Topical Review

Foundations of optical diagnostics in low-temperature plasmas

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Abstract

Over the past few decades many diagnostics have been developed to study the non-equilibrium nature of plasma. These developments have given experimentalists the possibility to measure in situ molecular and atomic densities, electron and ion densities, temperatures and velocities of species in the plasma, to just name a few. Many of the diagnostic techniques are based on the ‘photon-in, photon-out’ principle and were at first developed to perform spectroscopy on atoms and molecules. Much later they were introduced in the research of plasmas. In this foundation paper we will focus on optical-based diagnostics that are now for quite some time common use in the field of low-temperature plasma physics research. The basic principles of the diagnostics will be outlined and references will be given to papers where these techniques were successfully applied. For a more comprehensive understanding of the techniques the reader will be referred to textbooks.

Keywords: optical diagnostics, plasma, low-temperature plasma

1. Introduction

The diagnostic toolbox for the experimental low-temperature plasma physicist has been expanded enormously over the past decades. At first the toolbox consisted of a spectrometer to measure the emission lines of plasma excited species and a Langmuir probe to measure electron densities. But nowadays also mass spectrometers, to determine the composition of the plasma, and even advanced laser-based diagnostics are being used to determine e.g. time and spatially-resolved temperatures, densities and velocities of the plasma species, or even electric field strengths. Every diagnostic in the toolbox has its pros and cons, and all should be considered complimentary to each other. E.g. Langmuir probes are cheap, however, cannot always be applied, due to its intrusive character [¹]. In fact, a probe is measuring the disturbance by the probe on the charged species and a model is necessary to extract the electron density and temperature from the measurement. Mass spectrometry can give detailed information on both neutrals and ions but requires to sample part of the gas, which is a delicate procedure in case of quantitative measurements and perturbative especially at atmospheric-pressure [²]. Nevertheless, these non-optical techniques, which have been improved and further developed to overcome many of their limitations, are very successfully applied in the study of plasma [³]. Optical techniques, which can be divided into passive and active techniques, have also shown their merits in low-temperature plasma physics. In Plasma Spectroscopy by Griem [⁴] the working principle of several passive optical techniques is discussed. Demtroder [⁵] discusses many laser-based active spectroscopic techniques and their applications. Most of the laser-based diagnostics were first applied under
clean and well-determined conditions, and used to measure e.g. absorption cross-sections or lifetimes. But, while lasers were becoming more and more available to non laser-specialists, these techniques are now also shown to be applicable in harsher circumstances, like plasmas and flames. With active spectroscopic gas phase diagnostics like absorption spectroscopy and laser-scattering techniques, quantities like atomic and molecular densities, ion and electron densities, temperature of electrons and heavy particles, and their velocities, can be determined. Several review papers have been published over the years that show the applicability of optical diagnostic techniques for the study of different types of plasma [6–10]. A collection of papers has been published very recently in a special issue of the ‘Journal of Applied Physics D: Applied Physics’ on plasma diagnostics using spectroscopic methods highlighting some of the recent developments in optical diagnostics for measuring physical parameters in low-temperature plasmas, with a focus on atmospheric-pressure plasmas [11]. A review devoted to the spectroscopic detection of molecular radicals in atmospheric-pressure plasma has also recently been published [12].

It is clear from the above that many diagnostic techniques are available to the experimental (plasma) researcher and it is up to the researcher to find the right diagnostic that will deliver the information one is looking for. In this paper we will focus on a selection of optical-based diagnostics that have shown to be applicable to the study of low-temperature plasma. All of the techniques that will be described in more detail are already being used for many years in plasma physics, and are generally being regarded as a standard diagnostic. The experimental schemes of some of the basic diagnostic techniques have been extended to e.g. increase their sensitivity or applicability for dedicated plasma studies. These schemes will only be mentioned and appropriate references will be given.

