produced in an electrical discharge. The 2\(^3\)S level is metastable, being the lowest triplet and hence unable to radiatively decay to the ground state 1\(^1\)S because of the selection rule \(\Delta S=0\). The 2\(^1\)S level is metastable in that it cannot radiatively couple to the ground state since this would require \(\Delta l = 0\), which is not allowed for electric dipole transitions. Collisonal transfer to the nearby 2\(^1\)P level, which can radiatively couple to the ground state, then often determines the lifetime of the 2\(^1\)S level. The excitation energies of the 2\(^1\)S and 2\(^3\)S levels in helium are very close to the upper lasing levels 3s2 and 2s2 in neon, and so the rate coefficients for energy transfer are very fast, leading to a population inversion of the energy levels in neon (see Figure 9.4).
A similar mechanism is used in the case of the CO$_2$ laser. In this case, a vibrationally-excited nitrogen molecule transfers its energy to the upper lasing level of the CO$_2$ molecule, which can result in a population inversion and lasing near 961 cm$^{-1}$ (10.6 µm) or 1064 cm$^{-1}$ (9.60 µm) – see Figure 9.5.

**Dissociative excitation**

We can also create excited atoms and molecules (radicals) by “internal conversion”. In molecular gases that are undergoing dissociative reactions, a significant fraction of the daughter atoms can be produced in excited levels. We can illustrate the process by considering the case of hydrogen; from the potential curves we note that if the impacting electron has a kinetic energy of at least 15 eV, it can excite the H$_2$ molecule from the $X^1\Sigma_g^+$
ground level to an excited level; this level can be repulsive, resulting in the dissociation of the molecule, but with the production of a ground state atom and an excited atom:

$$e + H_2 \rightarrow e + H + H^*$$  \hspace{1cm} (9.6)

The excited atom will then radiate away this energy, giving rise to the characteristic atomic spectral lines:

$$H^* \rightarrow H + hv$$  \hspace{1cm} (9.7)

The reaction rate for the production of 2s in hydrogen is shown in Figure 9.6.

![Figure 9.6 Dissociative excitation of hydrogen [98]](image)

We should note that when the atom is created in a metastable state, it cannot radiatively decay to a lower level, and will stay in this level until it hits the wall of the plasma reactor. In the case of the hydrogen 2s level, we have seen that it is quickly transferred by collision to the 2p level, from which it can radiate.

When molecular radicals are produced during the dissociation of heavier molecules, they are often produced in vibrationally-excited states.
Radiative recombination

In this process, an ion captures an electron, and the excess of energy is radiated away:

\[ e + H^+ \rightarrow H + h\nu \]  

(9.8)

Since the electrons before the reaction have a continuous energy spectrum (we assume in general a Maxwellian distribution of velocities), the radiation will have a continuous spectrum, with a minimum energy, given by the ionization potential of the level to which the electron recombines. In the case of hydrogen, this "continuum edge" is at 91.1 nm (if the electron recombines into level \( n = 1 \)), and at 364.6 nm (if the electron recombines into \( n = 2 \)). The cross-section for this process is greatest at low energy, as can be seen in Figure 9.7, but even for electron temperatures below 1 eV, the rate coefficient is only about \( 10^{13} \) cm\(^3\)/s. It is thus a process which is significant for dense, highly-ionized plasmas. The rate coefficient is largest for recombination into the 1s level of the hydrogen atom, but it is also reasonably high for the \( n=2, 3, 4 \) levels. From these excited levels, there is a further emission of line radiation as the electron radiates away this “excess” energy.

![Figure 9.7 Radiative recombination in hydrogen [98]](image-url)
Three-body recombination

It is possible for three particles to participate in the recombination process, generally an ion and two electrons:

\[ e + e + H^+ \rightarrow e + H \]  \hspace{1cm} (9.9)

One of the electrons is captured by the ion, while the other is able to carry away the excess energy and momentum, the result being that there is no continuum radiation in this case. This process is the opposite of collisional ionization, and the rate coefficient can again be calculated by detailed balance.

Dissociative Recombination

Electrons can be captured by molecular ions, resulting in a transient excited molecule which subsequently breaks up, generally producing at least one excited atom in the process. The rate coefficient for this process is illustrated in Figure 9.8 for the case of electrons recombining with hydrogen molecular ions \( H_2^+ \):

\[ e + H_2^+ \rightarrow H + H^+ \]  \hspace{1cm} (9.10)
Again, we note that the rate coefficient is reasonably large only for electron temperatures lower than about 1 eV; the rate coefficient is, however, much greater than that for radiative recombination, and so this will be dominant for plasma in which there is a modest fraction of molecular ions.

**Dielectronic Recombination**

In plasmas with multiply-charged ions, the process of capturing a free electron can be accompanied by the internal excitation of a bound electron. This excitation allows for the conservation of energy and momentum, and so there is no continuum radiation. There will, however, be line radiation produced as the excited electrons cascade down to lower levels:

\[
e + A^{n+} \rightarrow A^{(n-1)+++} \\
A^{(n-1)+++} \rightarrow A^{(n-1)++} + h\nu
\]  

(9.11)

Here, \(A^{(n-1)+++}\) represents an ion having lost \((n-1)\) electrons, but with two excited electrons. Subsequently, these excited electrons cascade down to the ground state by the emission of photons.
The emission and absorption of radiation

9.1.2 Detailed Balance

There are several processes which affect the population of excited levels, and which are the inverse of each other: collisional excitation versus deexcitation, photoionization versus radiative recombination, emission versus absorption of radiation etc. The rate coefficients for these processes can be related by detailed balance (see Chapter 2). One imagines a situation where all processes are balanced by their inverse. This is what happens under conditions of thermal equilibrium. For the case of collisional excitation/deexcitation between a lower level i and an upper level j we have:

\[ n_j X_{ji}(T_e) = n_i X_{ij}(T_e) \]  (9.12)

Here \( X_{ji} \) is the rate coefficient for transitions from level j to level i (deexcitation), and \( X_{ij} \) the rate coefficient for excitation. But we know that in thermal equilibrium the populations of the energy levels are given by a Boltzmann relation:

\[ \frac{n_j}{n_i} = \frac{g_j}{g_i} \exp \left( -\frac{E_{ji}}{k_B T_e} \right) \]  (9.13)

From these two relations we can readily show:

\[ X_{ji}(T_e) = X_{ij}(T_e) \frac{g_i}{g_j} \exp \left( \frac{E_{ji}}{k_B T_e} \right) \]  (9.14)

Similar considerations can be used to relate the rate coefficients for other inverse processes.

9.2 Plasma Models

These excitation/deexcitation processes - both collisional and radiative - must be incorporated into numerical models to predict the densities of excited levels, and hence the intensity of the radiation emitted by different species in the plasma. Due to the large number of levels involved, and the number of possible processes, some approximations are always required. In the standard models described below, only electron collisions are considered. One must analyse the particular situation to verify whether or not the other molecular or atomic processes are negligible. If not, they must be included explicitly in the numerical model.

9.14
Local Thermodynamic Equilibrium (LTE) Model

At high densities, both the excitation and deexcitation transitions between the atomic levels are dominated by electron collisions. If the collision processes dominate the radiative transitions for all quantum levels of an atomic system, the level populations are then said to be in local thermodynamic equilibrium (the LTE regime), and the level populations are given by the classical Boltzmann relation:

\[
\frac{n_j}{n_i} = \frac{g_j}{g_i} \exp\left(-\frac{eE_{ji}}{k_B T_e}\right) = \frac{g_j}{g_i} \exp\left(-\frac{E_{ji}}{T_e}\right)
\]  

(9.2.1)

where \(E_{ji} (=E_{ij})\) is the energy difference between the levels \(i\) and \(j\) in eV, \(g_i\) and \(g_j\) are the statistical weights of the levels \(i\) and \(j\), \(T_e\) is the electron temperature in K, and \(T_e\) is the electron temperature in eV.

For plasmas in LTE, the balance between different ionization stages is determined by the Saha equation:

\[
\frac{n_0(z+1) n_e}{n_0(z)} = \frac{g_0(z+1)}{g_0(z)} 2 \left(\frac{2\pi m_e k_B T_e}{\hbar^2}\right)^{3/2} \exp\left(-\frac{e\chi(z)}{k_B T_e}\right)
\]  

(9.2.2)

where \(n_0(z+1)\) and \(n_0(z)\) are the ground state densities of charge state \(z+1\) and \(z\), respectively, having statistical weights \(g_0(z+1)\) and \(g_0(z)\), \(n_e\) is the electron density, and \(\chi(z)\) is the energy difference in eV between the states \(z\) and \(z+1\): the ionization energy of ions of species \(z\). \(T_e\) is in K.

The population of level \(i\) of the species \(z\) can also be related to the ground state density of the species \(z+1\) [102]:

\[
n_i(z) = n_0(z+1)n_e \frac{g_i(z)}{g_0(z+1)} \frac{1}{2} \left(\frac{\hbar^2}{2\pi m_e k_B T_e}\right)^{3/2} \exp\left(\frac{\chi_i(z)}{k_B T_e}\right)
\]  

(9.2.3)

If the equation (9.2.3) accurately describes the level populations for all levels \(i\), the system is said to be in complete LTE (cLTE). If, on the other hand, the relation only holds for levels above a certain minimum \((i \geq p)\), we have partial LTE (pLTE). Criteria for the validity of cLTE and pLTE have been derived by several authors. Griem [1] established a criterion for pLTE by posing that the collisional de-population rate should be at least ten times the radiative de-population rate: \(n_e X_{ji}(T_e) \geq 10 A_{ji}\), where \(A_{ji}\) is the radiative transition probability for a transition from an upper level \(j\) to a lower level \(i\), and \(X_{ji}(T_e)\) is the rate coefficient for collisional de-excitation. His criterion can be expressed as:
Here $n_e$ is in m$^{-3}$, $T_e$ is in K and $z$ is the nuclear charge. We see from equation (9.2.4) that pLTE holds for higher-lying levels, and that the value of $p$ varies slowly with both the temperature and the density. If we consider the case of a plasma having a modest density of $10^{18}$ m$^{-3}$ and a temperature of $5 \times 10^4$ K with $z = 1$, we find from equation (9.2.4) that levels above $p = 6$ should be in pLTE. Fujimoto and McWhirter [102] have revisited this question of the validity of the LTE criteria. Their criterion for pLTE is based on the premise that the actual level population (derived from a Collisional-Radiative model) does not deviate the pLTE value by more than 10%. They considered three cases: recombining plasmas, ionizing plasmas, and plasmas in ionization balance. For this latter case, their criterion for pLTE can be written:

$$p \geq 533.8 \left( \frac{T_e}{z^2} \right)^{0.1} \left( \frac{z}{n_e} \right)^{0.133}$$

(9.2.5)

As for the Griem criterion, $n_e$ is in m$^{-3}$, $T_e$ is in K and $z$ is the nuclear charge. Using the same values as above, we find a value $p = 6.4$ using equation (9.2.5). We see that for this case of a plasma in ionization balance, the criterion derived by Fujimoto and McWhirter (equation 9.2.5) is very similar to that derived by Griem (equation 9.2.4). The Griem and Fujimoto-McWhirter criteria are illustrated in Figure 9.2.1, where we have considered a relatively low density case where $\frac{n_e}{z^2} = 1 \times 10^{18}$ m$^{-3}$. We see that the two criteria give approximately the same value for this case, but the variation with $T_e$ is somewhat different.

Figure 9.2.1 Quantum number for establishing pLTE according to the Griem and Fujimoto-McWhirter criteria
Griem also considered a criterion for complete LTE, where collisional transitions dominate over radiative transitions for all levels. This criterion can be expressed as a density limit:

\[ n_e \geq 9.8 \times 10^{20} \ z^7 \left( \frac{T_e}{z^2} \right)^{1/2} \]  \hspace{1cm} (9.2.6)

If we consider the same example as above, with \( z = 1 \) and \( T_e = 5 \times 10^4 \) K, we find that the electron density necessary to establish complete LTE is \( 2.2 \times 10^{23} \) m\(^{-3}\). For complete LTE, the criterion derived by Fujimoto and McWhirter [102] can be expressed as:

\[ n_e \geq 1.5 \times 10^{24} \ z^7 \left( \frac{T_e}{10^5 \ z^2} \right)^a \ where \ a = 0.55 - \left( \frac{0.49}{z} \right)^{1.5} \]  \hspace{1cm} (9.2.7)

Using the same values as above, we find that the electron density necessary to establish cLTE according to the Fujimoto-McWhirter criterion is \( 8.1 \times 10^{23} \) m\(^{-3}\).

We can also estimate the density limit for the LTE model, by using analytic formulae for \( X \) formulated by Seaton (described in McWhirter [4]):

\[ X_{ij}(T_e) = \frac{6.5 \times 10^{-4}}{E_{ji} T_e^{1/2}} f_{ij} \exp \left( -\frac{e E_{ij}}{k_B T_e} \right) \]  \hspace{1cm} (9.2.8)

where \( X_{ij} \) is the excitation rate coefficient, \( E_{ij} \) is the excitation energy in eV, and \( f_{ij} \) is the absorption oscillator strength. From the discussion of detailed balance in section 9.1.2, we can write:

\[ X_{ji}(T_e) = \frac{g_i}{g_j} \ X_{ij}(T_e) \exp \left( \frac{e E_{ij}}{k_B T_e} \right) \]  \hspace{1cm} (9.2.9)

Using this along with the relation between the oscillator strength and the transition probability:

\[ A_{ji} = \frac{e^2}{4 \pi \epsilon_o} \ \frac{8 \pi^2 \ g_i^1 \ 1 \ f_{ij}^1}{m_e e g_j^1 \ \lambda_{ij}^2} = 6.67 \times 10^{-5} \ \frac{g_i^1 \ 1}{g_j^1 \ \lambda_{ij}^2} \ f_{ij} \]  \hspace{1cm} (9.2.10)

we can find an approximate lower limit for the electron density:

\[ n_e \geq 1.6 \times 10^{18} \ T_e^{3/2} \ E_{ij}^4 \ \text{m}^{-3} \]  \hspace{1cm} (9.2.11)

where \( T_e \) is in K and \( E_{ij} \) in eV. This relation was conveniently presented in graphical form (see McWhirter [4], P.207). The most restrictive case is that where we consider the transitions from the ground state (e.g. the lowest-lying 1S-2P transition in hydrogen).  

\[ 9.17 \]
since the energy difference is the greatest. We notice that the Griem criterion (equation 9.2.6) indicates that the density limit \( n_e \) depends on \( z^6 \), while the McWhirter criterion (equation 9.2.11) doesn’t contain \( z \) explicitly. If we note that the energy levels of hydrogen-like ions are given by \( E_n = -\frac{R}{n^2} z^2 \), we see that the dependence on the nuclear charge is the same, as is the dependence on \( T_e \). The Griem criterion is illustrated in Figure 9.2.2:

![Electron density required to establish cLTE according to Griem criterion](image)

**Figure 9.2.2 Electron density required to establish complete LTE according to the Griem criterion, assuming \( z = 1 \)

Except for high density plasma jets used for plasma spray processing etc., the majority of plasmas used in materials processing never attain the densities required to establish cLTE, and so for the low-lying levels this regime is generally irrelevant. As mentioned above, the relative importance of radiative transitions compared to electron collisions depends on the excitation level. The rate coefficient for collisional deexcitation can be written:

\[
X_{ji}(T_e) = 6.5 \times 10^{-4} \frac{g_i}{g_j} \frac{f_{ij}}{E_{ji} T_e^{1/2}}
\]  

(9.2.12)

For low-lying levels, electron collision rates are smaller because of the generally larger energy gap, whereas the radiative transition rates are large. For higher-lying levels, the energy gap becomes smaller, and hence the collisional transitions become more important, and the radiative rates decrease (see equation 9.2.10). Thus, low-lying levels may be well described by a corona model, or more generally a CR model, while the high-lying (Rydberg) levels near to the ionization limit can be distributed according to their statistical weights and a Boltzmann factor (equation 9.2.1). This is the situation in which we have "partial LTE" [8].
Coronal Model

At low electron densities, the density of an excited atomic level is determined by an equilibrium between collisional excitation and radiative decay, the so-called coronal limit. In this limit, the densities of the excited levels are given by:

\[
\frac{dn_j}{dt} = n_e n_X_j - n_j A_j \quad (9.2.13)
\]

\[
n_j = n_e n_X_j A_j^{-1} \quad (9.2.14)
\]

where \(n_j\) is the density in the excited level \(j\), \(n\) the ground state density, \(X_j\) the excitation rate coefficient from the ground state to the level \(j\), and \(A_j\) the total radiative decay rate from the excited level \(j\). The emissivity \(\varepsilon_\lambda\) (in units of photons per m\(^3\) per second per Sr) for a given line of wavelength \(\lambda\) of the species is then given by:

\[
\varepsilon_\lambda = \frac{1}{4\pi} n_j A_\lambda = \frac{1}{4\pi} n_e n_X_j \frac{A_\lambda}{A_j} \quad (9.2.15)
\]

where \(A_\lambda\) is the transition rate for the line of interest, and the quotient \(A_\lambda/A_j\) is called the branching ratio. A considerable amount of work has gone into determining the excitation rate coefficients for a number of species, since they are important for astrophysics and for fusion research.

