6. Molecular Spectroscopy Techniques Applied for Processing Plasma Diagnostics

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Optical diagnostics are between the most commonly used tools for the characterization of plasmas and for the better understanding of physical and chemical processes controlling their time and space dependencies. In this review paper the most popular spectroscopy techniques are described and examples of their applications to plasmas are indicated. An special emphasis is given to power saturation phenomena, encountered in laser based diagnostics. Numerical applications show that with commonly available lasers a great care must be taken to avoid saturation and to be really non-intrusive, as expected for a diagnostic tool.

Keywords: plasma diagnostics, optical saturation, actinometry, broad-band absorption, CRDS, cavity-enhanced absorption, LIF

6.1 Introduction

Low pressure glow discharges are widely used in new technologies and particularly for materials surface processing as: etching [1], deposition [2] of thin films and modification of surface properties like hardness [3], corrosion resistance [4] or wettability [5]. In particular, plasma processing has had the largest impact in silicon integrated circuit technology by making it possible to etch sub-100 μm sized features with vertical side walls in silicon [6]. However, to meet the requirements of material properties and the performances of sophisticated device structures, it is necessary to know the precise composition of the plasma in interaction with the surface of the material under process. Particularly, as the semiconductor industry continues to scale down the dimensions of ULSI circuits, a more and more precise control of the line shape profile of the etched features is required. These requirements can be achieved by in-situ diagnostics in the plasma gas-phase. Between different existing techniques, optical diagnostics are particularly well-suited for in-situ plasma diagnostic studies because they are non-intrusive, species-selective, and yield good space and time resolved information. Optical diagnostics can be divided in two categories, passive and active. In the first case, Optical Emission Spectroscopy (OES), the spectral and temporal analysis of the plasma induced emission provides information relative to the species present in electronically excited states. This information about species present in the plasma, is however not always related to atoms and molecules in their ground states, that form the majority of the medium. In active spectroscopy, an external light source is used and the response of the plasma to this source, that could be a diminution of the transmitted intensity, Absorption Spectroscopy (AS), or changes in spectrally resolved emission from the plasma, Laser Induced Fluorescence (LIF), contain information relative to the absorbing species. The light source is often a frequency tunable laser but it also could be another plasma or a lamp. These techniques can provide data relative to the ground state of molecules but to be non-perturbative, strict conditions regarding the spectral power density of the external source must be respected. After having described these different techniques, several recently applied examples will be presented and their results discussed.

6.2 Emission Spectroscopy

Easily implemented and cost-effective, Optical Emission Spectroscopy is the most popular plasma diagnostic technique. But it suffers from two main handicaps:

i) it is a sight of line measurement and the space resolution that it can provide is only in directions perpendicular to the observation. However, tomography technique [7], in which the Plasma Induced Emission (PIE) is first recorded from different observation directions and then the recorded files are inverted by numerical procedure, can give access to the space resolved data.

ii) the gathered information comes from the excited states of the species and not from the ground state molecules. To overcome this weakness, Coburn & Chen have proposed the well known Actinometry technique [8], in which a small, but precisely known, amount of a rare gas is introduced into the plasma and its PIE is recorded together with the PIE from the species of interest.

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6.2.1 Actinometry

This technique is used to follow changes (in space, with time or with experimental parameters) in the density of transient species present in the plasma. Provided that electron impact excitation from the ground state of specie X is the only excitation mechanism of the upper state of the observed radiation, the PIE signal of this specie, \( I_X \), writes:

\[
I_X \propto [X] n_e \int_{E_T}^{\infty} \sigma_X(\varepsilon) f(\varepsilon) v_\omega(\varepsilon) d\varepsilon
\]

(1)

where \( n_e \) is the electron density, \( \varepsilon_T \) the threshold energy for excitation of the light emitting state, \( \sigma_X(\varepsilon) \) is the energy dependent excitation cross section for the excitation of X by electrons of speed \( v_\omega(\varepsilon) \), and \( f(\varepsilon) \) the normalised electron energy distribution function (eedf). \( I_X \) therefore depends on both electron density and eedf. Actinometry offers the possibility to get rid of the electron density dependence by using the ratio:

\[
\frac{I_X}{I_A} = \frac{[X]}{[A]} \int_{E_T}^{\infty} \frac{\sigma_X(\varepsilon) f(\varepsilon)}{\sigma_A(\varepsilon) f(\varepsilon)} \tau d\varepsilon = \frac{F(\varepsilon)}{X} \frac{[X]}{[A]}
\]

(2)

where \([A]\), the density of actinometer, often argon but other rare gases have also been used, is known. However, the proportionality factor \( F(\varepsilon) \), that relates the measured intensities to the particles densities, strongly depends on eedf, to simplify, on electron temperature \( T_e \). Now, if threshold energies, \( \varepsilon_T \) and \( \varepsilon_A \) are close and if the energy dependence of \( \sigma_X(\varepsilon) \) and \( \sigma_A(\varepsilon) \) could be supposed to have the same shape, then \( F(\varepsilon) \) becomes independent of \( T_e \) and the density \([X]\) can be deduced from the measured intensity ratio.