2. General concepts

Generally speaking, optical diagnostic techniques can be separated into two categories: passive (see section 3) and active optical techniques (see section 4). In plasma studies, emission spectroscopy is one of the most commonly used passive optical diagnostic techniques. This technique is based on the recording of radiation emitted by excited species in the plasma that send out this radiation when spontaneously relaxing to a lower energetic state. From the recorded radiation the densities of excited species present in the plasma can be obtained. Information about the basic plasma parameters, i.e. the electron density and temperature, can be obtained from the measured densities of the excited species. However, a model is needed and assumptions have to be made on the (non-)equilibrium state in which the densities over the energy levels are distributed (see section 3). Information about e.g. the electron density or the translational temperature can under certain circumstances also be obtained from an accurate recording of the line shape of the emitted radiation (see section 3.2.1).

In a passive spectroscopic technique one relies on the excitation of species by the plasma. In case of active spectroscopic techniques one introduces light into the plasma, and determines the effect of the plasma on this light. In very general terms, the light can be absorbed, resulting in an excitation of species or the light can be scattered from species in the plasma. After absorption of the light by the plasma, the information can be extracted in two ways. One is to measure the intensity of the light before and after passing through the plasma. The information on the absorbing species in the plasma is directly obtained from the ratio of the two signals. This technique is called absorption spectroscopy (see section 4.1). And two is to record the light that might be emitted by the excited species when decaying to a lower energy state after absorption of the incoming light. This technique is called laser induced fluorescence (LIF) spectroscopy (see section 4.2). During a LIF experiment one extracts the information about the plasma from the spectral distribution of the emission or from the (total) emission intensity as function of the laser wavelength. In light-scattering techniques three processes are distinguished: Thomson, Rayleigh and Raman scattering. Thomson scattering is elastic scattering from free electrons, Rayleigh scattering is the elastic scattering from heavy particles, and Raman scattering is inelastic scattering from molecules. Although the cross-section for Thomson scattering is much smaller than for the other scattering processes, progress in lasers and spectrograph-detector combinations has allowed researchers to successfully apply Thomson scattering in many different plasmas, like low-pressure technological plasmas, high-pressure thermal plasmas and fusion plasmas, to just name a few. In general, the information on the electron temperature and density is extracted from the spectrally resolved scattered radiation: the width of the spectral profile is a measure of the average electron temperature, and the area under the profile can be related to the electron density (see section 4.3). Rayleigh scattering can be used to determine the total density and temperature of the heavy particles, while Raman scattering can e.g. give information about the density and temperature of a particular molecule (every molecule has at least one active Raman mode) in the plasma. In table 1 a non-exhaustive summary is given of the different parameters that can be obtained with optical diagnostics in non thermal plasma. In the table we use \( n_e, T_e \) for resp. electron density and temperature, \( E_{\text{field}} \) for electric field strength, and \( T_\text{rot}, T_g \) and \( T_\text{vib} \) for resp. rotational, gas and vibrational temperature. Only examples of the more commonly-used optical diagnostic techniques are given. It illustrates how versatile these techniques are and how crucial for understanding plasmas. In this paper a selection of some of these optical diagnostic techniques will be discussed in more detail. For the other optical techniques mentioned in the table the reader is referred to the references given in the last column.
3. Passive optical diagnostic techniques

Passive optical diagnostic techniques are based on the recording of radiation spontaneously emitted by the plasma. This spectroscopic technique is experimentally the most simple variant of the optical diagnostics that is discussed in this paper. The intensity, $I_{p,q}$, of radiation emitted when species in an excited state, $p$, spontaneously decay to a lower state $q$ can be expressed as follows:

$$I_{p,q} = A_{pq} h v_{pq} V N_p,$$  \hspace{1cm} (1)

Here, $A_{pq}$ is the Einstein transition probability of spontaneous emission from initial state $p$ to final state $q$ (vide infra), $h$ is Planck’s constant, $v_{pq}$ is the frequency of the emitted radiation, $V$ the volume from which the radiation is emitted, and $N_p$ is the number density of emitting species in the initial state. In practice, the radiation emitted by the plasma is typically dispersed and recorded by a spectrograph-detector combination. For a given light emission intensity emitted by the plasma, the intensity actually detected will depend on the solid angle of the light collection and the spectral response of the optical setup. The choice of the dispersive element and detector type in terms of sensitivity and/or time response is crucial and discussed for instance in [41, 42]. However, equation (1) clearly shows that the recorded intensity of the emitted radiation is proportional to the density of species in the excited state $p$. In case the excited state is predominantly populated through excitations from the ground state, a situation that is called the Corona balance, the measured intensity is to a good approximation also proportional to the density in the ground state. However, very often other plasma processes, like electron de-excitation processes, three-particle recombination, radiative recombination and electron impact ionisation, can play a role as well. In that case, collisional radiative models need to be used to extract information about the plasma from absolute plasma emission measurements [41, 43].