A possible exception to this simple relation occurs in the presence of metastable levels, which do not decay by the emission of radiation since such transitions are not allowed. Collisional excitation or de-excitation – or collision with the wall of the reactor - then determines the population of these levels.

In the corona model, a balance between ionization and radiative recombination determines the balance between ionization stages:

\[
n_e n(z) S(T_e, z) = n_e n(z+1) \alpha(T_e, z+1) \quad (9.2.16)
\]

or

\[
\frac{n(z+1)}{n(z)} = \frac{S(T_e, z)}{\alpha(T_e, z+1)} \quad (9.2.17)
\]

Here \(n_e\) is the electron density, \(n(z)\) is the density of ground-state ions of charge \(z\), \(n(z+1)\) the density of ground state ions of charge \(z+1\), \(S(T_e,z)\) is the ionization rate coefficient for ions of charge \(z\), and \(\alpha(T_e,z+1)\) is the recombination rate coefficient for ions of charge \(z+1\). We thus see that the distribution of ions between the charge states \(z\) depends only on the electron temperature, and not on the density, in contradistinction to the case of the LTE model.
At higher electron densities, we can no longer assume that the balance between ionization stages is determined by radiative recombination, since three-body recombination can play a role. Since the rate of radiative recombination producing ions of charge $z$ depends on the product $n_e n(z+1)$ while the rate of three-body recombination depends on $n_e^2 n(z+1)$, we see that three-body recombination can become dominant at high electron density. Also, at high electron density the transitions between excited levels no longer depend uniquely on radiative transitions; collisional transfer becomes important. The criterion for coronal equilibrium to apply for levels above level $j = 6$ in hydrogen-like ions has been proposed by McWhirter [4], using approximate formulae for the excitation rate coefficient. The criterion is based on the dominance of radiative transitions over collisions:

$$\sum_{i<j} A_{ji} \geq n_e X_{jk}(T_e)$$ (9.2.18)

If we consider hydrogen and hydrogen-like ions, the criterion can be written as:

$$n_e \leq 5.6 \times 10^{14} z^6 T_e^{1/2} \exp\left(\frac{1.164 \times 10^3 z^2}{T_e}\right) = 6.0 \times 10^{16} \frac{z^6}{T_e^{1/2}} \exp\left(\frac{0.1 z^2}{T_e}\right) \text{m}^{-3} \quad (9.2.19)$$

Here, $z$ is the charge of the ion ($z = 1$ for HI, 2 for HeII etc.), $T_e$ the electron temperature in K, and $\tilde{T}_e$ the electron temperature in eV. This relation was plotted by McWhirter ([4] Figure 1), and is redrawn in Figure 9.2.3.

---

**Density limit for coronal equilibrium**

![Graph showing electron density limit for coronal equilibrium for HI, HeII, BeIV, and CVI](image)

Figure 9.2.3 Electron density limit for coronal equilibrium

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9.20
We note that the plasma electron density should be below the values illustrated in Figure 9.2.3 for the corona model to be valid. As we can see by comparing Figures 9.2.2 and 9.2.3, the lower density limit for cLTE is about $10^6$ times as great as the upper density limit for the corona model.

**The Time-Dependent Corona Model**

We have assumed in the above discussion that the plasma is in steady-state. If the plasma parameters change, the distribution between the different charge states will change, as well as the distribution among the excited levels. If the plasma cools, for example, the ions in the higher charge states will recombine to form ions of lower $z$ (a “recombining” plasma). If the plasma becomes hotter, more ionization will occur, producing ions of higher charge state (an “ionizing” plasma). The relaxation time is determined by the slowest process: the lowest recombination or ionization rate. If we consider the case of an ionizing plasma, we have:

$$\frac{d n(z)}{d t} = n_e n(z-1) S(z-1) - n_e n(z) \alpha(z)$$  \hspace{1cm} (9.2.20)

with $n(z) + n(z-1) = \text{constant}$. The relaxation time for this simple case is given by:

$$\tau = \frac{1}{n_e [S(z-1) + \alpha(z)]}$$  \hspace{1cm} (9.2.21)

McWhirter [4] has estimated the values of $S$ and $\alpha$ for the case where $S = \alpha$, for a number of charge states. The value of $S$ (or $\alpha$) varies by less than an order of magnitude, and is approximately $10^{-12}$ cm$^3$/s. Thus, the relaxation time between charge states is given approximately by:

$$\tau \approx \frac{10^{12}}{n_e} \text{ seconds}$$  \hspace{1cm} (9.2.22)

The rate of change of the excited level population of charge state $z$ is given by:

$$\frac{d n_j(z)}{d t} = n_e n(z) X_j (T_e, z) - n_j(z) \sum_{i<j} A_{ji}(z)$$  \hspace{1cm} (9.2.23)

We see that the relaxation time for the excited level populations is approximately equal to the radiative lifetime of the excited level. This is generally of the order of several nanoseconds, and is generally much faster than the rate at which the charge states relax (the order of milliseconds, even for relatively high density plasmas). In the low density plasma for which the corona model is valid, the excited levels are “instantaneously” in equilibrium with the ground state.
Collisional-Radiative Model

At somewhat higher densities, depending on the species and slightly on the electron temperature, electron collisions between excited levels become important. The limit of this collisional-radiative (CR) regime has been well discussed in the review article by McWhirter [4]. In general, we must take into account both collisional and radiative transitions between a number of excited levels. The basic assumptions of the CR model are (McWhirter):

1. The free electrons have a Maxwellian velocity distribution.
2. Ionization can proceed from any bound level, and is partially balanced by three-body recombination into (generally) the ground state:

\[ n_i(z) + e \leftrightarrow n(z + 1) = e + e \quad (9.2.24) \]

where the reaction rates for ionization and three-body recombination are given as:

\[ n_e n_i(z) S_i(T_e, z) \]
\[ n_e^2 n(z + 1) \beta_i(T_e, z + 1) \quad (9.2.25) \]

3. There are electron-induced excitation and deexcitation transitions between bound levels. The reaction rate for the excitation process is given by:

\[ n_e n_i(z) X_{ij}(T_e, z) \quad (9.2.26) \]

4. Radiation results from transitions between bound levels and from radiative recombination. The reaction rates are given by:

\[ n_j(z) A_{ji}(z) \]
\[ n_e n(z + 1) \alpha_i(T_e, z + 1) \quad (9.2.27) \]

5. The plasma is optically thin.

Most plasmas of interest – in fusion experiments and those used for materials treatment - fall into the CR regime, and hence to get a complete description, there is a need for a great deal of atomic physics, most of which comes from theoretical calculations, supported by experimental measurements where possible. The level populations in a CR plasma are derived from a set of equations describing all these excitation/deexcitation mechanisms. Luckily, there are only a finite number of equations to be considered, since for higher-lying levels the collisional rates are dominant, and the level populations are reasonably well described by the LTE model.

9.3 Emission spectroscopy – atoms and ions
In general, a plasma contains relatively energetic electrons, which are capable of ionizing and exciting the atoms or molecules of the working gas; a plasma is generally luminous. Textbooks on plasma discharges describe the colours of the negative glows and positive columns for different gases. An analysis of the radiation spectrum emitted by the plasma can thus give us quantitative information on the species which exist in the plasma, and often we can do more: measure the temperatures of the ions and electrons and the electron density in the plasma. An important aspect of plasmas used for materials processing is the presence of many chemical species - molecules and radicals. The spatial distribution of these species in the plasma can give us valuable information about the processes which are important for dissociating the molecules which are used for deposition on (e.g. SiH₄) or etching of (e.g. Cl₂) substrates. The challenge, then, is to relate the observed radiation from the plasma to either the densities of the species of interest, or the electron density or temperature.

In principle, if we know all of the excitation processes and their rates, the electron density and the electron temperature (more generally the electron energy distribution function), then we can calculate the emissivity and hence determine the species density from a spectral measurement. Unfortunately, this is rarely the case, and so there are few situations where emission can be used to provide reliable absolute measurements of species densities. Argon and helium are notable exceptions, because of their importance to spectroscopic measurements, and the relative simplicity of their spectra. In spite of this, there have been many very interesting and useful applications of emission spectroscopy. Since optical detectors can be very fast, optical detection can be used to follow the temporal development of the RF discharge. Such measurements were carried out by Oelerich-Hill et al. [9], who were able to correlate the spatial distribution of the plasma emission with the form of the EEDF, and to follow the temporal development during the RF cycle. Another powerful application of emission spectroscopy is the availability of multi-channel detection systems, which can be used either to gather spectral information, or to obtain multi-chord intensity measurements. This latter approach allows one to calculate 2-dimensional emissivity profiles of the plasma via tomographic reconstruction, and thus to measure plasma inhomogeneities. The spatial-resolved distribution of excited species in a surface-wave produced plasma were obtained by Margot et al [10] and Besner et al [11], while Schielke et al [12] calculated 2-dimensional profiles for a parallel plate discharge employing a segmented cathode.

**Measuring plasma parameters**

In the case of a plasma under LTE conditions, the relative distribution among the excited levels is given by the Boltzmann factor (equation 9.2.1). The absolute population density of level i (of charge state z) can then be expressed as:

\[
n_i(z) = B g_i \exp\left(-\frac{E_i}{k_BT}\right)
\]

(9.3.1)

B is a constant. We want to relate the relative state populations to the total population density n(z):
\[
n(z) = \sum_i n_i(z) = B \sum_i g_i \exp \left( -\frac{eE_i}{k_B T} \right) \tag{9.3.2}
\]

If we define the partition function \( Q(z, T) \):

\[
Q(z, T) = \sum_i g_i \exp \left( -\frac{eE_i}{k_B T} \right) \tag{9.3.3}
\]

We can write the population density of level \( i \) as:

\[
n_i(z) = \frac{n(z)}{Q(z, T)} g_i \exp \left( -\frac{eE_i}{k_B T} \right) \tag{9.3.4}
\]

The absolute emissivity of the spectral line (in photons per m\(^3\) per second per Sr) can then be expressed as:

\[
\varepsilon_{ji} = \frac{1}{4\pi} n_j(z) A_{ji} = \frac{1}{4\pi} \frac{n(z)}{Q(z, T)} g_j A_{ji} \exp \left( -\frac{eE_j}{k_B T} \right) \tag{9.3.5}
\]

In terms of the specific intensity \( I_{ji} \) (Watts per m\(^3\) per Sr) we have:

\[
I_{ji} = n_j(z) A_{ji} \frac{h\nu_{ji}}{4\pi} = n_j(z) A_{ji} \frac{hc}{4\pi \lambda_{ji}} \tag{9.3.6}
\]

Here \( \nu_{ji} \) is the frequency of the \( j \to i \) transition, and \( \lambda_{ji} \) the corresponding (vacuum) wavelength. From this, we see that we can calculate the total density of the species from an absolute measurement of the emissivity, if we know the temperature, and hence are able to calculate the exponential factor and the partition function (equation 9.3.5). How do we measure \( T \)? If we consider radiative transitions from two different upper levels of the same ionization stage \( z \), we can derive from equation 9.3.5 that:

\[
\frac{\varepsilon_k}{\varepsilon_j} = \frac{g_k A_k}{g_j A_j} \exp \left( -\frac{e(E_k - E_j)}{k_B T} \right) \tag{9.3.7}
\]

We note that the ratio is independent of the ground state density. Since the atomic parameters are assumed known, the ratio of the line emissivities can be used to derive \( T \). We should note that the line ratio technique will be accurate if the energy difference between the two upper levels is (somewhat) greater than \( T \). The comparison of lines from a number of upper levels (a “Boltzmann plot”) is recommended to assure consistency. In such a “thermal” plasma, we assume that all species have the same temperature. \( T \) is thus the temperature of the electrons, ions and neutrals in the plasma. The “Boltzmann plot”
technique has been used to analyse different plasmas, including laser-produced plasmas [13], pulsed arc plasmas [14], inductively-coupled plasmas [15] and high-pressure (atmospheric pressure) plasmas [16, 17, 18, 19]). In high density plasmas, the excited levels can be significantly populated, so it is important to avoid self-absorption of the radiation (especially important for resonant transitions in which the lower level of the transition is the ground state). From equations (9.3.4) and (9.3.6) we have:

\[
\ln\left(\frac{I_{ji}}{g_j A_{ji}}\right) = \ln\left(\frac{\hbar c n(z)}{4\pi Q(z, T)}\right) - \frac{eE_j}{k_B T}
\]  

(9.3.8)

The slope of the plot will give the temperature, as shown in Figure 9.3.1 [15].

![Boltzmann plot using FeII lines in an inductively-coupled plasma](image)

Figure 9.3.1 Boltzmann plot using FeII lines in an inductively-coupled plasma [15]

We should note that even though the Boltzmann plot in Figure 9.3.1, taken from the experiments of Sung and Lim, seems to obey the correct exponential form, the use of FeI and FeII lines gave different values for the excitation temperature. These temperatures were also significantly different than the rotational temperature and the electron temperature in the plasma.