Several examples, where the density \([X]\) was simultaneously measured by absorption [9] or LIF [10], have shown that actinometry is not reliable. In a recent work, the density of silicon etch products, Si, SiCl and SiCl\(_2\) radicals, have been measured by broad-band absorption spectroscopy in an industrial high density process reactor and were compared to actinometry signals, obtained using argon [11]. Results shown in Fig. 1 indicate that when the variation with RF power is considered, the trend of density change is well reproduced by actinometry but when the density variation with the pressure is studied, the trends are totally opposite for all three cases. In fact, it is well known that in high density plasmas, the electron temperature doesn’t change with the power but decreases with increasing pressure [12]. As the threshold energy is about 13.5 eV for Ar and only 5.1, 4.2 and 3.7 eV for Si, SiCl and SiCl\(_2\), respectively, this leads to an enhancement of the excitation rates of the radicals, compared to argon (Eq. (2)). It has been shown that xenon, for which the \( \varepsilon_A \) value of its 828 nm line is only 9.9 eV, is much more appropriate for the actinometry of Cl atoms and Cl\(_2\) molecules [13,14]. To get rid of the pressure dependence of \( I_A \), the quenching rate coefficients of argon, measured for a large number of compounds [15] can be used. Another problem that often was encountered in plasmas of diatomic molecules, when following the evolution of atom density by actinometry, is the contribution to the emission intensity \( I_X \) from the dissociative excitation of molecules, for example in chlorine plasma [16]:

\[
\text{Cl}_2 + e \rightarrow \text{Cl} + \text{Cl}^* + e
\]

(3)

To take account of this extra excitation term, the time-resolved actinometry methods have been applied for the detection of CF\(_2\) radical [17] or O atoms [18]. In these techniques, the plasma producing power is modulated in rectangular-wave. Given that the time required for the establishment of the plasma is usually in the order of a few tens of \( \mu s \), during which the degree of dissociation of the molecule stays low, the \( I_X \) signal following the ignition corresponds to the dissociative excitation and the time evolution of \( I_X \) provides information about the time-variation during the plasma pulse of the \([X]\) density [18].

6.3 Absorption Spectroscopy

Absorption spectroscopy can provide direct measurement of the absolute densities of species in their ground state. However, this quantity is a line of sight averaged value. The spectral resolution, absolutely necessary in molecular spectroscopy which deals with vibrational and rotational...
structures of the transition, can be provided by the detection system (spectrometer) or by the frequency tunable light source (laser). The transmittance signal at frequency \( \nu \) is related to the absorbing species density according to the Beer-Lambert law:

\[
T(\lambda) = \frac{I(\nu)}{I_0(\nu)} = \exp\left(-\alpha(\nu) l_{\text{equiv}}\right)
\]

(4)

where \( I_0(\nu) \) and \( I(\nu) \) are the intensity at frequency \( \nu \) without and with absorbing species, \( l_{\text{equiv}} \) is the equivalent path length and \( \alpha(\nu) \) is the absorption coefficient. For a single line (atomic line or single rotational line), it is given by:

\[
\alpha(\nu) = k_\nu \phi(\nu) \left( N_l - \frac{g_l}{g_u} N_u \right)
\]

(5)

with \( N_l \) and \( N_u \) being the density of population in the lower and upper states of the transition, respectively, and \( g \) the statistical weights of these levels. \( \phi(\nu) \) is the normalized line profile, \( \left(\int \phi(\nu) d\nu = 1\right) \), whose simplest forms are Gaussian profile, \( \phi_G(\nu) \), resulting from the Doppler broadening due to the velocity distribution of absorbers (inhomogeneous broadening), and Lorentzian profile, \( \phi_L(\nu) \), due to limited lifetime of the electronic states and collisions (homogeneous broadening). They are given by:

\[
\phi_D(\nu - \nu_0) = \frac{2}{\sqrt{\ln(2)}} \frac{\nu - \nu_0}{\delta \nu_D}
\]

\[
\exp\left[-4\ln(2) \frac{(\nu - \nu_0)^2}{\delta \nu_D^2}\right]
\]

(6)

where the Doppler width (FWHM) is:

\[
\delta \nu_D (\text{Hz}) = \left(\frac{2 \nu_0}{c}\right) \sqrt{2 \ln(2) RT / M}
\]

\[= 7.16 \times 10^{-7} \nu_0 \sqrt{T / M}\]

(7)

where \( M \) is the molecular weight, and

\[
\phi_L(\nu - \nu_0) = \frac{2 \sigma_L}{\nu - \nu_0^2 + (\delta \nu_L / 2)^2}
\]

(8)

where the natural width (FWHM) is related to the lifetime:

\[
\delta \nu_L (\text{Hz}) = \frac{1}{2\pi \tau}
\]

(9)

When \( \delta \nu_D \) and \( \delta \nu_L \) are comparable, the line shape will have a Voigt profile [19], resulting from the convolution of Eqs. (6) and (8).