In general, the radiation emitted by a body at temperature $T$ can be described with Planck’s radiation law:

$$\rho_{p}(\nu, T) d\nu = \frac{8\pi h \nu^3}{c^3} \frac{d\nu}{(\exp(h\nu/kB T) - 1)}$$ \hspace{1cm} (2)

where the radiation density per unit of frequency (Hz), $\rho_{p}(\nu, T) d\nu$ is expressed in J m$^{-3}$ s$^{-1}$. In this equation $c$ is the speed of light (in m s$^{-1}$), $kB$ Boltzmann’s constant (in J K$^{-1}$), $h$ Planck’s constant (in Js), $T$ the equilibrium temperature (in K) and $\nu$ the frequency of the radiation (in Hz). If a plasma would be in thermodynamic equilibrium (TE), it could be treated as a black-body radiator. Consequently, the equilibrium temperature deduced from Planck’s radiation law is then the parameter that can be used to describe excited state densities using the Boltzmann distribution, ion densities (and electron densities because of charge neutrality) using the Saha equation, and energy distributions of the particles, since these follow a Maxwellian distribution. The Boltzmann distribution gives the relation between the populations, $n_p$ and $n_q$, in energy states, $E_p$ and $E_q$, of atoms and molecules at an equilibrium temperature, $T$:

$$\frac{n_p}{g_p} = \frac{n_q}{g_q} \exp \left[ \frac{(E_p - E_q)}{kT} \right]$$ \hspace{1cm} (3)

Here, $g_p$ and $g_q$ are the statistical weights of the energy states $p$ and $q$, resp. For high electron densities the excited levels are in equilibrium with the continuum. The population of an
excited state, \( p \), per statistical weight is then given by the Saha relation:

\[
\frac{n_p}{g_p} = \frac{n_e n_i}{g_e g_i} \left[ \frac{\hbar^2}{2\pi m_b k T_p} \right]^2 \exp \left( \frac{E_{\text{ion}}}{kT_p} \right),
\]

in which \( g_e, n_e \) and \( g_i, n_i \) are the statistical weights and densities of resp. the electron and the ion and is proportional to \( n_e^2 \) (assuming quasi-neutrality). The dependence on \( T_p \) is however different; the line to continuum ratio can be used as a measurement of \( T_p \). \( E_{\text{ion}} \) is the ionisation energy of state \( p \).

However, non-thermal plasmas are not in thermodynamic equilibrium, i.e. they have to be maintained by supplying energy and are therefore characterised by temperature and density gradients. Dense plasmas with a high electron density, locally follow Boltzmann, Saha and Maxwell equations. Dense plasmas with a high electron density, emission and absorption in the system is not equal, the law does not apply for the spectral distribution and the temperature cannot be extracted from the measurement of \( T_e \).

In the next sections the different types of emitted radiation are considered. As a consequence, the molecular emissions show up in the cross-section for radiative recombination is very small.

### 3.1. Continuum radiation

Within this type of radiation we distinguish free–free emission, also called Bremsstrahlung, and free-bound emission, also called recombination radiation.

Bremsstrahlung originates from Coulomb collisions. In those collisions the charged particles are accelerated and thereby emit radiation. In low-temperature plasmas the radiation arises almost solely from the electrons in the electron-ion interaction. The electron undergoes a transition between two free states, which is the reason why we call this radiation also ‘free–free’ radiation. It should be mentioned that electron-electron scattering does not lead to free–free radiation due to momentum conservation, and that the contribution of ion scattering from neutrals can be neglected due to the heavy mass of the ions. Also, electron-atom contributions to the free–free radiation is usually less important (it might be important in parts of the spectrum of plasma of low-ionisation degree (typically below \( 10^{-3} \)). As there are no bound states involved in the transition, the Bremsstrahlung is continuous in wavelength. For 10 eV electrons the maximum intensity of the radiation emitted in a Coulomb collision with ions is around 100 nm. It can be shown that for plasma at temperatures below a few 100 eV, Bremsstrahlung can be neglected [48].