If the radiation comes from two different charge states, the ratio of line emissivities from a cLTE plasma can be written as:

\[
\frac{\varepsilon_j(z+1)}{\varepsilon_i(z)} = \frac{1}{n_e} \frac{A_j g_j(z+1)}{A_i g_i(z)} \left(\frac{2\pi m_e k_B T}{\hbar^2}\right)^{3/2} \exp\left[-\frac{e(E_j + \chi_z - E_i)}{k_B T}\right]
\]  

(9.3.8)

where \(A\) are the Einstein coefficients, \(g\) the statistical weights of the upper levels having excitation energies \(E\) (in eV), \(\chi_z\) the ionization energy of species \(z\), and \(n_e\) the electron density. Assuming that \(n_e\) is the same for all the transitions, a Boltzmann plot of the intensity
ratios for a number of lines will allow a calculation of the (electron) temperature. The advantage in this case is that the energy difference is much greater and so the error in the calculation of \( T_e \) should be less. In addition, if the plasma is in cLTE, equation (9.3.8) can be used to calculate the electron density:

\[
n_e = \frac{e_i(z)}{\varepsilon_j(z+1)} \left( \frac{2\pi m_e k_B T}{\hbar^2} \right)^{3/2} \frac{g_j(z+1)}{g_i(z)} \frac{A_j}{A_i} \exp \left( -\frac{e(E_j + \chi - E_1)}{k_B T} \right)
\]  

(9.3.9)

Even in the case of lower density plasmas, the higher-lying levels can be in partial LTE as was discussed above. In this case, the intensity of the spectral lines emitted from these levels can be expressed as:

\[
I_{ji} = K g_j A_{ji} \exp \left( \frac{E_j}{T_{ex}} \right)
\]  

(9.3.10)

where \( E_j \) is the “excitation energy” of the upper level \( j \) (measured generally from the ground state) in eV, \( g_j \) its statistical weight, and \( A_{ji} \) the transition probability. In this case, we interpret \( T_{ex} \) as the “excitation temperature” (in eV), which may be conveniently calculated from a “Boltzmann plot”:

\[
\ln(I_{ji}) = \ln(K g_j A_{ji}) - \frac{E_j}{T_{ex}}
\]  

(9.3.11)

Even in plasmas having modest electron densities, the high-lying levels can be distributed according to a Boltzmann distribution. Very often a plot of the line intensity \( I_{ij} \) versus the excitation energy \( E_i \) gives a straight line for the higher-lying levels, but deviates from this for the lower-lying levels; the method is thus only valid when one uses the higher-lying levels. We also note that this method assumes that the plasma is uniform, such that the excitation temperature does not vary along the measurement chord. In such plasmas, there is usually a significant difference between the temperature of the heavy species (atoms, molecules, ions) and the electrons. It is generally tempting (and usually justified) to relate the excitation temperature to the electron temperature, since they are generally responsible for exciting the atoms.

In low density plasmas, we are generally forced to use a Collisional-Radiative model to calculate the level populations and hence the line emissivity or intensity. Brenning [20], for example, calculated the “excitation rate coefficient” \( S_{\lambda} \) for a number of HeI lines, applicable to low density plasmas. An example for the 501.6 nm line is shown in Figure 9.3.2.
We see that the rate coefficient varies rapidly with the electron temperature; a measurement of the absolute intensity of this spectral line should thus allow a good calculation of the electron temperature:

\[ I_{\lambda} = n_e n_{\text{HeI}} S_{\lambda} \left( \frac{hc}{\lambda} \right) \frac{hc}{\lambda} \text{ Watts m}^{-3} \text{ s}^{-1} \]  \hspace{1cm} (9.3.12)

Here, \( n_{\text{HeI}} \) is the total density of helium atoms, and so to know this density we must generally assume that the atomic density is relatively uniform throughout the plasma (i.e. a low density plasma).

There have been considerable advances in the development of Collisional-Radiative Models in recent years, to include non-Maxwellian electrons and even possibly plasmas which are not completely optically thin. For example, the intensity ratio between two spectral lines from the same species and from different species can be used to calculate the electron temperature \( T_e \) in laboratory plasmas. A good example quoted by Behringer [21] is that of the ratio of a HeI line at 667.815 nm and an ArI line at 667.728 nm. The ratio has been
calculated by Behringer using a C-R model, and is found to be a fairly sensitive function of $T_e$ (see Figure 9.3.3).

Figure 9.3.3 Ratio of photon numbers for (1) HeI 667.815 nm to ArI 667.728 nm, (2) HeI 667.815 nm to ArI 810.368, (3) HeI 667.815 nm to ArI 696.543 nm, as well as $N_2^+$ to $N_2$.

Measurements using this line ratio were used by Behringer to show the influence of gas pressure (Figure 9.3.4) on the electron temperature, and the perturbation introduced by inserting a probe into the plasma (Figure 9.3.5). We note that the electron temperature decreases as we increase the pressure, while it increases when the probe is inserted into the plasma.

Figure 9.3.4 Variation of the line ratio HeI 667.815 nm to ArI 667.728 nm as a function of pressure [21]
9.29

In some cases, however, it is not a good idea to compare the intensities from two different species. If the plasma is reasonably dense, the two species may exist in spatially different regions of the plasma, in which case the ratio of the measured intensities will not give the ratio of the local emissivities, which is required for the calculation of the line intensity ratios. In laboratory plasmas, the gas is generally weakly ionized, and so we can generally assume that the ground state (generally atomic) species are uniformly distributed throughout the plasma, and that the emission will be greatest where the electron density times the excitation rate coefficient is the greatest.

In the case where spatial variation could be important, it is best to compare the radiation from the same species. This is not always easy, but helium is a special case, where the levels are sufficiently well spaced to provide good resolution for temperature measurements, and where the atomic structure, having singlet and triplet levels, allows for two-step processes to be important, allowing a measurement of the electron density. Calculations using CR models showing that line ratios in HeI can be used to calculate electron densities and temperatures have been reported by Schweer et al [22] and Sasaki et al [23]. These techniques have been developed for measuring n_e and T_e profiles in the edge of tokamaks. More recent work by Boivin et al. [24] compared the experimentally-measured line intensity ratios to the calculated ratios of the 471.3, 492.2 and 504.8 nm Hel lines over a range of plasma densities; the comparison was judged to be “from poor to good”. This indicates that although such techniques are promising, good C-R models are required.

9.4 Emission and absorption by molecules

In general, we can have pure rotational transitions, rotation-vibration transitions, or electronic-vibration-rotation transitions. Rotational transitions give rise to radiation of about 1 cm⁻¹, lying in the microwave region of the electromagnetic spectrum. Vibrational levels are spaced about 1000 cm⁻¹, so the resulting radiation falls in the IR region of the spectrum.
The electronic levels are spaced much the same as atomic levels (30,000 cm\(^{-1}\)), and so the electronic transitions fall in the visible region of the spectrum (see tables by Herzberg [7]).

**Rotation-vibration spectra**

The excitation energies of the vibrational levels are given by:

\[
E_v = \hbar c G(v)
\]

\[
G(v) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2
\]

(9.4.1)

where \(v\) is the vibrational quantum number (=0,1,2…) and the molecular constants can be found in Herzberg. Some examples:

<table>
<thead>
<tr>
<th>(\omega_e \text{ cm}^{-1})</th>
<th>(\omega_e x_e \text{ cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2(\text{X}))</td>
<td>4396</td>
</tr>
<tr>
<td>(\text{N}_2(\text{X}))</td>
<td>2360</td>
</tr>
<tr>
<td>(CH)(X)</td>
<td>2861</td>
</tr>
</tbody>
</table>

We note that room temperature corresponds to a thermal energy (\(k_B T\)) of about 200 cm\(^{-1}\), and so the vibrational energy levels for light molecules are spread more widely than \(k_B T\). Thus, in rotation-vibration spectra, where one works with gas cells, furnaces etc., the energy levels will be populated by collisional processes; since all species are at the same temperature, the distribution among the excited levels will be given approximately by a Boltzmann factor characterized by this common temperature (see Herzberg P.123):

\[
N_v = \frac{N}{Q_v} \exp\left(-\frac{G(v)\hbar c}{k_B T}\right)
\]

\[
Q_v = 1 + \exp\left(-\frac{G(1)\hbar c}{k_B T}\right) + \exp\left(-\frac{G(2)\hbar c}{k_B T}\right) + \ldots
\]

(9.4.2)

Here \(Q_v\) is the partition function for the vibrational levels. From the table we can see that for most diatomic molecules, the vast majority are in the ground state (\(v=0\)). In principle, from a measurement of the line intensity as a function of the energy spacing, we can calculate the temperature \(T\). In a plasma, there are many more processes which come into play, and the vibrational levels are not necessarily populated by collisions with thermal particles. As we have seen, electron collisions can produce dissociation (for example the dissociation of a polyatomic molecule resulting in an excited diatomic molecule) and recombination processes; often the resulting molecule is vibrationally excited with an anomalous “vibrational excitation temperature”.

The rotational levels, on the other hand, are spaced much closer together – in general the energy spacing is much less than the thermal energy. In this case, many excited rotational
levels will be populated. We must also consider the statistical weight of the levels, in addition to the Boltzmann factor. Each state of the system having a total angular momentum \( J \) consists of \( 2J+1 \) levels that coincide (in the absence of an external field). The number of molecules in the rotational level defined by \( J \) is thus proportional to:

\[
(2J+1) \exp \left( -\frac{F_v(J)\hbar c}{k_B T} \right)
\]

(9.4.3)

The rotational energy levels have an energy spacing (see Herzberg [7]):

\[
F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2
\]

\[
B_v = B_c - \alpha_c (v + \frac{1}{2}) + ... 
\]

(9.4.4)

\[
D_v = D_c + \beta_c (v + \frac{1}{2}) + ...
\]

We thus see that the most highly populated level is not, in fact, the level \( J=0 \) (Herzberg [7] P.124). We find that, by assuming the simplest form for \( F(J) \) (\( F(J)=BJ(J+1) \)) that the maximum of the level population occurs for:

\[
J_{\text{max}} = 0.5896 \sqrt{\frac{T}{B}} - \frac{1}{2}
\]

(9.4.5)

If we write:

\[
Q_e \approx 1 + 3e^{\frac{2B\hbar c}{kT}} + 5e^{\frac{6B\hbar c}{kT}} + ...
\]

(9.4.6)

then the level populations can be written:

\[
N_J = \frac{N}{Q_r} (2J+1) e^{\frac{BJ(J+1)\hbar c}{kT}}
\]

(9.4.7)

NOTE: for \( T \) sufficiently high or \( B \) sufficiently small, we can write:

\[
Q_r \approx \int_0^\infty (2J+1) e^{\frac{BJ(J+1)\hbar c}{kT}} dJ = \frac{kT}{B\hbar c}
\]

(9.4.8)

The intensities of the lines in a rotation-vibration band are given approximately by the distribution among the rotational levels. For the case of emission spectra, this corresponds to the upper level \( J' \). It is assumed that the transition probability is the same for all lines of a band. This is given by an integral of the dipole moment times the wavefunctions, and this generally doesn’t change during the transition. There is also a slight dependence on \( J'' \),

9.31
which can be taken into account by using $J' + J'' + 1$ instead of $2J' + 1$ (see Herzberg [7] P.125). Thus we have:

$$I_{\text{emission}} = \frac{C_{\text{emission}} v^4}{Q_\nu} \frac{B_{\nu}(J'+1)hc}{kT} (J'+J''+1)e^{\frac{-B_{\nu}(J'+1)hc}{kT}}$$

$$I_{\text{absorption}} = \frac{C_{\text{absorption}} v}{Q_\nu} (J'+J''+1)e^{\frac{-B_{\nu}(J'+1)hc}{kT}}$$

(9.4.9)

We recall that the selection rule for $J$ requires:

$$\Delta J = \pm 1 \quad (\Lambda = 0)$$

$$\Delta J = 0, \pm 1 \quad (\Lambda \neq 0)$$

(9.4.10)

$\Delta J=0$ gives the Q branch (and only exists for NO among diatomic molecules), while $\Delta J=\pm 1$ gives the R branch and $\Delta J=-1$ gives the P branch. We note that for a rotation-vibration band, the B values are essentially the same (the same harmonic oscillator structure). Thus, the R and P branches extend to either side of the “origin”.

**Electronic Bands**

In this case, an electronic transition is involved, in addition to a rotation-vibration transition. The result is a number of vibration bands having a structure determined by the distribution among the rotational levels. An important difference in this case is that the vibrational structure and the rotational spacing (the B values) can be significantly different between the upper and lower electronic states (different harmonic oscillators), and hence the spacing is no longer uniform. The overlap of the wavefunctions and the Franck-Condon principle result in a distribution in intensities among the vibrational bands (see Herzberg [7] P.195,197).

There is no selection rule for the vibrational quantum number, but we must still obey the selection rules for $\Delta J$. Thus we have (approximately):

$$\nu = \nu_0 + B_\nu J'(J'+1) - D_\nu J'^2(J'+1)^2 - \left[ B''_\nu J''(J'' + 1) - D''_\nu J''^2(J'' + 1)^2 \right]$$

(9.4.11)

Here $\nu_0$ is the frequency corresponding to the transition from the lowest vibrational levels in both the upper and lower levels. We again have the possibility of a Q branch ($\Delta J=0$, which requires $\Lambda\neq0$), an R branch ($\Delta J=\pm 1$) and a P branch.

In general, $B_\nu \neq B''_\nu$ and so the spacing of the lines is not uniform. The band “expands” or “contracts” depending on the shape of the potential curves in the upper and lower electronic levels. This gives rise to band spectra which are degraded to the blue or degraded to the red. If, for example, if $B_\nu \neq B''_\nu$ the lines in the R branch will be increasingly spread out as $J$
increases, while the P branch will be “turned around” by the nonlinear $J^2$ term. This effect is described graphically by the Fortrat parabola (see Fig. 9.4.1).

![Fig. 9.4.1 Fortrat parabola for CN band at 388.3 nm [7]](image)

The line shape will still be determined by the distribution of among the upper (in the case of emission) and lower (in the case of absorption) levels. In emission, for example, we have:

$$\ln \left[ \frac{I_{\text{em}}}{{J'}+{J''}+1} \right] = A - \frac{B J (J+1) \hbar c}{kT}$$ (9.4.12)

Thus, a plot of the intensity of a line (characterized by $J'$ and $J''$) divided by $J'+J''+1$ versus $J'(J'+1)$ gives a straight line from which we can determine the rotational temperature $T$. If the spectrum is more complicated, it is still possible to simulate the observed spectrum using the molecular constants. This has been done for the (0,0) Swan band of C$_2$ by Pellerin et al. [25], where they have also taken into account the finite linewidth of the measurement apparatus.

### 9.5 Absorption Spectroscopy

**Radiation transfer**

We have assumed that the photons emitted by the atoms or molecules will freely escape from the plasma – the plasma is optically thin. This is generally a good assumption for most laboratory plasmas, but although the probability of reabsorption may be small, it is not zero, and we can make use of this to measure properties of the species comprising the plasma.
We consider a small surface da in the plasma, with radiation propagating in a cone dΩ around the direction \( \hat{s} \) (see Figure 9.5.1). The energy flux in this cone, in a frequency interval dω around the frequency \( \omega \) is given by:

\[
(dP_v(\hat{s}) = I_v(\hat{s}) \cos \xi \; d\Omega \; d\nu \; da)
\]

(9.5.1)

\( I_v(\hat{s}) \) is the specific intensity (Watts/m² Sr Hz).