\( k_0 \) is related to the absorption, \( B_{lu} \), and emission, \( A_{ul} \), transition probabilities [20], (Einstein coefficients), the oscillator strength of the line, \( f_{lu} \), or the transition dipole moment, \( \mu \), according to the relation:

\[
k_0(\nu) = \frac{h \nu_0^3}{c} B_{lu} = \frac{g_u}{8 \pi} \frac{\lambda_0^2}{8 \pi} A_{ul}
\]

\[= \frac{1}{4 \pi \epsilon_0} \frac{\pi e^2}{m_e c} f_{lu} = \frac{g_u}{8 \pi} \frac{2 \pi^2}{3 \epsilon_0 h} A_{ul} \left| \mu \right|^2
\]

(10)

where different terms have their usual meanings [21].

Remark: All above mentioned equations and quantities are in International System, \( \nu \) [s\(^{-1}\)], \( l \) [m], \( N \) [m\(^{-1}\)], \( k_0 \) [m\(^2\) s\(^{-1}\)], \( B \) [J\(^{-1}\) m\(^{-1}\) s\(^{-2}\)]. Some authors and books use \( \omega = 2\pi \nu \), or \( \sigma = 1/\lambda = \nu/c \) as frequency unit and give slightly different equations [20,21].

Equation (5) evidences that the measured absorption is always related to the population difference between the lower and upper states of the transition. When dealing with electronic transitions, where the energy difference is much larger than the gas temperature, \( T_e \), the condition \( [N_u] \ll [N_l] \) is usually satisfied. But infrared absorption on vibrational transitions has been used to measure the density of molecules like CH \(_3 \), [22], CF \(_2 \), [23], SiH \(_3 \), [24] or NO, [25]. In this case, if \( T_e \) is high, the above mentioned condition could not hold. As an example, lines of the \( \Delta \nu_0 = 1 \), \( Q(n, n) \) band of CH \(_3 \) radical, with \( \lambda \approx 16.5 \mu m \), are often used to measure the density of this radical in hydrocarbon plasmas [22]. Assuming Boltzmann equilibrium within vibrational levels, we can calculate \( [N_u]/[N_l] \approx 0.17 \) if \( T_e = 500 \) K, or 0.64 for \( T_e = 2000 \) K. It is obvious that under these conditions \( [N_u] \) can be neglected in Eq. (5). In the following, we will consider electronic transitions and will assume that \( [N_u] \) is negligible.

Applied to diatomic molecules, equations (4) to (10) lead to [26]:

\[
\int \ln \left[ \frac{I_0(l)/I(\nu)}{I(\nu)} \right] d\nu = \left[ \frac{g_u}{8 \pi^2} \frac{\lambda_0^2}{4} A_{ul}^{v',v} \right] \left[ \frac{S_{J',J}}{2J'+1} \right] \left[ \frac{g_{v',v}}{g_{v,v}} \right] \equiv \frac{c}{2\pi} \left[ N_{v',v} / \phi(\nu) \right]
\]

(11)

where the integral is over the single rotational line between \( v' \), \( J' \) of the upper and \( v, J \) of the lower electronic states,

\[
A_{ul}^{v',v} = A_{ul} \sum_{v',J'} v' q_{v',v} q_{v',v'}
\]

(12)

is the transition probability between the vibrational levels \( v' \) of the upper and \( v \) of the lower states, with \( q_{v',v} \) being the Franck-Condon factor [26]. \( S_{J',J} \) is the Hönig-London factor of the line [27] and \( g_{v,v} \) is the nuclear spin statistical weight of the rotational level in the lower state [26]. In polyatomic molecules, due to the existence of several vibrational and rotational modes, equation (11) will be slightly different [28].