Recombination radiation is generated when an electron recombines with an ion to form the excited state or ground state of the corresponding atom (or the \( \text{Z}^+ \) charged ion forms the \( \text{(Z–1)}^+ \) charged ion). This component is called ‘free-bound’ continuous emission. It has been observed that the chance of radiative recombination decreases fast with increasing quantum number, i.e. decreasing ionisation energy, of the resulting atom. This means that the most energetic photons are produced with highest probability. Since the photon has to take care of both energy and momentum conservation, the cross-section for radiative recombination is very small.

### 3.2. Line radiation (‘bound–bound’)

Line radiation arises from transitions in atoms or molecules between two bound states. For an atomic plasma, the spectral distribution of the radiation, in short the spectrum, consists of individual lines at well-defined frequencies. The transitions occur between different electronic states. For molecules the same is true. However, since molecules, in contrast to atoms, can vibrate and rotate, they have a much denser energy level scheme. As a consequence the molecular emissions show up in the form of bands, which (in the visible part of the spectrum) are in fact congestions of ro-vibronic transitions in the molecule. In figure 1 an optical emission spectrum is shown that has been recorded during etching of an amorphous hydrogenated carbon layer by means of an Ar/H\(_2\) plasma expansion. The low-pressure recombining Ar/H\(_2\) plasma expansion impinges in the subsonic part of the expansion on a carbon surface. The emission of atoms and molecules is recorded just in front of the carbon surface that is exposed to the plasma. Ro-vibronic emissions of CH (electronic
transitions $A \rightarrow X$ and $B \rightarrow X$) and $C_2$ (denoted with the change in vibrational quantum number, $\Delta v$, in the electronic transition $d \rightarrow a$) radicals are clearly observed. These species are formed in the plasma etching process of the carbon layer. For more information on the plasma expansion and the plasma chemistry in this system the reader is referred to the PhD thesis of T. Hansen [49].

3.2.1. Line shapes. None of the spectral lines in a spectrum is Dirac delta function. Without any interaction with other particles, the population in an excited state will decrease because of spontaneous emission to a lower energy state. The probability of this transition process is described by the Einstein coefficient $A_{pq}$ (see also equation (1)), $p$ depicting the upper state and $q$ the lower state. The sum of the transition probabilities for radiative decay to all levels $q < p$ determines the natural lifetime $\tau$ of state $p$ in the following way:

$$\tau = \frac{1}{\sum_{q < p} A_{pq}}. \quad (5)$$

Through the Heisenberg uncertainty relation this life time is related to the natural line width, $\Delta \nu_{\text{nat}}$, of the transition: $\Delta \nu_{\text{nat}} = (2\pi)^{-1}$. The line profile, $\phi(\nu)$, i.e. the spectral intensity distribution of the radiation, is Lorentzian:

$$\phi(\nu - \nu_0) \propto \frac{\Delta \nu_{\text{nat}}}{(\nu - \nu_0)^2 + (\Delta \nu_{\text{nat}}/2)^2}, \quad (6)$$

with $\nu_0$ the centre frequency of the transition and $\Delta \nu_{\text{nat}}$ the full width at half-maximum (FWHM) of the distribution.

There are several processes that lead to a change in width of the natural line profile, but can also show their effect in a change in shape of the line profile. E.g. collisions with other particles will lead to a shortening of the life time of the excited state, and thus (Heisenberg uncertainty relation) a broadening of the line profile. To a very good approximation this collision-induced line broadening (also called pressure broadening) can be expressed as follows:

$$\Delta \nu_{\text{col}} \approx \frac{p_{cp}}{\sqrt{T}} \quad (7)$$

with $p_{cp}$ the partial pressure of the collision partner and $T$ the temperature of the gas. Another process that leads to broadening is the interaction of the excited state with the charged particles in the plasma: this is called Stark broadening. Looking at an spectrally-isolated single transition, all the previously described processes lead to Lorentzian spectral intensity distributions. The total line broadening for the single transition will be again Lorentzian, with a width equal to the sum of the individual line widths. In figure 2 an example of a Lorentzian line profile is plotted. Here, the $x$-axis is plotted in wavenumbers (cm$^{-1}$), as this is the most commonly used unit in spectroscopy, i.e. the true frequency, $\nu$, divided by the speed of light. The FWHM of the Lorentzian line profile in figure 2 is 30 GHz, which is equal to 1 cm$^{-1}$.