The total flux through the surface is then given by:

\[
P_v = \int I_v(\hat{s}) \cos \xi \; d\Omega \quad \text{with} \quad d\Omega = \sin \xi \; d\xi \; d\phi
\]

(9.5.2)

If there are no losses in the medium, but we allow a refraction of the rays (i.e. \( \xi_1 \neq \xi_2 \)), all the energy which is incident on the surface in the cone \( d\Omega_1 \) will leave in the cone \( d\Omega_2 \). Thus we have:

\[
I_v \; da \cos \xi_1 \; d\Omega_1 \; d\omega = (I_{o1} + dI_{i1})da \cos \xi_2 \; d\Omega_2 \; d\nu
\]

(9.5.3)

The solid angle \( d\Omega_1 = \sin \xi_1 \; d\xi_1 \; d\phi \) and \( d\Omega_2 = \sin \xi_2 \; d\xi_2 \; d\phi \). The angle \( d\phi \) does not change. In addition, we assume the rays refract according to Snell’s law:

\[
N_1 \sin \xi_1 = N_2 \sin \xi_2 = A
\]

(9.5.4)

\( N_1 \) and \( N_2 \) are the indices of refraction at the positions 1 and 2 in the medium, respectively. From this we can calculate that:

\[
N_1 \cos \xi_1 d\xi_1 = N_2 \cos \xi_2 d\xi_2 = B
\]

(9.5.5)

From the above relations we can find that:

\[
\frac{d\Omega_1 da}{A \; N_1 \cos \xi_1} = \frac{d\Omega_2 da}{B \; N_2 \cos \xi_2} = \text{constant}
\]

(9.5.6)

Thus, we find that \( N^2 \cos \xi \; d\Omega \; da \) is constant along the ray path. Since \( I_v \cos \xi \; d\Omega \; d\omega \; da \) is also constant, we deduce that \( I_v / N^2 \) is also constant along the ray: the conservation of energy.

However, in a medium which is emitting and absorbing photons, the intensity of the beam can be either reduced or increased; to take this into account we have to introduce the coefficients of absorption (\( \alpha_\nu \)) and emission (\( j_\nu \)). In traversing a distance ds, a small amount of the energy of the ray is absorbed:

\[
9.34
\]
At the same time, the small volume element is a source of radiant energy:

\[ j_\nu \, ds \, d\Omega \cos \xi \, dv \]  

(9.5.8)

\( j_\nu \) is defined as the energy emitted (per unit volume) in the frequency interval \( dv = 1 \) Hz, in the cone having a solid angle \( d\Omega = 1 \) (Sr), in the direction \( \vec{s} \). Thus we have for the energy in the ray:

\[
\begin{aligned}
(I_\nu + dl_\nu) \, da \cos \xi_2 \, d\Omega_2 \, dv = \\
I_\nu \, da \cos \xi_1 \, d\Omega_1 \, dv & \quad \text{incident flux} \\
- \alpha_\nu \, da \, I_\nu \, da \cos \xi_1 \, d\Omega_1 \, dv & \quad \text{absorption} \\
+ j_\nu \, da \, d\Omega_1 \, dv & \quad \text{emission}
\end{aligned}
\]  

(9.5.9)

If we use the relation (9.5.6) above, we find:

\[
\frac{I_{\nu 2}}{N_2^2} = \frac{I_{\nu 1}}{N_1^2} + j_\nu \frac{ds}{N_1^2} - \alpha_\nu I_{\nu 1} \frac{ds}{N_1^2}
\]  

(9.5.10)

Since

\[
\frac{I_{\nu 2}}{N_2^2} - \frac{I_{\nu 1}}{N_1^2} = \frac{d}{ds} \left[ \frac{I_{\nu}}{N^2} \right] 
\]  

(9.5.11)

we can rewrite equation (9.5.10) as:

\[
N_2^2 \frac{d}{ds} \left[ \frac{I_{\nu}}{N^2} \right] = j_\nu - \alpha_\nu I_{\nu}
\]  

(9.5.12)

This is known as the equation of radiative transfer. We can also write this in a more convenient form if we define the “source function”:

\[
S_\nu = \frac{1}{N^2} \frac{j_\nu}{\alpha_\nu}
\]  

(9.5.13)

and the “optical depth” \( \tau \) via:

\[
d\tau = -\alpha_\nu \, ds
\]  

(9.5.14)

The equation of radiative transfer then becomes:
\[
\frac{d}{d\tau} \left[ \frac{I_\nu}{N^2} \right] = \frac{I_\nu}{N^2} - S_\nu
\]  
(9.5.15)

A solution of this can be shown to be:

\[
\frac{I_\nu(A)}{N^2(A)} = \frac{I_\nu(B)}{N^2(B)} \exp(-\tau(B)) + \int_{\tau(A)}^{\tau(B)} S_\nu(\tau) \exp(-\tau) d\tau
\]  
(9.5.16)

If we consider a slab of plasma, for example, extending from A to B, with \( N=1 \), with a beam of intensity \( I_\nu(B) \) incident on the “back side”, we find that the intensity measured from the “front face” is:

\[
I_\nu(A) = I_\nu(B) \exp(-\tau_0) + \int_0^{\tau_0} S_\nu(\tau) \exp(-\tau) d\tau
\]  
(9.5.17)

The first term represents the incident flux which is attenuated by the intervening plasma, while the second term represents the emission from the plasma.

If we consider the case of a plasma which emits a spectral line by making a transition from level 2 to level 1, the emission coefficient can be written as:

\[
j_\nu = \frac{1}{4\pi} n_2 A_{21} h\nu_{21} g(\nu)
\]  
(9.5.18)

The absorption coefficient can be written as:

\[
\alpha_\nu = (B_{12} n_1 - B_{21} n_2) \frac{h\nu_{21}}{c} g(\nu)
\]  
(9.5.19)

The function \( g(\nu) \) represents the line shape of the emitted line, and is normalized to 1:

\[
\int_{-\infty}^{\infty} g(\nu) d\nu = 1
\]  
(9.5.20)

NOTE: for a collimated beam, \( I = \rho c \), where \( \rho \) is the energy density of the radiation.

NOTE: if we assume a system in equilibrium, we have:

\[
\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp\left(-\frac{h\nu}{k_BT}\right)
\]

\[
A_{21} = 8\pi \frac{h\nu^3}{c^3} B_{21}
\]  
(9.5.21)

\[
g_1 B_{12} = g_2 B_{21}
\]
This allows us to write the source function as:

\[ S_\nu = \frac{j_\nu}{a_\nu} = \frac{1}{2} \frac{\nu^3}{c^2} \exp\left(\frac{\nu}{k_B T}\right) \equiv L^B(\nu, T) \]  

(9.5.22)

Thus, in equilibrium, the source function is equal to the Planck (black body) function.

The increase in the intensity of the beam in traversing a distance \( dx \) in the plasma is then given by:

\[ \frac{dI_\nu}{dx} = \frac{A_{21}}{4\pi} n_2 h\nu g(\nu) - \frac{B_{12}}{c} n_1 I_\nu h\nu \left[ 1 - \frac{B_{21} n_2}{B_{12} n_1} \right] \]  

(9.5.23)

In absorption spectroscopy, the spontaneous emission and the induced emission are usually negligible, and so we can write:

\[ \frac{dI_\nu}{dx} = -\frac{B_{12}}{c} n_1 I_\nu h\nu g(\nu) = -k(\nu) I_\nu \]  

(9.5.24)

Here, \( k(\nu) \) is the absorption coefficient at the frequency \( \nu \). We note that from equation (9.5.24) we can write very generally:

\[ k(\nu) = \frac{B_{12}}{c} n_1 h\nu g(\nu) = \frac{A_{21}}{8\pi} \frac{g_2}{g_1} \frac{c^2}{\nu^2} n_1 g(\nu) = \frac{A_{21}}{8\pi} \frac{g_2}{g_1} \lambda^2 n_1 g(\nu) \]  

(9.5.25)

The spectral line shape influences the absorption coefficient at a given frequency, but the integral over the absorption coefficient depends only on the atomic parameters and the density of the lower level \([26]\):

\[ \int k(\nu) d\nu = \frac{A_{21}}{8\pi} \frac{g_2}{g_1} \lambda^2 n_1 \int g(\nu) d\nu = \frac{A_{21}}{8\pi} \frac{g_2}{g_1} \lambda^2 n_1 \]

(9.5.26)

Absorption spectroscopy of atoms and molecules

While emission spectroscopy is ultimately limited to the measurement of radiation from excited levels, the majority of the species in the plasma exist in the ground state. Most of the atoms, molecules, ions, or radicals that strike the surface will thus be in the ground state. The ultimate goal, then, of emission spectroscopy is to calculate the ground state density from the plasma emissivity. This is not simple, as we have seen in sections 9.2 and 9.3.
On the other hand, by measuring the absorption of radiation passing through the plasma, the ground state densities can be calculated. This was treated in the previous section, and is discussed in the texts by Mitchell and Zemansky [26], Corney [27], and Thorne [8]. Essentially, a photon causes a transition from a lower state 1 to an upper state 2, the rate depending on the Einstein coefficient for stimulated absorption and the photon density. A precaution: If the density of the upper level becomes sufficiently high, we will also have to take into account the stimulated emission (equation 9.5.23).

In absorption spectroscopy, a parallel beam of light is passed through the plasma, and the atoms in the plasma absorb some of the photons at wavelengths corresponding to optical transitions. Beer’s law determines the transmission of the radiation of frequency \( \nu \) through the plasma:

\[
I(\nu) = I_0(\nu) \exp(-k(\nu) l)
\]  

(9.5.27)

where \( I_0(\nu) \) is the intensity distribution of the incident radiation, \( l \) is the path length, and \( k(\nu) \) is the absorption coefficient of the plasma at the frequency \( \nu \). If the incident radiation has a very narrow frequency spread compared to the absorption line, then the absorption at frequency \( \nu \) can be determined, and by sweeping the frequency of the incident radiation, the profile of the absorption line can be determined. At the other extreme, when the incident radiation is broad-band, the spectrum of the transmitted light will be determined by \( k(\nu) \). The width of the absorption line will be determined by several processes (Doppler-broadening, pressure and Stark broadening...), but the integral over the line is determined uniquely by the density of the absorbing species and atomic parameters (equation 9.5.26).

In general we have to consider the transmission of radiation having a finite linewidth through a plasma whose absorption coefficient also has a finite linewidth. In this case we measure the "absorption" \( A \) of the radiation:

\[
A = 1 - \frac{I}{I_0} = \frac{\int I_0(\nu)[1 - \exp(-k(\nu) l)]d\nu}{\int I_0(\nu)d\nu}
\]  

(9.5.28)

where \( I \) is the total intensity of the transmitted radiation, and \( I_0 \) that of the incident radiation. In this calculation, the line shapes of both the incident radiation \( I_0(\nu) \) and the absorption coefficient \( k(\nu) \) are important. Ideal cases, when \( I_0(\nu) \) and \( k(\nu) \) are given by Gaussian (Doppler-broadened) profiles, are given in Mitchell and Zemansky [26]. In general, the line shapes are somewhat more complicated, and it is best to do the calculation numerically [28]. The profile of the incident radiation must be known, and an estimate of the absorption line shape is necessary; what is derived will then be the central (peak) value \( k_0 \). In the case of Doppler-broadened lines \( k_0 \) can be written as:

\[
k_0 = 1.62 \times 10^{-33} \lambda^3 \frac{g_2}{g_1} n_i A_{21} \left( \frac{\mu}{T} \right)^{\frac{1}{2}} \text{m}^{-1}
\]  

(6.5.29)
Here $\lambda$ is the wavelength of the transition in nm, $g_1$ and $g_2$ are the statistical weights of the lower and upper levels, $A_{21}$ is the Einstein coefficient, $n_1$ is the density of the lower level, and $\hat{T}$ the temperature of the absorbing species (of atomic mass $\mu$) in eV. As an example, we consider the case of the absorption of Lyman-$\alpha$ photons (121.6 nm) by hydrogen atoms. If the atomic density is $10^{18}$ m$^{-3}$, and the temperature of the atoms is 1 eV, we find $k_0 = 5.46$ m$^{-1}$. For a plasma of thickness 0.2 m, we have $k_0 = 1.09$. Thus, for relatively modest densities, if the temperature is not too high, there can be a significant amount of absorption.

For most atoms and atomic ions, the transitions from the ground state occur in the vacuum UV region of the spectrum, and so the measurements are difficult. An important application is the measurement of hydrogen atoms in the edge region of fusion reactors. H.F. Dobele and his group have carried out some elegant experiments to measure the densities of H and D atoms. Their system employs a pulsed dye laser which is frequency doubled in a BBO crystal. The resulting radiation at 223 nm is then focused into a gas cell and a number of Stokes and anti-Stokes orders are produced by stimulated Raman scattering. The ninth anti-Stokes radiation is used to probe the plasma; the wavelength is swept by varying the wavelength of the dye laser. A schematic of their set-up is shown in Fig. 9.5.2, and a spectrum of the absorption by hydrogen atoms is illustrated in Fig. 9.5.3. We see that the atomic hydrogen density is high enough to “saturate” the absorption curve. If a small amount of deuterium is added to the mixture, the experimental results show an unsaturated absorption peak (Fig. 9.5.4).

![Figure 9.5.2 Production of VUV light](image)
Absorption spectroscopy is also valuable in measuring molecular species. Experiments have been carried out by several groups using various techniques. The source can generate a narrow line, swept across the absorption band. Another approach is to use a broadband source, with a spectrograph to provide the spectral discrimination; this is the approach used by Goyette et al. [30], shown in Figure 9.5.5.
This approach was used to measure the density of C$_2$ molecules in a plasma discharge, as shown in Figure 9.5.6.

Another convenient approach is to measure the absorption from metastable levels. It has been found that excitation transfer from metastable levels can be very important in determining the discharge kinetics, and so the population of these levels is of some
importance. For molecules and molecular ions and radicals, the transitions occur in the UV and visible region of the spectrum, and so the measurements are much more convenient. Ibbotson et al. [31] have used such techniques to measure the absolute densities of Br in a discharge. They found that the results compared favourably with those obtained from actinometry, but that the Br emission did not give reliable results for the bromine concentration. Gousset et al. [28] measured the densities of O, O₂, and O₃ by measuring the absorption of radiation emitted by a discharge lamp. High sensitivity absorption spectroscopy using a Xe arc lamp as a source of continuum radiation was developed by Wamsley et al. [32]. Using a sensitive array detector, digital subtraction to discriminate against the light emitted by the "absorbing" plasma, and a high dispersion spectrograph, they were able to measure fractional absorptions of 10⁻³. A similar approach was used by Erickson et al. [33] to measure the line-average density of methyl radicals (CH₃) in plasma-assisted diamond growth facility.

Since many of the species of interest in laboratory plasma reactors are molecules and radicals, IR absorption can be a valuable technique, using transitions between vibrational and rotational levels. (We should note, however, that IR absorption is not possible for homonuclear molecules, where pure vibrational transitions are forbidden.) High resolution studies were carried out by Knights et al. [34] using a 1 m long cell, the absorption of a continuous source was measured by a Fourier Transform Infra-Red (FTIR) spectrometer. From their results they were able to calculate the vibrations and rotational temperatures of SiH radicals. Cleland and Hess [35] used a similar technique to analyze an RF discharge, but with lower resolution, but were still able to estimate the rotational temperature of N₂O. Richards et al. [36] calculated the concentration of Cl atoms in a plasma reactor by measuring the absorption of an IR tunable diode laser beam resulting from a transition between the 2P₁/₂-2P₃/₂ spin-orbit levels, and compared these results to densities predicted by actinometry. They used a multi-pass optical system, as did Maruyama et al. [37], who measured the absorption by the CF₃ radical in an RF discharge. Oh et al. [38] used wavelength modulation spectroscopy (WMS) to measure the single-pass absorption by CF₂ and CF₂O in a gaseous electronics reference cell. Recent developments by Sun et al. [39, 40, 41] have led to a technique which combines WMS and frequency modulation spectroscopy (FMS), resulting in high spectral resolution and high sensitivity, while reducing the effects of fringes caused by external surfaces.

**9.6 The Broadening of Spectral lines**

We have regarded the transition between two energy levels as if this gave rise to an infinitely sharp spectral line. Spectral lines have, however, finite widths, which can be the result of several processes: natural broadening, Doppler broadening, pressure broadening, Stark splitting or broadening, Zeeman splitting, and self-absorption. We can often obtain useful information about the emitting atoms (or molecules) and the plasma from a study of the line shape resulting from these different mechanisms.