6.3.1 Broad-band absorption

Broad-band absorption spectroscopy (BBAS) has been proven to be a very powerful technique for determination of the absolute (line-averaged) density of species produced in plasmas. Absorption rates down to 0.01%, corresponding to absorption coefficients of \( 1 \times 10^{-5} - 1 \times 10^{-4} \text{ cm}^{-1} \), can be easily measured when light from a xenon arc lamp (in UV) or a tungsten filament (in the visible spectrum) is decomposed with a grating spectrometer and detected with a CCD, or diode array camera [29,30]. The main advantage of the
The technique is to record in one shot the absorption lines, or bands, in the whole spectral range covered by the camera. The absorbing species density is deduced using Eq. (11) and when the spectral resolution of the spectrograph is high enough the gas temperature can be deduced from the rotational distribution [29]. However, with commonly used spectrographs the spectral resolution (~0.1 nm) is usually very poor compared to the Doppler width of the absorption lines (in the range of 10–3 nm). Also, given the large spatial extension of light sources used in BBAS, the spatial resolution perpendicular to the optical path is often limited to several millimeters. This technique has been widely used in hydrocarbon [31,32], fluorocarbon [29,33], and chlorine based [30,34] process plasmas. Particularly, LIF enabled the detection of ground-state SiO, SiCl, and SiCl₂ radicals. Due to the low resolving power of the spectrometer, the rotational structure of the bands is not resolved and the population density [N_{i,v}'] in vibrational v' levels of SiO and SiCl is deduced by the integration of Eq. (11) over rotational lines of the v' – v" transition to obtain [30]:

$$
\int \ln \left( \frac{I_{i,v}}{I(\lambda)} \right) d\lambda = \left( \frac{g_u}{g_l} \right) \frac{\lambda^4}{8\pi} A_{ul} \equiv N_{i,v'}
$$

(13)

For the seek of clarity, in Eq. (13) the units was changed from v' to \( \lambda \). For SiCl₂ radical, the vibrational bands are also not resolved and the whole structure can be integrated [30] to deduce the total density of this radical:

$$
\int \ln \left( \frac{I_{i,v}}{I(\lambda)} \right) d\lambda = \left( \frac{g_u}{g_l} \right) \frac{\lambda^4}{8\pi} A_{ul} \equiv N_{i}
$$

(14)

### 6.3.2 Fundamentals of laser based absorption

Since the development of tunable lasers in 1970s, laser-based diagnostic techniques made a tremendous contribution to the understanding of elementary processes occurring in plasmas. Particularly, LIF enabled the detection of ground-state, or long-lived excited states, of atoms and molecules. The first step in all the different techniques using lasers is the absorption of laser radiation by the specific specie present in the plasma volume to be detected. This will inherently reduce the population density in the lower state of the transition to which the laser frequency is tuned and increase the density in the upper state. To be considered non-intrusive, the modification of population densities must be small enough to let the measured signal be representative of the initial density of the lower state. To treat the influence of the laser radiation on measured signal, we consider a two levels system in interaction with a laser tuned between them. Rate equations governing the evolution of the populations of these states under laser radiation write [20]:

$$
dN_{i,l} / dt = \left( B_{al} \rho + A_{al} \right) N_{u} - \left( B_{ul} \rho + \Sigma_q k_{l,q} M_q \right) N_{i} + C_{l} 
$$

(15)

$$
dN_{u} / dt = B_{ul} \rho N_{i} - \left( B_{al} + \Sigma_{q=lower} A_{ul} + \Sigma_q k_{u,q} M_q \right) N_u + C_u
$$

(16)

where \( A_{al} \) is the spontaneous emission Einstein coefficient, \( B_{il} \) and \( B_{ul} \) are Einstein coefficients for absorption and stimulated emission, respectively, related one another by \( B_{ul} = g B_{il} \), where \( g = (g_l/g_u) \), and to \( A_{al} \) according to Eq. (10). \( \rho \) is the spectral energy density by frequency unity, \( \tau \) is the transit time of the lower state particle through the laser beam, \( k_{l,q} M_q \) represents the collisional depletion of the state \( | i \rangle \) by collision with specie \( q \), whose density is \( M_q \) and \( C_l \) is the population rate of state \( | i \rangle \) by different channels, including diffusion transport from the outside of the beam volume, electron impact excitation, radiative cascades and collisional transfers from the neighbor states. We define the total population relaxation rates of states \( | l \rangle \) and \( | u \rangle \), and the mean relaxation rate, \( \mathcal{R}^* \) as:

$$
\mathcal{R}_l = 1/\tau_l + \Sigma_q k_{l,q} M_q
$$

(17)

$$
\mathcal{R}_u = \Sigma_{i=lower} A_{ul} + \Sigma_q k_{u,q} M_q
$$

(18)

$$
\mathcal{R}^* = \mathcal{R}_l \mathcal{R}_u / (\mathcal{R}_l + \mathcal{R}_u)
$$

(19)