When the radiating particles are isotropically moving in all directions, e.g. due to temperature, the spectral intensity distribution of the emission will appear as a Gaussian line shape:

$$\phi(\nu - \nu_0) \propto \exp \left( - \frac{(\nu - \nu_0)^2}{(\Delta \nu_{\text{D}})^2} \right), \quad (8)$$

in which $\Delta \nu_{\text{D}}$, i.e. the FWHM of the distribution, is the so-called Doppler width. For a particle with molar mass $M$ (in amu), in a gas with temperature $T$ (in Kelvin), and a transition at a frequency $\nu_0$, the Doppler width can be shown to be [5]:

$$\Delta \nu_{\text{D}} = 7.16 \times 10^{-7} \nu_0 \frac{T}{\sqrt{M}}, \quad (9)$$

In figure 2 an example of a Gaussian line profile with a FWHM of 30 GHz ($\Delta \nu = 1$ cm$^{-1}$), is plotted.

As the spectral distribution of the emission reflects the process(es) that play a role in the broadening of the distribution, an accurate recording of the profile can be used diagnostically to obtain plasma parameters like heavy particle...
temperature, velocity, and electron density. Critically depending on the relative importance of the different processes that are responsible for the line broadening, the line shape in general can be described with a Voigt profile (see figure 2), i.e. a convolution of a Lorentzian and Gaussian profile. In figure 2 it is clear from the comparison of the three line profiles, all plotted with the same FWHM and normalised to 1, that the differences are most pronounced in the wings of the profiles.

3.2.2. Line distributions. Among the parameters measured with optical emission spectroscopy, the rotational temperature \((T_{\text{rot}})\) of molecular bands is one of the most commonly studied. The reason is that it is a very simple way to measure the gas temperature \((T_g)\) when equilibrium between \(T_{\text{rot}}\) and \(T_g\) can be assumed. This equilibrium is likely to occur because the energy difference between rotational levels is in the order of the gas temperature (few tens of mK). In order to be able to define \(T_{\text{rot}}\) as a ‘temperature’, the population densities of the rotational energy levels of the excited state considered have to be in equilibrium and thus follow a Boltzmann distribution shown in equation (10)

\[
N_u = \frac{N_{0}g_{u}}{Q(T_{\text{rot}})} \exp\left(\frac{-E_u}{k_BT_{\text{rot}}}\right). \tag{10}
\]

Here, \(N_0\) and \(N_u\) denote resp. the number density of molecules in the ground state and in level \(u\) with statistical weight \(g_u\) and energy \(E_u\), and \(Q(T_{\text{rot}})\) is the partition function. By measuring the relative density of several levels with known Einstein coefficients and energy, \(T_{\text{rot}}\) can be deduced. However, in a non-thermal plasma the assumption \(T_{\text{rot}}\) equals \(T_g\) is not always valid, either because of the mechanisms populating the excited state or because of the depopulating processes. The short lifetime of the excited states observed through optical emission sometimes prevents the thermalization to happen before the excited state has decayed. For this reason, it can be more interesting to measure the rotational distribution of ground state molecules that usually have much longer life times and thus enough time to reach equilibrium with the surrounding gas. This, however, requires active optical diagnostic techniques such as Raman scattering or absorption spectroscopy (see section 4). Even if the rotational distribution measured by emission spectroscopy is a Boltzmann distribution, this does not always mean that it is in equilibrium with \(T_g\). It is always important to compare the effective life time of the radiative level (including collisional de-excitation) with the characteristic time of rotational energy transfer. The conditions under which the rotational structure of a molecular emission band can be used to estimate the gas temperature are discussed in detail in [32, 33].