**9.6.1 Natural Broadening**
Since the emission of radiation involves a (random) transition from the upper level to the lower level, this time uncertainty must be associated with an uncertainty in the energy i.e. the frequency. This gives rise to a “natural broadening” of the spectral lines. This phenomenon can be analysed in the classical framework by considering the radiative process to correspond to a damped oscillator. The electric field of the radiation field will then be given by the Fourier transform of the time-dependent intensity; this results in a line exhibiting a (normalized) Lorentzian profile:

\[
I_\nu = \frac{\gamma/2\pi}{(\nu - \nu_{21})^2 + (\gamma/2)^2}
\]

(9.6.1)

where \(\nu_{21}\) is the Bohr frequency for the transition between states 1 and 2. The “damping” parameter \(\gamma\) is related to the lifetime of the levels 1 and 2:

\[
\gamma = \gamma_1 + \gamma_2 = \frac{A_1}{2\pi} + \frac{A_2}{2\pi}
\]

(9.6.2)

where \(A_i\) represents the transition rate from the level \(i\) (the sum of the Einstein coefficients). We can see from the formula that the full width at half maximum of the line is \(\gamma\). Since the Einstein coefficients for many lines are of the order of \(10^8\) s\(^{-1}\), we see that the linewidth is only of the order of \(10^8\) Hz. This is generally much smaller than the width associated with other broadening mechanisms, and can often be neglected.

### 9.6.2 Doppler Broadening

It is important to note that every atom or ion emits radiation at its characteristic frequency \(\nu_0\) (the Bohr frequency) in its own reference frame. If the emitting atoms are in motion, an observer will measure this radiation at a slightly different frequency, because of the Doppler effect. The observed frequency is given by:

\[
\nu = \nu_0 - \nu_0 \frac{\bar{v} \cdot \hat{z}}{c} = \nu_0 \left(1 - \frac{v_z}{c}\right)
\]

(9.6.3)

If the emitter is moving toward the observer, the radiation will appear blue-shifted, while if it is moving away the radiation will be red-shifted. From an ensemble of particles, each emitting at the frequency \(\nu_0\) in its own rest frame, the line profile is related to the distribution function of the emitters in the direction \(z\):

\[
I(\nu) d\nu = f(\nu_z) dv_z
\]

(9.6.4)

If the velocity distribution function of the atoms or ions is Maxwellian (thermal motion), the resulting spectral line exhibits a Gaussian line profile:
\[ I(v) = I_0 \exp \left[ -\frac{mc^2(v - v_0)^2}{2k_BTv_0^2} \right] \quad \text{or} \]
\[ I(\lambda) = I_0 \exp \left[ -\frac{mc^2(\lambda - \lambda_0)^2}{2k_BT\lambda_0^2} \right] \quad (9.6.5) \]

where \( I_0 \) is the maximum intensity. In terms of the integrated line intensity \( I \) we get:
\[ I(v) = I \frac{c}{\nu_0} \sqrt{\frac{m}{2\pi k_B T}} \exp \left[ -\frac{mc^2(v - v_0)^2}{2k_BTv_0^2} \right] \quad (9.6.6) \]

For the case of Doppler broadening, the full width at half maximum (FWHM) can be expressed as:
\[ \frac{\Delta v}{v_0} = \frac{\Delta \lambda}{\lambda_0} = \sqrt{\frac{8k_B T \ln 2}{mc^2}} = 7.719 \times 10^{-5} \sqrt{\frac{T(\text{eV})}{\mu}} = 7.165 \times 10^{-7} \sqrt{\frac{T(\text{K})}{\mu}} \quad (9.6.7) \]

where \( \hat{T} \) is the temperature in eV and \( T \) the temperature K, and \( \mu \) is the atomic (or ionic) mass (in atomic mass units). By measuring the width of a Doppler-broadened line, we can thus measure the temperature of the emitting species. If we consider argon atoms (\( \mu = 40 \)) with a temperature of 0.2 eV, we find that the FWHM of a line at 600 nm is 2.73x10^9 Hz; we thus see that Doppler broadening is significantly greater than natural broadening. (We note that at a wavelength of 600 nm this corresponds to a very small broadening, only 3.28x10^{-3} nm. This is beyond the resolution of most spectrographs, but by using narrow-band lasers, however, such a line width is easily measured.)

On the other hand, in processes such as molecular dissociation, the product atoms are released with significant kinetic energy, resulting in appreciable (but not thermal) Doppler broadening. A classic case is that of hydrogen, the dissociation of which results in two “Franck-Condon” energetic atoms:
\[ e + H_2 \rightarrow e + H + H, \quad \text{with } \Delta E \approx 4 - 5 \text{eV} \quad (9.6.8) \]

This will give rise to a non-Doppler profile which can be used to determine the presence of these energetic atoms.

### 9.6.3 Pressure Broadening

It is found that spectral lines emitted by a gas at high pressure are broader than (and sometimes shifted with respect to) those lines emitted by the same gas at lower pressure. This broadening occurs because its neighbours perturb the emitting atom. The theories of
pressure broadening are classified as “impact (or interruption) broadening” or “quasistatic broadening” [6]. In the impact theory, the time between collisions is much greater than the duration of the collision, and only binary collisions are considered. This theory is thus most pertinent for low pressure gases. In the statistical theory, the emitting atom is considered to be in a constant state of perturbation, the atom and its neighbours forming a quasistatic aggregate or a pseudo-molecule. This theory would thus be expected to be more applicable in the case of high pressure gases.

Consider first the case of impact broadening. We assume the radiating atom to emit an infinitely long wave train (in the absence of collisions); the collisions are “instantaneous” events that interrupt the wave train, with the phase changing randomly during the collision. The probability density of a time between collisions $t$ is given by:

$$f(t) = \frac{1}{\tau} e^{-\frac{t}{\tau}} \quad (9.6.9)$$

where $\tau$ is the mean time between collisions. During the time 0 to $t$, the emitted wave is sinusoidal, and so we have:

$$E(t) = E_0 e^{i\nu_0 t}$$

$$E(\nu) = \frac{1}{2\pi} \int_0^t E_0 e^{i\nu_0 t} e^{-i\nu t} dt = \frac{E_0}{2\pi} \frac{e^{i(\nu_0 - \nu) t} - 1}{i(\nu_0 - \nu)} \quad (9.6.910)$$

The intensity is then given by:

$$I(\nu) = |E(\nu)|^2 = \frac{E_0^2}{2\pi^2} \frac{1}{(\nu - \nu_0)^2 + \left(\frac{1}{\tau}\right)^2} \quad (9.6.11)$$

The full width at half maximum of this Lorentzian line is thus given by $\Delta\nu_p = 2/\tau$. The mean time between collisions can be estimated as:

$$\tau = \frac{1}{\sqrt{2\sigma \nu n}} = \frac{\sqrt{\pi \mu k T}}{4P\sigma} \quad \text{giving} \quad \Delta\nu_p = 2.981 \times 10^{25} \frac{P\sigma}{\sqrt{\mu T}} \quad (9.6.12)$$

where $\sigma$ is the “optical” cross section in m$^2$, $P$ the pressure in Pa, $\mu$ the atomic mass, and $T$ the temperature in Kelvins.

In the quasistatic theory, the energies of both the upper and lower levels are perturbed during the impact – much as the potential energy curves during the formation of molecules. If the atom makes a transition during the interaction time, the energy of the emitted photon can be less than or greater than the Bohr energy – it depends on the relative deformation of the levels. We would thus expect to see a pronounced shift as well as a broadening of the spectral line.
9.6.4 Stark Broadening

When the perturbers are charged particles, we speak of “Stark broadening”. In this case, the electric field of the perturber results in a Stark shift of the atomic levels. The Stark widths of many spectral lines have been studied by Griem and others. The most important case is that of atomic hydrogen, which shows a linear Stark effect. In this case the half width of the line is given by:

\[ n_e \left( m^{-3} \right) = C \Delta \lambda_{1/2}^{3/2} \quad \text{where } \Delta \lambda_{1/2} \text{ is in nm} \]  \hspace{1cm} (9.6.13)

Values for C can be found in Griem. Figure 9.6.1 gives values for C for the H\(\beta\) line for a range of densities and temperatures.

More recent work [42, 43] has resulted in a formula relating the electron density \(n_e\) and the full width at half maximum \(\Delta \lambda_{1/2}\) of the Doppler-broadened H\(\beta\) line:

\[
\log(n_e) = 22.758 + 1.478 \log(\Delta \lambda_{1/2}) - 0.144 \left[ \log(\Delta \lambda_{1/2}) \right]^2 - 0.1265 \log(T_e) \]  \hspace{1cm} (9.6.14)

Other elements and lines have also been studied, and the agreement between theory and experiment is generally quite good. In general, the spectral line is both broadened and shifted by the microfields in the plasma. An example is the HeI line at 728.1 nm, where the experimental results of Pérez et al. [14] are found to be in good agreement with calculations of Griem [44]. They find the line broadening (with a width \(w\)) and shift (with a shift \(s\)) proportional to the electron density:

Figure 9.6.1 Coefficient C for the broadening of the H\(\beta\) line of hydrogen
w(nm) = 8.96(±0.14)\times10^{-24} \ n_e\left(\text{m}^{-3}\right) + 0.0282(± 0.0108) \ \text{and} \\
s(nm) = 4.29(0.09)\times10^{-24} \ n_e\left(\text{m}^{-3}\right) \hspace{1cm} (9.6.15)

Since it is possible to resolve a spectral line having a width of 0.1 nm, this would suggest that Stark broadening (of the HeI line) is useful for calculating the electron density if it is greater than about 10^{22} \text{ m}^{-3}. On the other hand, we see that the electron density required to produce the same broadening (0.1 nm) of the H\beta line is only 3.8\times10^{20} \text{ m}^{-3}.

### 9.6.5 The Zeeman Effect

The Zeeman Effect describes the splitting of the energy levels when an atom or molecule is placed in a magnetic field. It results in a series of closely-grouped spectral lines, and correctly speaking does not give rise to a broadening of the lines. The line spacing is generally quite small, and so, when using an instrument which is unable to resolve the structure, the line will appear broadened.

The electric dipole interaction between an atom or ion and an electromagnetic field involves transitions between states in which the change in magnetic quantum number M_J is either 0 or ±1. These transitions involve absorption or emission of radiation which is linearly polarized if \Delta M_J = 0 or circularly polarized if \Delta M_J = ±1. In the absence of any external field, atomic states which differ only with respect to M_J are degenerate in energy. In the presence of a magnetic field, a preferred direction is established and the magnetic moment of the atom results in a splitting of the energy levels of the previously degenerate states. The shift in energy depends on the total (J), orbital (L) and spin (S) angular momentum of the atomic state, and results in a splitting of optical transitions into multiple lines closely grouped around the original line if the magnetic interaction is weak compared to other elements in the Hamiltonian operator describing the energy levels of the states in question. Viewed along the z-axis determined by the magnetic field, an atom absorbs or emits radiation that is either right- or left-circularly polarized, corresponding to transitions with \Delta M_J = +1 or -1 (\sigma transitions). Viewed perpendicular to the z-axis, there is a third component, with polarization parallel to the z-axis, corresponding to \Delta M_J = 0 (\pi transitions). In general, the wavelengths of all three components differ; moreover, each polarization is often further split depending on the values of M_J of the upper and lower levels involved. Atoms pumped by a laser with polarization perpendicular to the z-axis will only absorb light on \sigma transitions, while atoms pumped with a polarization parallel to the z-axis will absorb only \pi transitions. The energy shift of an atomic level characterized by LS coupling, with the quantum numbers S, L and J, in an external magnetic field is given by:
\[ \Delta E_{LSJM} = \mu_B B g_J M_J \]

where

\[ \mu_B = \frac{e\hbar}{2m_e} \]

is the Bohr magneton

\[ B = \text{magnetic field (T)} \]

and

\[ g_J = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \]

(9.6.16)

g\_J is called the Landé g factor. The atomic levels are split into \(2J+1\) magnetic sublevels having equal energy separation. In case of singlet \((S = 0)\) terms, \(J = L\) and \(g_J = 1\), so the energy spacing of the upper and lower levels is the same. The Zeeman pattern then consists of a single \(\pi\) component \((\Delta M_J = 0)\) which is unshifted, and a pair of \(\sigma\) components \((\Delta M_J = \pm 1)\) having an energy spacing of \(\pm \mu_B B\). This is known as a “normal Zeeman triplet”. Most situations are somewhat more complicated; an example is shown in Figure 9.6.2 [6].

![Figure 9.6.2 Zeeman effect (From [6])](image-url)
9.6.6 Self-absorption

When the optical depth of the plasma for a given transition (equation 9.5.14) becomes large enough, the photons have a finite probability of being reabsorbed before they can escape from the plasma. This has an effect on the line intensity, but also on the line shape. If we consider the case of the emission from a slab of plasma, the intensity of the radiation emitted from the “front face” of the slab is given by:

\[ I_v(A) = \int_0^{\tau_0} S_v(\tau) \exp(-\tau) d\tau \]  \hspace{1cm} (9.6.17)

We see that for the emission of spectral lines (equations 9.5.18 and 9.5.19), the source function is independent of frequency, but the optical depth is frequency dependent. The intensity is then:

\[ I_v(A) = S\int_0^{\tau_0} \exp(-\tau) d\tau = S[1 - \exp(\tau_0)] \]  \hspace{1cm} (9.6.18)

If the optical depth is very small, we can express this as:

\[ I_v(A) = S\tau_0 = S\alpha_s I \]  \hspace{1cm} (9.6.19)

From equations (9.5.18) and (9.5.19) and assuming that \( n_2 << n_1 \), we obtain:

\[ I_v(A) = \frac{1}{4\pi} n_2 A_{21} h\nu g(\nu) \]  \hspace{1cm} (9.6.20)

This is exactly what to be expected if each volume in the plasma emits completely independently. On the other hand, if the optical depth is very large, the intensity approaches \( S \), which in the case of an equilibrium population approaches the emission from a black body (equation 9.5.21). This is illustrated in Figure 9.6.3.

![Fig. 8.1. Effect of increasing optical depth on line profile (a) in emission and (b) in absorption.](image)

Figure 9.6.3 Effect of optical depth on a spectral line profile
For intermediate cases, we find that the line is “flattened” at the top – it saturates at the level of the Planck function. The line shape is thus distorted compared to its “natural shape”, as shown in Figure 9.6.4.

![Figure 9.6.4 Spectral line profile as we approach saturation](image)

If the plasma has a non-uniform temperature distribution, we find that in the case where absorption is important, the line can be “self reversed”: the absorption from the edges of the plasma (where the line is generally narrower) gives rise to a “dip” in the intensity at the center of the line.