Equations (15) and (16) could be solved analytically for the general case but in this paper we consider only the steady-state solution, \( dN_{i,l} / dt = 0 \), fulfilled when using a cw laser or, when \( 1/(\rho B_{il}) \), the characteristic time for the optical pumping, is well shorter than the characteristic time for the variation of the laser intensity. The steady state solutions are:
\[
N_i = \frac{C_1 (gS + \mathcal{R}_u / \mathcal{R}_l) + C_2 (gS + A_{ld} / \mathcal{R}_l)}{S \left( \mathcal{R}_u - A_{ld} + g \mathcal{R}_l \right) + \left( \mathcal{R}_l + \mathcal{R}_u \right)} \quad (20)
\]

\[
N_u = \frac{C_1 S + C_2 (S + \mathcal{R}_u / \mathcal{R}_l)}{S \left( \mathcal{R}_u - A_{ld} + g \mathcal{R}_l \right) + \left( \mathcal{R}_l + \mathcal{R}_u \right)} \quad (21)
\]

where \( S \) is the saturation parameter defined as:

\[
S = B_n \rho / \mathcal{R}^* \quad (22)
\]

From these equations, we can deduce the “statistically weighted population difference” of the levels, related to the absorption coefficient \( \alpha(v) \) through Eq. (5):

\[
\Delta N = N_i - g N_u = \Delta N^0 \left( 1 + S \frac{\mathcal{R}_u - A_{ld} + g \mathcal{R}_l}{\mathcal{R}_l + \mathcal{R}_u} \right) \quad (23)
\]

where \( \Delta N^0 \) is the population difference in the absence of laser, \( \rho = 0 \), then \( S = 0 \), given by:

\[
\Delta N^0 = N_i^0 - g N_u^0 = \frac{C_1}{\mathcal{R}_u} - \frac{C_2}{\mathcal{R}_l} \left( g - A_{ld} / \mathcal{R}_l \right) \quad (24)
\]

According to (23), the actual absorption coefficient, given by Eq. (5), depends on saturation parameter \( S \) and can tend to zero for large \( S \) values, even when the population difference, \( \Delta N^0 \) is important.

Due to the optical coupling of states \( | l \rangle \) and \( | u \rangle \) by the radiation field, the homogeneous line width of the transition (Eq. 8) is broadened and becomes [20]:

\[
\delta \nu_h (\text{FWHM}) = \delta \nu_l \sqrt{1 + S} \quad (25)
\]

### 6.3.3 Numerical applications

Molecular spectra are composed of many individual rotational lines possessing different transition probabilities (see Ref. [27] for diatomic molecules and G. Herzberg [36] for polyatomic molecules). It is therefore necessary to estimate the saturation parameter for each individual line. Examples given here below are for a \( \phi = 2 \text{ mm} \) laser beam tuned on a transition with \( \lambda = 600 \text{ nm} \) and \( A_{ld} = 1 \times 10^7 \text{ s}^{-1} \), the radiative lifetime of the upper state \( \tau_{lu} = \sum_{\gamma < \text{lower}} (1/A_{ld}) = 20 \text{ ns} \) and \( g = (g_l/g_u) = 1 \).

(1) **When a pulsed laser is used**

We consider a laser pulse with \( \Delta t = 4 \text{ ns} \) duration, \( E_{\text{laser}} = 1 \text{ mJ} \) energy and \( \Delta \nu_h = 0.2 \text{ cm}^{-1} \) = 6 GHz spectral bandwidth. The spectral energy density and the Einstein coefficient \( B_{lu} \) of the transition are:

\[
\rho = \frac{E}{\Delta \nu_sc \Delta \nu_h} = \frac{10^{-7}}{4 \times 10^{3} \pi (10^{-3})^2 \cdot 3 \times 10^7 \cdot 6 \times 10^9} = 4 \times 10^{-3} \text{ J m}^{-3} \text{ s}^{-1} \quad (26)
\]

\[
B_{lu} = \frac{g_u^2 \mathcal{A}_{ul}}{8 \pi \hbar} = \frac{10^6 \times 10^{-9}}{8 \pi \cdot 6.6 \times 10^{-16}} = 1.3 \times 10^{20} \text{ m}^{-3} \text{ J}^{-1} \text{ s}^{-2} \quad (27)
\]