As shown above, spontaneous emission spectroscopy is a powerful diagnostic tool to study plasma. And in combination with collisional radiative models, which use absolute densities of excited species, plasma parameters such as the electron density, the electron temperature and the density of atomic ground state species can be determined. However, to determine the absolute density of excited species, an absolute measurement of the emission between two levels is necessary. To perform absolute emission measurements quite some experimental efforts are required. E.g. one needs to determine the collection angle, the spectral transmission of the system, the response of the detection system, etc. Still, when this calibration is carefully performed, the absolute density of the excited levels can be compared with a collisional radiative model, and plasma quantities like e.g. heavy particle and electron temperature and ground state densities can be determined [50].

3.2.3. Actinometry. A classical technique to retrieve plasma parameters from intensity ratios from emission lines is called actinometry. Actinometry is a widely used passive optical diagnostic technique that has been successfully applied to plasmas in which the population in excited states of atomic species can be described with the so called Corona model, i.e. excitation is solely by electron impact and de-excitation by radiative decay (and not through collisions). Typically, a known amount of a rare gas is added to the plasma under study. The density of this ‘actinometer’ \((a)\) in the gas mixture being known, its emission intensity is used as a tracer of variation of electron density and energy responsible for the population of the excited levels of the specie \((s)\) being studied. The relative line intensities \(I\) of the excited states of \(s^*\) and \(a^*\) allow, under certain plasma conditions, to infer the density of the emitting species. If the light collection angle is the same for both \(s\) and \(a\), and the spectral transmission of the optical system is well calibrated, the density of \(s\), \([s]\), is obtained using a simple equation of the type:

\[
\frac{I_s}{I_a} = \frac{C_s}{C_a} \frac{\hbar \nu_{ij} A_{ij}^s k_s^s \sum A_{ij}^{s*} [s]}{\hbar \nu_{ij} A_{ij}^a k_a^a \sum A_{ij}^{a*} [a]} = C_s [s] \tag{11}
\]

where \(C_s\) are constants that depend on the detection system and that must be calibrated at the wavelengths of the lines used for \(s\) and \(a\), \(A_{ij}\) is the Einstein coefficient for the observed transition and \(\sum A_{ij}\) is the sum of all Einstein coefficients of the radiative transition from the \(i\)th level. The density of \(s\), which is determined from the line intensity ratio, depends on the electron excitation rate coefficients \(k_e\) of both the actinometer and the atom being measured. \(k_e\) can be calculated from the integration of the collision cross section \(\sigma(e)\) with threshold energy \(e_0\) and the electron energy distribution function \(f(e)\) (EEDF) with the expression [51]:

\[
k_e^s = \left(\frac{2e}{m}\right)^{1/2} \int_{e_0}^{\infty} \sigma(e)f(e)e de. \tag{12}
\]

The final density obtained for the specie \(s\) is therefore depending on the accuracy of the EEDF which depends on the Boltzmann solver and the set of cross sections used for this calculation. It is also preferable to choose an excited state of the actinometer having a threshold energy \(e_0\), for its excitation cross section \(\sigma(e)\) close to the one of the excited state of \(s\) in order to prevent possible artefacts induced by complex EEDFs. Equation (11) can be adapted in case the emitting level is also depopulated by non-radiative quenching but then quenching coefficients and densities of the quenchers...
need to be known [25]. In plasmas with molecular fragments atomic emission can result from dissociative recombination of molecular ions. In that case classical actinometry cannot be applied. In a topical review of Donnelly [52] the possibilities of this technique are extensively discussed, showing that under certain conditions electron temperature and energy distributions can be determined for non-equilibrium plasmas. For instance, by using several lines of both s and a and using the variation of the excitation coefficient \( k_e \), one can infer the electron energy [16]. In a paper of Lopaev et al [53] the applicability of actinometry for measuring absolute concentrations of atomic oxygen, nitrogen and fluorine in an ICP plasma is reported.