### 9.6.7 Observed Line Shapes and Convolution

The measured widths of the spectral lines which we observe are always the result of the inherent line width resulting from the processes discussed above, as well as the extra broadening produced by the measuring apparatus. The measured line width is thus a convolution of all these processes – which are assumed to be independent. Natural broadening is an example of “homogeneous broadening”, where all the atoms in the plasma are subject to the same broadening mechanism. On the other hand, Doppler broadening is an example of “inhomogeneous broadening” since a certain group of atoms having a given velocity will produce radiation with a corresponding frequency (or wavelength) shift. The “instrument function” depends on the device used to measure the line width: a (grating) spectrograph, a Fabry-Perot interferometer, a laser etc. (see section 12). Very often, for example, the instrument function of a grating spectrograph with narrow slits approaches a Gaussian distribution. If the spectral line we want to examine has a line profile $g(\lambda)$ centered at $\lambda = 0$, while the spectrograph has an instrument function (by which we mean the transmission as a function of the wavelength) $T(\lambda-\lambda_0)$ centered at the wavelength $\lambda = \lambda_0$, then the measured signal is given by:

$$S(\lambda_0) = \int_{-\infty}^{\infty} g(\lambda)T(\lambda-\lambda_0) d\lambda$$

(9.6.21)
The resulting measured line profile will thus be broader than either of the functions g or T. The integral in equation is known as a convolution. It can be shown that the convolution of two Gaussian profiles results in another Gaussian, which has the composite half width \( \Delta \lambda \):

\[
\Delta \lambda^2 = \Delta \lambda_1^2 + \Delta \lambda_2^2 \tag{9.6.22}
\]

Here, \( \Delta \lambda_1 \) and \( \Delta \lambda_2 \) are, for example, the half widths of the line emitted by the plasma and the half width of the instrument function. If the line emitted by the plasma has a Lorentzian profile while the instrument function is a Gaussian, the resulting profile is known as a Voigt profile. To a good approximation, the FWHM of a Voigt profile varies with the ratio of the Lorentzian half width to the Gaussian half width:

\[
\Delta \lambda_V \approx \Delta \lambda_G \left( 1 - c_0 c_1 + \sqrt{\varphi^2 + 2c_1 \varphi + c_0^2 c_1^2} \right) \tag{9.6.23}
\]

Here \( \Delta \lambda_V \) is the FWHM of the Voigt profile, \( \Delta \lambda_G \) is the FWHM of the Gaussian profile, and \( \varphi = \frac{\Delta \lambda_L}{\Delta \lambda_G} \), where \( \Delta \lambda_L \) is the FWHM of the Lorentzian profile. The parameters \( c_0 \) and \( c_1 \) are given by: \( c_0 = 2.0056 \) and \( c_1 = 1.0593 \).

### 9.7 Actinometry

A very useful technique for measuring species densities - the ground state densities - in reactive plasmas by spectroscopy is actinometry, which was introduced by Coburn and Chen [45], and which has been discussed by many authors (see, for example d’Agostino et al. [46], Gottscho and Donnelly [47] and Granier et al. [48]). This technique is based on the introduction of a small, but known, concentration of inert gas (often argon) to the discharge, and monitoring the emission from the excited noble gas as well as from the reactive species of interest. If the excitation energy of the upper levels responsible for the emission from both species is approximately the same, then the excitation efficiencies will be similar and will have the same dependence on plasma parameters. We can thus express the intensities from the two species as:

\[
\begin{align*}
\varepsilon_\lambda(X) &= n_e \eta_X [X] \\
\varepsilon_\lambda(Ar) &= n_e \eta_{Ar} [Ar]
\end{align*} \tag{9.7.1}
\]

Here \([Ar]\) represents the Argon density, \([X]\) the density of species X, and \( \eta \) the excitation efficiencies which depend on the electron temperature. From these two relations, assuming that the excitation efficiencies have the same dependence on \( T_e \), we obtain:

\[
\frac{[X]}{[Ar]} = a(X,Ar) \frac{\varepsilon_\lambda(X)}{\varepsilon_\lambda(Ar)} \tag{9.7.2}
\]
Thus, the (unknown) density of species X can in principle be calculated from the known Ar density; \( a(X,\text{Ar}) \) is a proportionality constant related to the ratio of the rate coefficients for excitation. As pointed out by Donnelly [49], this constant is often not measured. Gas-phase titration is sometimes used, and recently Donnelly has used rare-gas actinometry to measure the dissociation of Cl\(_2\) in a helical resonator plasma, using a mixture of He/Ne/Ar/Xe as the actinometer gas. This provides a range of upper excited level energies with which to make comparisons. The constant \( a(X,\text{Ar}) \) was determined by taking measurements at very low power, where the density of the Cl\(_2\) molecules is well known.

There is, however, one important caveat to the use of this technique: the excitation mechanism for both species is assumed to proceed via electron-impact excitation from the ground state. This is the only way to assure that the excitation efficiencies are about the same. There are several excitation mechanisms which can have an important influence on the excited level densities: chemiluminescence, dissociative excitation (e.g. polyatomic molecules), excitation transfer from the actinometer gas itself (since the rare gases have metastable levels which can be highly populated). If these excitation mechanisms are dominant, actinometry is not useful. It has been found, for example, that Ar can be used as an actinometer for determination of F densities in CF\(_4\)/O\(_2\)/Ar plasmas, but not necessarily for determining Cl densities in the sheath in Cl\(_2\)/Ar plasmas [47]. This latter conclusion was based on an analysis of the broadening of the spectral lines in the sheath. The line shape can provide information about the processes that give rise to these radiating molecules and radicals. For example, the production of excited species by dissociative excitation will often give broader lines than those produced by electronic collisional excitation from the ground state of the emitting species. On the other hand, it seems that actinometry can give useful results if the observed region is restricted to the center of the plasma, away from the sheaths. This technique was used by Aydil and Economou [50] to measure Cl concentrations, using the 837.6 and 808.7 nm lines in Cl, along with a 811.5 nm line in Ar.

St-Onge and Moisan [51] used actinometry to determine the density of atomic hydrogen in RF and microwave discharges, and examined the conditions under which actinometry could be used with confidence. They found that the Ar flow should be kept to a small fraction of the hydrogen flow (they used 1%) in order not to perturb the discharge. Another problem is the contribution of dissociative excitation to the production of excited hydrogen atoms. This contribution is not negligible, especially in warmer plasmas (\( T_e > 2\text{eV} \)), and suggests the use of higher \( n \) Balmer series lines rather than H\(_\alpha\) or H\(_\beta\).

In spite of what was said above about the limits of validity of actinometry, it is possible to extend the technique somewhat if a good model can be developed to describe the excitation mechanisms. In addition, if the excitation of the species is shown to be describable by actinometry, then we can infer the excitation process.

**Trace Rare Gas – Optical Emission Spectroscopy (TRG-OES)**

In this technique, small amounts of rare gases are introduced into the discharge – not enough to perturb the discharge, but enough to produce measurable emission. Rather than using the
line intensities to estimate the density of a given species in the plasma, the aim here is to try
and measure the electron temperature, and possibly get an idea of the electron distribution
function. The radiation from a number of spectral lines from several species (Ne, Ar, Kr,
Xe) is measured. The excitation mechanisms for the upper levels of these species have been
studied exhaustively, and are constantly being upgraded. The intensities of these lines are
compared to a model, and the temperature which provides a best fit to all the data is chosen
as “the electron temperature”. Since the population of some levels is more affected by
energetic electrons than others, by comparing these “energetic levels” it is possible to get
some idea of the presence or lack of energetic electrons: is the electron distribution function
Maxwellian. This method has been thoroughly discussed by Donnelly [52].

This method thus represents an extension of actinometry, as well as an extension of the
“Boltzmann plot”.

9.8 Laser spectroscopy - Laser Induced Fluorescence

Laser spectroscopy is ideally suited for the measurement of several important parameters in
processing plasmas, with high spatial and (under some circumstances) temporal resolution.
There are several laser-based techniques that have found or could find application in
materials processing plasmas. We can mention Laser-Induced Fluorescence (LIF), laser
optogalvanic spectroscopy (LOG), Cavity Ring-Down Spectroscopy (CRDS), infrared laser
absorption (see section 9.5), Raman and Coherent Anti-Stokes Raman Spectroscopy
(CARS) and Degenerate Four-Wave Mixing (DFWM). Not all of these techniques have
found wide application for (low pressure) plasmas, because of the low particle densities in
this case.

Of these, LIF is by far the most employed technique, because of a combination of desirable
attributes: high spatial resolution, high sensitivity and good temporal resolution. LIF is
based on the resonant excitation of a particle (atom, ion, or molecule) by laser radiation. In
this sense it is like absorption spectroscopy, except that we measure the light which is
radiated from the upper level. The particle is excited to an upper level by the absorption of a
photon; it will then spontaneously radiate another photon which we measure. In some cases,
with strong pumping, stimulated emission will also come into play. The spatial resolution is
a result of the combined use of a probing beam and an optical detection system that collects
photons from the irradiated volume (see Figure 9.8.1). The common volume can be small
(the order of mm³), limited only by the signal level. The temporal resolution can be 10-20
ns, if a pulsed dye laser pumped by a doubled-YAG or excimer laser is used. In principle,
LIF can furnish detailed information on relative and absolute ion densities, the distribution
among vibrational and rotational levels in molecules, measurements of the ion, atom and
molecular velocity distribution functions, and electric fields in the plasma.
The probability that an ion in level 1 will absorb a photon depends on many factors. These include the laser intensity; the spectral distribution of the laser radiation; the electronic configuration of the atom, which determines the discrete energy levels accessible to the ion by emission or absorption of a photon; the physical environment surrounding the ion; and finally, the ion velocity. The ion environment includes external fields and other particles with which the ion may interact; these interactions can cause a shift or broadening of the ionic energy levels. The ion velocities cause the effective photon energies observed in the rest frame of the ion to be shifted by the quantity \( \Delta \nu = \frac{v_0 \nu}{c} = \frac{v}{\lambda} \) where \( \nu \) and \( \lambda \) are the frequency and wavelength of the transition, respectively, and \( v \) is the ion (or atom) velocity directed toward the observer. The probability that an ion in level 2 will make a transition to level 3 depends only on the ionic energy levels; these levels are determined by the surrounding environment and by the ion electronic configuration. The total transition probability from level 2 to level 1 depends also on the energy density of the radiation which induced the transition from level 1 to level 2. The type of information one retrieves depends on the relative widths of the incident laser radiation and the absorption line of the species to be analysed. (We assume that the dominant line broadening mechanism is Doppler broadening.) When the laser line is very narrow, only a small fraction of the ions will be excited: those with the correct velocity, lying within a narrow band of velocities around the laser frequency \( \nu_L \):

\[
\nu_L - \nu_0 = \frac{v}{c} \quad (9.8.1)
\]

On the other hand, if the linewidth of the pumping radiation is broader than the absorption linewidth, essentially all of the ions in the volume can be pumped. This is illustrated in Figure 9.8.2.
In this case, we can describe the pumping process by a number of rate equations. Consider for simplicity an isolated 2-level system (Figure 9.8.1). If we neglect collisional losses, and radiation to/from levels other than those indicated, we have:

\[
\frac{dn_2}{dt} = n_1 B_{12} I(\nu) - n_2 B_{21} I(\nu) - n_2 A_{21}
\]  

(9.8.1)

Here \(I(\nu)\) is the incident laser intensity. If we consider the lossless case where \(n_2(0) = 0\) and \(n_1(0) = n\), with \(n_1 + n_2 = n\), we then find a simple solution to this equation:

\[
n_2(t) = n \frac{B_{12} I(\nu)}{B_{12} I(\nu) + B_{21} I(\nu) + A_{21}} \left( 1 - \exp\left( -\frac{t}{\tau}\right) \right)\]

(9.8.2)

The time constant \(\tau\) is given by:

\[
\tau = \frac{1}{(B_{12} + B_{21}) I(\nu) + A_{21}}
\]

(9.8.3)
Thus, after a short time (possibly significantly shorter than the radiative lifetime \( \tau_{12}^{-1} \)) the levels 1 and 2 attain an equilibrium which depends on the laser intensity. If the laser intensity is very high, we see that the populations of levels 1 and 2 approach the values:

\[
\begin{align*}
n_2 & \rightarrow \frac{B_{21}}{B_{12} + B_{21}} n \\
n_1 & \rightarrow \frac{B_{12}}{B_{12} + B_{21}} n
\end{align*}
\] (9.8.4)

Thus, the populations of the two levels are in the ratio of their statistical weights: the process is “saturated”. We can express the equilibrium population of level 2 as a function of laser intensity:

\[
n_2 = n \frac{g_2}{g_1 + g_2} \frac{S}{1 + S}
\] (9.8.5)

Here we have introduced the (dimensionless) saturation parameter \( S \) (a function of frequency) which is related to the laser intensity and is given by:

\[
S = \frac{g_1 + g_2}{g_1} \frac{B_{21} I(\nu)}{A_{21}} = I(\nu) \frac{g_1 + g_2}{g_1} \frac{c^2}{8\pi h \nu^3}
\] (9.8.6)

The laser intensity required to saturate a given transition can be estimated by taking \( S = 1 \):

\[
I_{sat}(\nu) = \frac{g_1}{g_1 + g_2} \frac{8\pi h \nu^3}{c^2}
\] (9.8.7)

It is usually more convenient to express in terms of the wavelength, in which case the laser intensity (Watts per m² per m) is:

\[
I_{sat}(\lambda) = \frac{g_1}{g_1 + g_2} \frac{8\pi h c^2}{\lambda^5}
\] (9.8.8)

We thus see that it is much more difficult to saturate a transition at shorter wavelengths. Examples of the power levels required [53]:

\[
\begin{align*}
\lambda &= 302.0 \text{nm (Fe I)} \quad I(\lambda) = 300 \text{ MW per m}^2 \text{ nm} \\
\lambda &= 121.5 \text{nm (L}_\alpha \text{)} \quad I(\lambda) = 14000 \text{ MW per m}^2 \text{ nm}
\end{align*}
\]

The fluorescence intensity measured in the experiment is given by \( n_2 A_{23} \), and so we see that it increases almost linearly with the laser power for low laser intensities, but that it saturates for increasing \( S \). Thus, we don’t increase the fluorescence signal if we pump harder.
The most practical arrangement for measuring laser-induced fluorescence is to use a 3-level process (see Fig. 9.8.1). An ion or atom initially in level 1 absorbs a laser photon of energy $\hbar \nu_{12}$ and is excited to level 2. From level 2, there is a probability that the atom will spontaneously decay to level 3 by the emission of a photon of energy $\hbar \nu_{23}$; there is also a probability that it will decay by either spontaneous or stimulated emission back to level 1. Ideally, before applying the pumping pulse, level 1 is densely populated and level 2 is empty; it is also desirable that the spontaneous transition probability from level 2 to level 3 be high, and that the wavelength of the transition $\hbar \nu_{12}$ (the laser frequency) be sufficiently far from that of $\hbar \nu_{23}$ that the fluorescence may be observed without contamination by the laser radiation. In this case, we see that with sufficient pumping the populations of both levels 1 and 2 will approach zero: all the atoms are pumped from level 1 to level 3. The fluorescence signal from level 2 is then time-dependent, and the question arises as to whether we can relate this signal to the initial (total) density in level 1.

Measurements of Concentrations

As seen above, at higher intensities with a broad enough pumping line, all the ions will be pumped, the stimulated transitions dominate, and the signal saturates. The population densities in levels 1 and 2 are then determined by the statistical weights of the two levels. Under these conditions, the fluorescence signal will not depend strongly on the intensity distribution of the laser beam. If the laser pulse lasts sufficiently long (generally a few times longer than the radiative lifetime of the upper level) we find that all of the atoms have been pumped to level 3. A measurement of the total time-integrated fluorescence signal then allows us to calculate the density of the species we have pumped. A precise measure of the absolute atom or ion density is important when we want to quantitatively compare rate processes, such as the absolute etching efficiency or the sputtering yields. The atoms that can be directly pumped from the ground state by the absorption of a single photon are generally metals, where visible and near UV transitions from the ground state are available, and hence absolute density measurements can be made. Such measurements have been used to measure the density of metal atoms near the walls and limiter surfaces in fusion experiments (see Bogen and Hintz in 53 and 54), and to measure the rate of atomic sputtering from surfaces bombarded with energetic ions. In the case of many molecules and radicals, the transitions from the ground state lie in the visible and the near UV, and so absolute densities can be measured.