The rate of population transfer from the lower to the upper state, \( \rho B_{lu} \geq 5 \times 10^7 \text{ s}^{-1} \), is much larger than \( 1/\Delta \nu_h \approx 2.5 \times 10^8 \text{ s}^{-1} \) and as the lifetimes of the states are long compared to \( \Delta \nu_h \), the system behaves almost like a closed one, with conservation of the total number of particles. In this case, the relaxation rate is \( \mathcal{R}^* = (\mathcal{R}_l + \mathcal{R}_u)/2 \) (see page 91 of Ref. [20]). At low pressure, when collisional transfers are negligible, \( \mathcal{R}_u = 5 \times 10^7 \text{ s}^{-1} \) and \( \mathcal{R}_l = (1/\text{transit time inside the laser beam}) \approx 2.5 \times 10^5 \text{ s}^{-1} \). These values lead to a saturation parameter \( S \equiv 2 \times 10^3 \), a very big number. If the gas pressure is about one Torr, due to collisional transfers between rotational levels, \( \mathcal{R}_u \) will become about \( 2 \times 10^7 \text{ s}^{-1} \) and \( \mathcal{R}_l \) will slightly increase but these will lower \( S \) by less than a factor of two. Consequently, under laser irradiation the initial population of the lower state will be immediately shared between the two states, proportional to their statistical weights, and the absorption signal, which is proportional to \( \Delta N = N_i - g N_u \) will be almost zero. The other consequence of the high \( S \) value is the much larger power broadened linewidth of the transition, that could be observed from the spectral profile of the LIF signal when scanning the laser wavelength. According to (9) and (25), \( \delta \nu_h \) is about 5.6 GHz. This linewidth is much larger than the Doppler width at room temperature, commonly in the range of 1 GHz, and consequently prevents the determination of the gas temperature from the Doppler profile. However, even at this high saturation regime, the LIF signal, which is proportional to \( N_u = N_l^0 \mathcal{R}_u / (\mathcal{R}_l + \mathcal{R}_u) \), but independent of laser power, can provide the relative populations of different levels when the laser is successively tuned on corresponding transitions. As an example, Davis and Gottscho probed by LIF the rotational distributions in the ground sates of both CCl radicals and N\(_2\) discharges [37]. They concluded that at each position in the discharge the rotational temperature was strongly dependent upon both the applied rf power and the surface temperature of the electrodes. They also observed a thermal gradients near the electrode surfaces. However, with decreasing laser power one can move to low saturation regime where the LIF signal becomes laser power dependent.

Gilles *et al.* demonstrated that the relevant parameter to be used when comparing the LIF signals of two systems is \( \rho B_{lu} \) and not the laser power alone [38].

(2) **When a single mode cw laser is used**

The same above mentioned open system is considered with a \( \Delta \nu_h = 1 \text{ MHz} \) single mode \( P_{\text{laser}} = 10 \text{ mW} \) continuous laser. \( \Delta \nu_h \) being much smaller than the Doppler width, only a small part of the particles, whose velocity component along the beam propagation axis, \( V_z \), satisfy the condition \( (V_z/V_h)/\nu_h \) will interact with the laser radiation. As \( \Delta \nu_h \) is much smaller than the homogeneous Lorentzian line width of the transition, \( \delta \nu_h \), the spectral density to be considered is...
the population of the lower state will be reduced significantly. The majority of particles transferred by laser absorption to the upper state will be almost zero. As we are considering an open system, it is still a large number and consequently the absorption signal is saturated, as defined in (22) will be 

\[ \delta v = \frac{1}{2\pi\tau_u} = \frac{\Re_v}{2\pi} \]

As

\[ \int \rho(v)dv = \rho_0 \frac{\pi\delta v}{2} = \frac{P_{\text{laser}}}{s\pi c} \quad (30) \]

we then calculate the laser power density:

\[ \rho_0 = \frac{4P_{\text{laser}}}{s\pi c\Re_v} = \frac{4 \cdot 0.01}{\pi \left(10^{-3}\right)^2 \cdot 3 \times 10^3 \cdot 5 \times 10^7} = 8.5 \times 10^{-13} \text{ J m}^{-2} \text{s}^{-1}. \]

In steady-state conditions, the mean relaxation rate \( \Re_v \) is given in Eq. (19). At low pressure, when collisional transfers are negligible, \( \Re_v \approx 1/\text{transit time inside the laser beam} \) and then \( \Re_v \approx 2.5 \times 10^5 \text{ s}^{-1} \). The resulting saturation parameter, as defined in (22) will be \( S \approx 440 \), which is still a large number and consequently the absorption signal will be almost zero. As we are considering an open system, the majority of particles transferred by laser absorption to the upper state will radiate down to other states and consequently the population of the lower state will be reduced significantly, as seen from (20). However, according to (25), now \( \delta v_s \approx 21 \times \delta v = 0.17 \text{ GHz} \) and if the width of the line profile is in the range of 1 GHz, or larger, the velocity distribution profile of the absorbers can easily be deduced from the LIF signal by scanning the laser wavelength. The velocity distribution in high density plasmas of metastable atoms of argon [39] and chlorine [41] have so been deduced and allows to measure the photon lifetime in the cavity. This « ringdown time » \( \tau \) is measured while the laser wavelength is tuned across absorption features of the sample. Considering the reflection coefficient \( R \) of the mirrors (1 – \( R \) < 10\(^{-4}\) for good ones) and the absorption coefficient of the sample, \( \alpha \), the decay rate of the trapped photons is:

\[ l/\tau = (1 - R + c\alpha)/(L/c) = l/\tau_0 + (c/L)\alpha \quad (31) \]

where \( c \) is the speed of the light, \( l \) is the length of the absorbing sample and \( L \) the cavity length. \( l/\tau_0 \) is the decay time when the laser wavelength is set outside of absorption features. \( l/\tau \) has a broadband smooth baseline which can be easily distinguished from the rapidly varying spectral features of the sample. These later provide \( \alpha(v) \) from which species density can be deduced. Very often, YAG or Excimer pumped tunable pulsed lasers are used in CRDS experiments and the spectral resolution is limited by the linewidth of the laser. But with a cw-single-mode laser (diode laser, dye or Ti:Sapphire lasers), which has a linewidth of less than 10 MHz (\( \pm 0.01 \)) pm), CRDS can provide the profile of the absorption lines, from which the structure of the line, or the gas temperature related to the Doppler broadening of the line, can be deduced [48]. In cw-CRDS, an acousto-optic modulator is used to provide the train of laser beam pulses to be injected into the cavity [48]. The repetition rate of these pulses can be more than one order of magnitude higher than that of the usual pulsed lasers.
drawback of the high sensitivity and good spectral resolution of cw-CRDS is the large time often needed to scan the spectral range of interest.

Since its discovery, CRDS has been very widely used in plasma diagnostics, of which we can mention the detection and/or the density measurement of $N_2^+(X^2Σ^+; \nu = 0)$ ions [49,50] and $N_2(X^2Σ^+; \nu = 18)$ vibrationally excited molecules [51] in nitrogen plasmas, Si and SiH radical [52], as well as SiH radical and nano-particles [44,53] in SiH$_2$ containing plasmas, CH and CH$_3$ radicals in diamond deposition plasmas [54-56], CF, CF$_2$ and SiF$_2$ radicals in silicon etch CF$_4$ plasma [57] and O$^-$ and H$^-$ negative ions in different plasmas [58,53]. Temporally resolved version of CRDS can provide the time variation of the absorbing molecules concentration even when their lifetime is comparable to the decay time $\tau$ of the CRDS signal [59].

(3) Cavity Enhanced Absorption Spectroscopy (CEAS)

CEAS does not rely on determination of the decay time $\tau$ of the light leaking from the cavity, but rather on the intensity of integrated light transmitted through the cavity. When scanning the laser, the radiation is coupled into the cavity via accidental coincidences of the laser frequency with one of the cavity modes and the absorption spectra is extracted from the frequency-dependent light intensity transmitted by the cavity [60]. The drawback of this extreme simplicity of CEAS is the need for an independent determination of the mirrors reflectivity to access to the absorption coefficient $\alpha(\nu)$. This can be accomplished by running one CRDS experiment in empty cavity [61]. In this reference CEAS was used to measure the density of $N_2^+(X^2Σ^+; \nu = 0)$ ions in an ICP reactor. Vankan et al. also employed this technique to measure the density of ammonia formed in the expanding beam of an N$_2$–H$_2$ plasma generated in a cascaded arc source [62].

(4) Broad-Band Cavity Enhanced Absorption Spectroscopy (BBCEAS)

This very recent technique combines the multipass advantages of the cavity enhanced technique with the broad spectral ability of the BBAS or ICLAS. It uses a self-mode-locked tunable Ti:Sa laser that provides a train of about 82 MHz laser pulses of $\pm 100$ femtosecond duration forming a comb of 82 MHz ($\pm 1.75 \times 10^{-4} \text{ nm at 800 nm}$) frequency spaced modes enclosed within a few nm wide envelope [63,64]. This broad-band laser source can be coupled to an absorption Fabry-Perot cavity if the length of this cavity is precisely adjusted in such a way that its free spectral range becomes a multiple of the $82 \text{ MHz}$ frequency spacing of the laser comb. The light leaking from the other mirror of the cavity is then dispersed with a spectograph and detected by a CCD or diode array device. So, the cavity enhanced absorption spectra in the whole spectral range covered by the laser envelope, or by the optical detection system, can be recorded in only one shot. Another interesting feature of the fs laser source is the facility of its frequency doubling with a simple BBO crystal to obtain violet radiation. Figure 3 shows the absorption spectra on the well known 1st negative $0 \rightarrow 0$ band of nitrogen ions recorded in a 1 Torr; 5 mA glow discharge with $R = 98\%$ reflection coefficient mirrors [64]. The effective path length was therefore 50 times the real plasma length. This figure results from the concatenation of three spectra of one nm wide each recorded for three successive settings of the spectrometer. This is because only 1 nm was covered by the 1024 pixels of the photodiode array. The total time for recording the whole spectra was less than 100 seconds. The insert in Fig.3 shows that thanks to the high resolution of the spectrometer the Spin-doubling on rotational lines is well resolved for the high rotational lines.