On the other hand, we must accept that the majority of atoms cannot be pumped directly from the ground state. In some cases, pumping from excited levels is often the most practical approach, from which the total density can be calculated using a reliable model to relate the excited level densities with the ground state density. Accurate measurements of the electron density and temperature are generally required, since the excited level populations are determined by electron collisions. One example of where this has been used with good accuracy is the determination of the atomic hydrogen densities in fusion plasmas. For these calculations, reliable collisional-radiative models exist, such as those due to Johnson and Himno [55] and Fujimoto et al [56, 57]. In the case when molecular
dissociative excitation contributes to the production of excited atoms as well as atomic excitation, however, the problem becomes more complicated and one has to model all the plasma processes. In this case as well, however, reasonable estimates of atomic densities can be obtained. In some cases, the relative spatial distribution of metastable ions can be used to measure the (spatial) variation of the total ion density. In these cases, however, we must know the mechanisms which populate the metastable levels. For example, in the case of ArII, the metastable level density has been found to vary quadratically with the electron density. In this case, the square root of the LIF intensity should allow an estimate of the spatial variation of the electron density. This is particularly useful, for example, in the sheath or near-presheath region of the plasma, where probe measurements would be doubtful. (see Figure 9.8.3 for an example of this.) We see that, in fact, the electron density – related to the square root of the LIF signal – decreases by a factor 2 from the upstream plasma and the target. This is agreement with the 1D models of flow in the presheath.

![Relative Density Variation from LIF Signal](image)

**Figure 9.8.3** Electron density variation through the pre-sheath as derived from the LIF signal [58]

Measurements of the absolute density of CH radicals in an ECR discharge have been performed by Jacob et al [59] using a broad-band dye laser pumping an entire rotational band. The absolute calibration was obtained from a comparison with the LIF signal from $N_2^+$ molecular ions, whose density was in turn measured by microwave interferometry.

For measurements of light atoms such as H, C, F, O, there is a large energy gap between the ground state and the first excited level. Direct pumping generally requires photons in the
extreme UV range, for which laser sources are not convenient. In addition, the power required to saturate the transition increases dramatically as we reduce the wavelength, and so measurements made in the UV or VUV are generally below saturation, requiring a calibration depending on laser power. An example of this approach is that of Mertens and Silz [60], who use a frequency-tripled dye laser beam at 121.5 nm to pump hydrogen atoms. The absolute density is obtained from a calibration using Rayleigh scattering in argon. The aim of their experiment is to measure the density of atomic hydrogen near the edge of the TEXTOR tokomak.

Another solution to this problem is to use two-photon excitation (TALIF or Two-photon Absorption Laser-Induced Fluorescence). The laser wavelengths are then in the 200-300 nm range, where efficient frequency-doubling crystals can operate. It is then possible to use two-photon absorption to populate the upper level, while observing the fluorescence in the visible region. This technique has been reviewed by Amorim, Baravian and Jolly [61]. This technique has been most often applied to the measurement of atomic hydrogen densities [62, 63, 64], but has also been used to detect Cl, CO and O [65, 66]. In the case of hydrogen, either two 205 nm photons are absorbed, populating the n=3 (3d^2D) level, or two 243 nm photons followed by pumping at 656.3 nm. The resulting H_α radiation at 656.3 nm is observed, allowing absolute values for the atomic densities to be obtained, as well as their spatial distribution. In the case of O atoms, two photons at 226 nm pump the atoms from the 2p^3 3P ground state to the 2p^4 3P excited level, while the fluorescence radiation at 844.6 nm is observed perpendicular to the pump beam. In the paper by Hancock and Toogood, they emphasize the presence of stimulated emission (SE) at 844.6 nm, in the same direction as the pump beam, under strong laser irradiation. Since this stimulated emission affected the fluorescence (FL) signal, they suggest that such experiments be carried out at low energy conditions, where SE is absent. The absolute calibration of the fluorescence measurement was done by comparison of the FL signal with that obtained using a flow tube wherein the O concentration was well known from gas-phase titration measurements. These experiments by Hancock et al show that the emission at 844.6 nm from excited oxygen atoms is affected by dissociative excitation at higher molecular concentrations, whereas the two-photon LIF technique gives a more reliable estimate of the ground state oxygen density. In the work by Brockhaus et al [66], the absolute number density is obtained by calibrating the optical system using Raman scattering in hydrogen, and using a rate equation model to relate the excited level density to the total density, knowing the laser parameters.

A review paper by Muraoka et al [67] includes a useful table which gives a résumé of the species which have been measured by LIF.

High quality dye lasers have traditionally been used to provide the pumping radiation, although diode lasers have been used for recent work wherein high spectral resolution has been obtained, and Optical Parametric Oscillators (OPOs) could find increasing application due to their broad wavelength tunability. For spatially-resolved measurements, one can scan both the pumping beam and the detection optics to map out the spatial variation, but it is often easier to translate the plasma source, leaving the optics fixed. Expanded beams and multiple pass optics have also been used, along with detector arrays, to obtain spatially-
resolved distributions of the induced fluorescence. Such techniques could be valuable tools in measuring the spatial uniformity of different species in plasma processing discharges.

Measurements of Ion Motion

One of the great attributes of dye lasers (and other tunable lasers) is their ability to generate a narrow linewidth. The linewidths can be sufficiently narrow to measure the translational energy of atoms, ions and molecules in the discharge. In order to deduce the velocity distribution from the LIF data, we need an accurate measurement of the frequency spectrum of the laser. This factor may then be separated from the Doppler shift and broadening caused by the motion of the ions. In this case, the laser samples a small part of the velocity distribution function – only those ions with the correct velocity can be pumped. The probability of absorbing a photon in the frequency band \((\nu, \nu + d\nu)\) in a time \(dt\) is given by:

\[
P_{ij} = \frac{B_{ij}}{4\pi} L(\nu, v_{ij}, \Delta v_{ij}, \nu) d\nu \, dt
\]  

(9.8.9)

Here \(B_{ij}\) is the Einstein coefficient for stimulated absorption for isotropic radiation, and \(L\) represents the absorption profile. If the ion is modeled as a harmonic oscillator with external excitation, the absorption profile \(L\) is Lorentzian:

\[
L(\nu, v_{ij}, \Delta v_{ij}, \nu) = \frac{2 \Delta v_{ij}^2}{4 \left[v - v_{ij} \left(1 + \frac{\nu}{c}\right)ight]^2 + \Delta v_{ij}^2}
\]  

(9.8.10)

\(\Delta v_{ij}\) is the FWHM of the line, and \(\frac{\nu}{c}\) is the Doppler shift. The number of transitions from the lower level \(i\) in the time \(dt\) is obtained by the product of \(P_{ij}\), the laser intensity \(I(\nu, t)\), and the density of the ions with velocity \(v\). Integration over the frequency then gives the variation of the levels \(i\) and \(j\):

\[
-\frac{df_i(v, t)}{dt} = \frac{df_j(v, t)}{dt} = f_i(v, t) \frac{B_{ij}}{4\pi} \int d\nu L(\nu, v_{ij}, \Delta v_{ij}, \nu) I(\nu, t)
\]  

(9.8.11)

In a similar way, we have to include the effects of stimulated and spontaneous emission. Other processes such as collisions (electron-ion, ion-ion, ion-neutral) and cascades from upper levels have also to be taken into account, but we assume that these effects are negligible. For such a 3-level system we then have a series of rate equations for the 3 coupled levels:
\[
\frac{df_1}{dt} = -f_1 B_{12} \Phi + f_2 \left[ B_{21} \Phi + A_{21} \right]
\]
\[
\frac{df_2}{dt} = f_1 B_{12} \Phi - f_2 \left[ B_{21} \Phi + A_{21} \right] - A_{23}
\]
\[
\frac{df_3}{dt} = f_2 A_{23} \quad \text{where}
\]
\[
\Phi = \frac{1}{4\pi} \int dv \nu \left( \nu, \nu', \Delta \nu, \nu \right) f \left( \nu, t \right)
\]

These equations can be solved if we know the atomic parameters and the intensity distribution of the laser. The fluorescence signal (number of measured photons) is then given by:

\[
N = \frac{d\Omega}{4\pi} A_{23} \int d^3x \int d^3v \int dt f_2 \left( x, v, t \right)
\]

Figure 9.8.4 shows schematically the effect on the velocity distribution functions for levels 1 and 2 for pumping under various laser intensities.
We see that with a low intensity, narrow laser line only a small part of \( f_1 \) is sampled – we are able to resolve the structure of the velocity distribution function. Experimentally, we scan the laser wavelength, allowing a measurement of \( f_1(v) \). However, we note from the figure that as the intensity of the laser increases, more and more of the distribution function is sampled – the resolution is degraded. This is called “power broadening”, and it occurs when the rate of stimulated emission approaches that of stimulated absorption, both being greater than spontaneous emission. Experimentally, we must find a recipe for determining the optimum value of the laser intensity. If it is too low, the fluorescence signal will be weak, while if it is too high, we lose the ability to measure the velocity distribution function. Goeckner and Goree [68] solved the differential equations (9.8.12), and applied their results to the experimental situation, suggesting methods for optimizing the laser intensity and avoid power broadening:

1. Measure the LIF spectral profile for different laser powers. Trace the FWHM of the LIF signal on a log-log plot. It is generally of the form:

\[
\log_{10}(\text{FWHM}) = \sigma \log_{10}(I_L) + C
\]  

(9.8.14)

The optimum laser intensity is chosen to give \( \sigma = 0.015 \).

2. Trace the LIF signal as a function of the laser intensity. The curve has 2 asymptotes, one for low power and one for high power. The optimum laser power is found at the point equal to half of the point of intersection of these two asymptotes.

3. Measure the LIF signal with respect to the saturation level. We then choose a laser power such that the LIF signal is 0.2 of the saturation value.
The velocity distributions of particles coming from a target or going towards it can be measured. An example of the former case is the measurement of the atoms sputtered by ion bombardment (see Husinsky et al [69]). An interesting study is that of Park et al [70], where the thermalization of atoms sputtered in a magnetron discharge was measured. A successful application of LIF to measure velocity profiles of particles moving toward a surface is the work of Goeckner et al [71], where the ion velocity and density in the sheath was measured. Goeckner et al [72] have also measured the ion velocities and temperature in a magnetron discharge. A number of experiments have been done to measure the ion velocities in ECR discharges, notably by Den Hartog et al [73], Davis and Gottscho [74], Trevor et al [75], Nakano et al [76], Sadeghi et al [77]. In the experiment by Gulick [78], measurements of the ion velocity distribution have been made in the pre-sheath, showing ion acceleration towards the sheath edge, in general agreement with a 1D fluid model including recycling and ionization. A result from experiments by Khodr [58] showing the LIF signal as the laser wavelength is scanned is shown in Figure 9.8.5. The spectrum is fitted by two Gaussians – one shows a velocity drift, while the other shows the presence of low energy ions which are created by ionization.

Figure 9.8.5 LIF spectrum of ArII ions showing a low energy component and a drifting component [58]
From the measured velocity shift as a function of position in front of the target, we can plot the ion velocity, as shown in Figure. 9.8.6; as we can see, the ion velocity approaches the sound speed as we approach the sheath edge.

![Figure 9.8.6 Ion velocity in front of a target derived from LIF][58]

It should be mentioned that high-resolution optical emission spectroscopy can also be used to measure ion motion [79, 80], but this approach measures chord-integrated spectra, and thus cannot provide the same spatial resolution as LIF.

**Measurements of Internal Energy**

In addition to the measurement of kinetic velocities, LIF is well adapted to the measurement of internal energy of molecules and molecular radicals. Narrow-line laser pumping, combined with wavelength scanning systems, allows one to measure the distribution amongst the vibrational and rotational levels in molecules. From this, the rotational or vibrational temperature can be measured. Such measurements allow a comparison of the energy distributions obtained for different species, and are important for elucidating the discharge kinetics. In the work of Brockhaus et al [66], the emission band strength is plotted against the vibrational energy of the upper level $v'$, allowing a calculation of the vibrational temperature $T_{vib}$ in $N_2$ and $N_2^+$. The value of $T_{vib}$ turned out to be the same for both molecules, 7100 K. They also measured the intensities of the rotational lines in the (0,0) band of $N_2^+$. The intensity of the R branch is given by:
\[ I_R = I_0 g(K'' + 1)\exp \left[ -\frac{\hbar c B_{v'} K'' (K'' + 1)}{kT_{rot}} \right] \]  

(9.)

where \( g \) is the statistical weight of the lower rotational levels designated by the quantum number \( K'' \), \( B_{v'} \) is the rotational energy constant of the upper level, and \( T_{rot} \) is the rotational temperature. The experimental results showed a rotational temperature of 770 K, which is relatively close to the translational temperature. Similar results have been reported by Fukuchi et al [103].

**Measurements of Electric Fields**

The electric field distribution near surfaces is an important parameter in all discharge sources. Because of their non-perturbing nature, and the possibility of very good spatial resolution, LIF measurements are especially appropriate for measuring the electric fields in sheaths. In one approach, the spectrally-resolved LIF signal from Stark-mixed parity levels in BCl radicals is measured, and the presence of the normally forbidden Q(11) transition is compared to the allowed P(12) and R(10) transitions [81, 82]. The ratio can be used to determine the electric field. It is estimated that fields as small as 4 kV/m can be measured. Maurmann et al [83] have used a similar technique using CS molecules, generated outside the discharge vessel. They were able measure electric fields in the range 10 \( \leq E \leq 120 \) kV/m. Oda and Takiyama [84] and Takiyama et al [85] have developed a technique wherein the polarization of the \( 3^1D-2^1P \) fluorescence emitted when metastable He atoms are pumped from the metastable \( 2^1S \) to the \( 3^1D \) level. This forbidden transition is accessible due to both the Stark effect and the electric quadrupole transition. They have performed measurements in a hollow cathode discharge, where they obtain a resolution of about 20 kV/m; the diagnostic is being developed for measurements in the edge region of tokamaks. Hebner et al. [86] measured spatially and temporally resolved electric fields using LIF measurements of the Stark structure of \( n = 11 \) singlet Rydberg manifold. Using this approach, they were able to measure with good precision the electric fields in the sheath of an RF capacitive discharge.

Other approaches, not based on LIF, have also been used to measure electric fields. Shoemaker et al [104] have measured the Stark splitting, and Ganguly and Garscadden [87] the Stark broadening of Rydberg levels in He by LOG. They estimate resolutions of 200V/m and 100V/m, respectively. Barbeau and Jolly [88] have measured spectroscopically the Stark broadening in H, and estimate a precision of 5 kV/m.

The most recent approach is that of “laser-induced fluorescence-dip spectroscopy”. A first laser beam is used to excite an atom from a lower level 1 to an upper level 2; a second laser is then used to further pump the atom from level 2 to a highly excited Rydberg level. The fluorescence from level 2 is observed as the wavelength of this second laser is scanned over a number of Rydberg levels; whenever the laser encounters an allowed transition, the atoms will be pumped to the upper (Rydberg) level, and so there will be a decrease of the
fluorescence from level 2. The Rydberg levels are broadened, shifted and possibly split by the electric field in the plasma. Using a known calibration, this can be used to measure the electric field with precise spatial resolution.