Instead of fs laser, it is also possible to use an incoherent high-brightness arc lamp as a broad-band source [65] but to the detriment of longer acquisition time, due to the weaker transmitted light, and lower signal to noise ratio.

(5) Saturation phenomena in cavity enhanced absorption spectra

Like all laser spectroscopy methods, cavity enhanced absorption techniques could be subject to saturation phenomena as was described in 6.3.2. This is mainly due to the high light power than can be stored inside the Fabry-Perot cavity and the long interaction time of this light with absorbing species, which make the problem similar to the cw-laser case, even when a short duration laser pulse is used. This point was analyzed in Ref.[51] for the CRDS experiments done with an Excimer pumped dye laser. Figure 4 illustrates the saturation phenomena observed in a cw-CRDS experiment [66] with a diode laser source tuned on 653.288 nm (3p[1/2]$_{1} \rightarrow 3P_{0}$) line, absorbing from the Ne*($^3P_{0}$) metastable state in a 0.1 Torr, 0.4 mA glow discharge in a 60% neon, 40% argon gas mixture. Figure 4(A) shows an example of the CRDS signal decay curves for different laser frequencies (indicated as $\nu_1$ to $\nu_4$ in Figure 4(B)). When the discharge is off, the decay, due only to the mirrors loss ($\tau_0$), is a perfect exponential. With the discharge on and laser set on the absorption line, we observe a faster and non exponential decay. To build the absorption profiles, shown in Fig. 4(B), the slopes of the decay curves are deduced for different RD signal (proportional to the light
power inside the cavity, indicated as horizontal lines in Fig. 4(A) and the corresponding $\alpha(\nu)$ values are calculated. The shoulder at about 1.5 GHz results from absorption by $^{22}$Ne isotope. The higher the light power inside the cavity is, the smaller the absorption coefficients, $\alpha(\nu, I) = \alpha(\nu, 0)/\sqrt{I+S}$, are [20]. According to Eq. (22), $S$, the saturation parameter, is proportional to the light intensity which is continuously decreasing during the ringdown time. We also observe Lamb dips at the center of the line, when atoms crossing perpendicular to the cavity axis absorb photons traveling in both directions. Therefore, the laser depletion is twice for metastable atoms with this velocity component [20]. Note that the saturation free curve is obtained for less than 4 $\mu$W laser power inside the cavity. The density of Ne($^3P_0$) atoms deduced from this curve (largest $\alpha(\nu)$) is about $1 \times 10^6$ cm$^{-3}$.

### 6.4 Laser Induced Fluorescence (LIF) Techniques

Single photon LIF has been extensively used for monitoring species density and internal energy of molecules in plasmas. Ref. [67] gives a non-exhaustive list of plasma interest atoms (Al, As, Cu, Fe, Ge, Mo, Si, Zn) and molecules (BCl, CCl, CF, CF$_2$, Cl$_2$$^+$, CH, CN, FeO, N$_2$$^+$, NH, NO, OH, SiCl, SiH, SiH$_2$, SiN, SiO) that have been detected by LIF, and their respective wavelengths. To this list one can add H$_2$ molecule [80] and C [81] and F [82] atoms. This difficulty can be overcome with Two Photon Absorption LIF (TALIF) technique, in which two photons are simultaneously absorbed to excite the molecule. The list of wavelengths that could be used to detect H, O, N, C, Cl, F, S and Xe atoms by TALIF are given in Ref. [67], to which one can add Kr [83] and Ar [15]. As the two-photon absorption cross section is extremely small, TALIF doesn’t suffer from saturation phenomena as described in 6.3.2. However, because it always require high power pulsed lasers, a third photon can interact with atoms in the excited state to induce further ionization [84] or induce Amplified Stimulated Emission (ASE) [85]. These both mechanisms lead to a diminution of the LIF signal, a phenomenon in some sort similar to the saturation effect. The absolute density of H, N and O atoms can be deduced by calibrating their TALIF signal with the TALIF signal from Kr or Xe, introduced in the discharge cell at known amount [86,87]. A modified version of TALIF, known as 2 + 1 laser induced fluorescence-deep, has been developed for the measurement of very week electric fields in the sheath region of hydrogen plasmas [88,89].

Another useful laser based technique for the determination of the vibrational and rotational population distribution in the ground state of homonuclear molecules, for which vibrational and rotational transitions are forbidden, is the Coherent Anti-Stokes Raman Scattering (CARS). It has been successfully applied to hydrogen [90] and nitrogen [91].

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