This technique has been developed by Czarnetzki et al. [89] and by Barnat and Hebner [90, 91, 92]. In the work by Czarnetzki et al., they used hydrogen atoms, pumped from the ground state to the \( n = 3 \) level by Doppler-free two-photon absorption. An IR laser further pumped the H atoms from \( n = 3 \) to higher levels – as high as \( n = 55 \). The (inverted) fluorescence signal when pumping to \( n = 30 \) is shown in Figure 9.8.7. It is estimated that an electric field as small as 5 V/cm can be measured by this technique. We should also emphasize that this is a local measurement, allowing measurements of electric fields with high spatial resolution.

![Figure 9.8.7 Broadening and splitting of the Rydberg levels by an electric field [89]](image)

Barnat and Hebner have optically pumped argon atoms, and have used the technique to measure electric fields with high precision near metal-dielectric interface [90, 91] and around a biased electrical probe in a plasma [92].

### 9.9 Laser Spectroscopy - Cavity Ring down Spectroscopy

This technique is a specific application of absorption spectroscopy, making use of the precise directionality and narrow linewidth of laser sources. The plasma is placed in an optical cavity formed by two highly reflecting mirrors. Laser light at a precise frequency is shone into the cavity through one of the mirrors, and bounces back and forth between the mirrors, gradually leaking out of the cavity because of the finite reflectivity of the mirrors. The original configuration of the method, and that which is easiest to analyse, is that wherein a pulsed laser is used, and the pulses at the output of the cavity are monitored. The advantage of this technique resides in the fact that (i) the measurement of a decay time involves a large number of pulses, thus giving an inherent averaging, (ii) the variation of the intensity of the source affects all the pulses equally, and so is not
important, (iii) the effective path length in the cavity is very long, thus allowing a small absorption to be measured.

If we consider an energy density $\rho$ (J.m$^{-3}$) at a given wavelength in the cavity, the radiant flux on each of the mirrors is then $0.5\rho c$ W.m$^{-2}$ and the loss from the cavity is $0.5\rho cA[(1-R_1) + (1-R_2)]$ W. If the length of the optical cavity is $L$, then we find that the energy density in the cavity decays away:

$$\frac{d\rho}{dt} = -\frac{0.5\rho c(2 - R_1 - R_2)}{L} \quad \text{or} \quad \rho = \rho_0 \exp\left(-\frac{t}{\tau_c}\right) \quad (9.9.1)$$

The time constant of the cavity is given by:

$$\tau_c = \frac{2L}{c(2 - R_1 - R_2)} \quad (9.9.2)$$

If the two mirrors are identical, then we have $R_1 = R_2 = R$, giving:

$$\tau_c = \frac{L}{c(1 - R)} \quad (9.9.3)$$

It is possible to purchase low-loss dielectric-coated mirrors having $R=0.9999$; in a cavity having a length of 0.5 m, this gives a “ring-down” time of 16.7 $\mu$s. This corresponds to about 10,000 round trips in the cavity, and a total path length in the cavity of 5 km!

The plasma (or other medium) to be analysed is placed within an optical cavity comprising 2 highly reflecting concave mirrors. The mirror curvature is chosen so that we have a stable cavity – the beam within the cavity is spatially confined. A beam of light is then injected from an external source; the simplest case to consider is that of a short duration pulse. If the pulse width is shorter than the round trip time within the cavity ($2L/c$) the pulse will simply bounce back and forth between the mirrors. A typical set-up is shown in Fig. 9.9.1.
Fig 9.9.1 Typical set-up for CRD measurements [93]

With a cavity 0.5 m long, the pulse should thus be less than 3.3 ns. Only a small fraction (1-R) of the incident laser pulse will enter the cavity; in general this can be easily measured. What will be the signal measured at the output of the cavity? If we have an incident intensity $I_0$, then the intensities of the first and subsequent pulses measured by the detector will be:

\[
I_1 = T_1 T_2 I_0 = (1 - R_1)(1 - R_2)I_0 \quad \text{at time 0}
\]
\[
I_2 = T_1 R_2 R_1 T_2 I_0 = R_1 R_2 I_1 \quad \text{at time } \frac{2L}{c}
\]
\[
I_3 = T_1 R_2 R_1 R_2 R_1 T_2 I_0 = (R_1 R_2)^2 I_1 \quad \text{at time } \frac{4L}{c}
\]
\[
\text{etc.}
\]

Thus, we have a sequence of pulses characterized by:

\[
I_n = (R_1 R_2)^{n-1} \quad \text{at times } t_n = \frac{2(n-1)L}{c}
\]  

(9.9.4)

(9.9.5)

From this we can calculate the pulse intensity as a function of time:

\[
I_n(t_n) = (R_1 R_2)^{\frac{cn}{2L}}
\]  

(9.9.6)

If we now consider an absorbing medium, with absorption coefficient $\alpha$ at the frequency of the laser, we see that the intensities of the detected pulses will be attenuated:
\[ I_1 = T_1 \exp(-\alpha t)L_1I_0 = (1 - R_1)(1 - R_2)\exp(-\alpha t)L_0 \] at time 0

\[ I_2 = T_1 \exp(-\alpha t)R_2 \exp(-\alpha t)\exp(-\alpha t)L_0 = R_1 R_2 \exp(-2\alpha t)L_1 \] at time \( \frac{2L}{c} \) \hfill (9.9.7)

\[ I_3 = (R_1 R_2)^2 \exp(-4\alpha t)L_1 \] at time \( \frac{4L}{c} \)

etc.

The pulse heights as a function of time then become:

\[ I_n(t_n) = (R_1 R_2)^{n} \exp\left(-\frac{\alpha L}{L} t_n\right) \] \hfill (9.9.8)

A typical waveform is shown in Fig. 9.9.2.

![Figure 9.9.2 Typical waveform in CRD experiment [93]](image)

Here, we distinguish between the cavity length \( L \) and the path length in the absorbing medium \( l \). If we plot this on a log scale, we get:

\[ \ln(I(t_n)) = \ln(R_1 R_2) - \frac{\alpha L}{L} t_n \] \hfill (9.9.9)

We note that \( R_1 \) and \( R_2 \) are less than 1, and so \( \ln(R_1 R_2) \) is negative. The overall dependence thus gives an exponential decay with a time constant:

\[ \tau_D = \frac{2L}{-c \ln(R_1 R_2) + 2\alpha L} \] \hfill (9.9.10)
We note that for $R_1 = R_2 = R \approx 1$, $-\ln(R) \approx 1-R$, and so we write this in a form which is compatible with equation (9.9.3):

$$
\tau_D = \frac{L}{c(1-R + \alpha l)}
$$

(9.9.11)

The “ring down” time constant of the cavity must first be measured in order to extract the contribution due to the absorption. If we consider mirror reflectivities of 0.9999, with $l = 0.2$ m, and $L = 0.5$ m, we find that the absorption component is equal to the cavity component of the decay time for $\alpha = 5 \times 10^{-4} \text{ m}^{-1}$. This represents a very small absorption, and so we can conclude that with high quality mirrors, very small absorptions can be measured. It has been estimated [93] that absorptions of less than 1 part in $10^7$ per pass can be measured (i.e. $\alpha l$ of the order of $10^{-6}$).

If we use longer laser pulses, then there will be overlapping of the pulse with itself within the cavity; there will be interference. The cavity will then begin to take on the characteristics of a Fabry Perot cavity, with axial modes. This situation is somewhat more complicated to analyse, but various CW techniques have been developed.

CRD spectroscopy has been used to measure a broad range of molecular species, comprising basic molecular spectroscopy [93], to environmental monitoring [94], to measuring radicals in plasma reactors [95, 96].

### 9.10 Laser Spectroscopy – photodetachment

In some plasmas, there is a significant fraction of negative ions. This is especially true of plasmas containing electronegative species (oxygen, chlorine, fluorine) that are especially useful in provoking chemical reactions – such as etching. Another case where the negative ions are important is that of hydrogen. In this case these ions are important for the production of negative ions beams – and subsequently the efficient production of beams of neutral atoms. The $\text{H}^-$ ions is weakly bound – only 0.75 eV, so the photodetachment cross-section is quite high through the visible spectrum (see Figure 9.10.1):

Thus, Nd:YAG, ruby and doubled-Nd:YAG lasers can all be used to remove the electron from the ion. To detect the presence of the $\text{H}^-$ ions, we then must detect the electrons liberated from the ions. Usually this is done by inserting a collector (a Langmuir probe) into the plasma near the laser beam. The generation of electrons by the beam will be registered as a current pulse on the probe (which should be biased so as to collect the electrons). A typical pulse is shown in Fig. 9.10.2):

The initial pulse indicates the photo-generated electrons, while the negative-going part is a result of the redistribution of the plasma after the initial injection of electrons.
The total number of electrons liberated in the focal region depends on the laser power and the pulse duration, as shown in Fig. 9.10.3:

Other techniques for measuring the photo-detached electrons have been developed, based on Thomson scattering (see section 11.).

9.11 Laser Spectroscopy - Non-linear interactions

Voir texte de A Bertrand Grenier

9.12 Abel Inversion and Tomography

Several diagnostics give chord-averaged values of given quantities. Examples are absorption spectroscopy, interferometry, and emission spectroscopy. It is often of interest to try and extract the local values of density, emissivity etc. If the plasma has a cylindrical symmetry, this can be done through Abel inversion.

If we consider the case of emission spectroscopy with an optically thin plasma (see Figure 9.12.1):

The measured signal is given by

$$ S(p) = 2 \int_0^\sqrt{R^2-p^2} \varepsilon(x) \frac{\Omega}{4\pi} da dx $$  

(9.12.1)

Here, $R$ is the radius of the plasma column, $p$ the impact parameter, $\varepsilon(x)$ the local emissivity (e.g. in photons per m$^3$ per s), $\Omega$ the solid angle for the optical collection, and $da$ the area of the defining aperture in the plasma. It can be shown that the product $\Omega da$ is a constant (called the étendue) if there are no apertures or absorbing media in the optical path. We can thus represent the measured signal (in this example, in photons per s) as:

$$ S(p) = 2 \Omega da \frac{\int_0^\sqrt{R^2-p^2} \varepsilon(x) dx}{4\pi} $$  

(9.12.2)

Since the emissivity is a function of radial position $r$, it is more convenient to put this equation as an integral over $r$ instead of $x$:

$$ S(p) = 2 \Omega da \frac{\int_p^R \frac{\varepsilon(r) r dr}{\sqrt{r^2 - p^2}}}{4\pi} $$  

(9.12.3)
S(p) is the measured quantity, but we want to evaluate the local emissivity \( \varepsilon(r) \). Formally this can be done through the Abel transformation:

\[
\varepsilon(r) = -\frac{1}{\pi} \int_{r}^{R} \frac{dS(p)}{p} \frac{dp}{\sqrt{p^2 - r^2}}
\]

(9.12.4)

There are several practical difficulties in using this equation. The chordal measurements are obtained at a number of discrete values of \( p \). Thus, the derivative of \( S(p) \) cannot simply be evaluated from the experimental data, since calculating differences between discrete points will increase the noise on the signal. Several methods for treating this problem have been devised [97]. Let us consider the paper by Barr as an example. He presented the equivalent formulation for the inversion:

\[
\varepsilon(r) = -\frac{1}{2\pi} \frac{dF(r)}{dr} \quad \text{where}
\]

\[
F(r) = 2\int_{r}^{R} S(p) \frac{dp}{\sqrt{p^2 - r^2}}
\]

(9.12.5)

The signal \( S_n \) is measured at discrete points \( p_n = n\Delta \), with \( r_k = k\Delta \) and \( R = N\Delta \). He then fitted the results in each interval \( n,n+1 \) by:

\[
S(p) = a_n + b_np^2
\]

(9.12.6)

From this, he was able to determine coefficients \( \beta \) which he could use to obtain the function \( f \) using \( S(p) \):

\[
f_k = \frac{1}{\pi\Delta} \sum \beta_{kn}S_n
\]

(9.12.7)

(See the paper by Barr [97] for the values of the coefficient \( \beta \).)

We note that the Abel inversion is valid only for systems which have cylindrical symmetry. Some work has been done to extend this approach to non-cylindrical configurations, but one has to know the shape of the plasma (i.e. the surface of constant emissivity) beforehand. We assume that the plasma is composed of layers of constant emissivity – we could call this the “onion-skin” model. This method works best if there are many observational chords through the plasma – a relatively straightforward problem with high performance CCD detectors. We start with the outside layer – assuming there is no emission from farther out. The path length through the layer is calculated, allowing a calculation of the emissivity of this layer. For the next layer in, we subtract the contribution from the first layer, allowing a calculation of the emissivity of the second layer. This procedure is repeated from the outside to the inside.
If we do not know ahead of time the symmetry of the plasma, we need extra camera views to examine non-symmetric distributions. We then use an approach called tomography. In essence this provides a Fourier-type analysis to the azimuthal asymmetries. To provide more resolution – to obtain higher azimuthal modes - more camera angles are required. Such approaches are routinely used to study the rotating non-axisymmetric modes in the X-ray emission from tokamaks, but there have also been some cases wherein laboratory plasmas have been studied.

Appendix 9.1: Chordal measurements

We note that the phase shift for a chord of an interferometer passing through the plasma is given by:

$$\Delta\varphi = \frac{2\pi}{\lambda n_c} 2 \int_{0}^{R_{p}} n_e(x)\,dx$$  \hspace{1cm} (9.A.1.1)$$

where $\lambda$ is the wavelength of the beam, $n_c$ the critical density and $n_e$ the plasma electron density. We thus see that it has the same form as the chord-integrated intensity of spectroscopic measurements.

Appendix 9.2: Gaussian, Lorentzian and Voigt profiles

A normalized Gaussian profile can be expressed as:

$$G(x,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left( -\frac{x^2}{2\sigma^2}\right)$$  \hspace{1cm} (9.A.2.1)$$

where:

$$\int_{-\infty}^{\infty} G(x,\sigma)\,dx = 1$$  \hspace{1cm} (9.A.2.2)$$

The full width at half maximum of the Gaussian profile is given by:

$$\Delta x_{1/2}^G = 2\sigma\sqrt{2 \ln 2} \hspace{1cm} \text{or} \hspace{1cm} \sigma = \frac{\Delta x_{1/2}^G}{2\sqrt{2 \ln 2}}$$  \hspace{1cm} (9.A.2.3)$$

A normalized Lorentzian profile can be written as:

$$L(x,\gamma) = \frac{\gamma}{\pi(x^2 + \gamma^2)}$$  \hspace{1cm} (9.A.2.4)$$
From this, we see that the full width at half maximum of the Lorentzian profile is given by:

\[ \Delta x_{1/2}^L = 2\gamma \quad \text{or} \quad \gamma = \frac{1}{2 \Delta x_{1/2}^L} \]  

(9.A.2.5)

The Voigt profile is given by a convolution of the Gaussian and Lorentzian profiles:

The full width at half maximum of the Voigt profile depends on the relative contributions of the Gaussian and Lorentzian components. It has been shown () that a reasonably good approximation, good to about 2.4% for \( \varphi = 0-10 \), is given by:

\[ \Delta x_{1/2}^V \cong \Delta x_{1/2}^L \left(1 - c_0 c_1 + \sqrt{\varphi^2 + 2c_1 \varphi + c_0^2 c_1^2}\right) \]  

(9.A.2.6)

Here:

\[ \varphi \equiv \frac{\Delta x_{1/2}^L}{\Delta x_{1/2}^G} \quad \text{and} \quad c_0 = 2.0056, c_1 = 1.0593 \]  

(9.A.2.7)
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