4. Active optical diagnostics

4.1. Absorption spectroscopy

Absorption techniques are based on the measurement of the intensity decrease of a light beam that passes through a medium. If only linear effects are considered, one can show that the intensity decrease as function of path length through the medium can be written as:

\[
I(\nu) = I_0(\nu)\exp(-\sum_n n_j \sigma_f(\nu) \times L) .
\]  

This is the so-called Lambert–Beer law. \( I(\nu) \) is the intensity after passing through the medium, \( I_0(\nu) \) the intensity before passing through the medium, \( n_j \) is the density of the absorbing species \( j \), \( \sigma_f(\nu) \) the absorption cross section of a transition around center frequency \( \nu_0 \) can be expressed as:

\[
\sigma_f(\nu - \nu_0) = S(T) \cdot \phi(\nu - \nu_0), \tag{14}
\]

with \( S(T) \) the line strength of the transition and \( \phi(\nu - \nu_0) \) the normalised line profile (see figure 2). \( S(T) \) can very often be found in literature or databases and simulation programs [54–56]. The shape of the line profile is determined by the mechanisms responsible for the broadening of the line (see section 3.2.1). As mentioned in section 3.2.1, depending on the most important mechanisms responsible for the shape, the profile can be Gaussian, Lorentzian or a combination of both, leading to a Voigt profile.

This is very often rewritten in terms of absorbance, \( A(\nu) \), defined as:

\[
A(\nu) = \ln \left( \frac{I_0(\nu)}{I(\nu)} \right) = \sum_n n_j \sigma_f(\nu) L = \sum_n \kappa_j(\nu) L, \tag{15}
\]

with \( \kappa_j(\nu) \) the absorption coefficient at frequency \( \nu \) for species \( j \). Integrating \( \kappa_j(\nu) \) over one transition of a single species, one obtains an integrated absorption coefficient, \( K \)

\[
K = \int_{-\infty}^{\infty} \kappa(\nu) d\nu = \frac{1}{L} \int_{-\infty}^{\infty} A(\nu) d\nu. \tag{16}
\]

One of the great advantages of this technique over the other diagnostic techniques is: when the cross section of the absorbing medium is known, the density can be directly determined from the ratio of \( I(\nu) \) and \( I_0(\nu) \), and no calibration is necessary (\textit{vide infra}). However, the absorption measurement is not a zero-background measurement, in contrast to e.g. laser induced fluorescence (see section 4.2). One has to record small changes, i.e. \( \Delta I(\nu) = I_0(\nu) - I(\nu) \) on a large signal \( I_0(\nu) \). The absorption measurement is also a so-called line-of-sight measurement, which means that spatial resolution cannot be obtained from one measurement.

There are many different absorption detection schemes reported in literature, all having their advantages and disadvantages. One can make a rough distinction between schemes in which a broad band light source is used or a narrow band light source.

4.1.1. Absorption spectroscopy with a broad band light source. When a broadband light source is used in an absorption experiment the light can be analysed by means of a monochromator, which disperses the light [57–59], or with a Fourier transform spectrometer, in which the intensity of the light after passing a Michelson interferometer is measured [60, 61]. When a photo multiplier is used as the detector behind a monochromator, every wavelength has to be recorded one after the other. However, nowadays very often a CCD camera is used, which allows recording a range of wavelengths at the same time. In a Fourier transform spectrometer a collimated beam from a light source is divided into two by a beamsplitter and sent to two mirrors. These mirrors reflect the beams back along the same paths to the beamsplitter, where they interfere. If the optical path difference between the two beams is zero or a multiple of the wavelength of the light then the light beams will constructively interfere and the output will be bright, but if the optical path difference is an odd multiple of half the wavelength of the light then the light beams will destructively interfere and the output will be dark. In one arm the light is reflected to the beam splitter after travelling a fixed distance, while in the other arm the light is reflected to the beam splitter from a mirror of which the position is changed during the experiment. After interference of both beams on the beam splitter the beam is directed through the sample and the intensity of the light is recorded as function of the optical path length difference introduced by the moving mirror, i.e. a so-called interferogram is recorded. The Fourier transform of this interferogram shows the intensity of the light at every wavelength, as in the case of the monochromator. During an experiment two interferograms are recorded, i.e. one with and one without sample in the beam. The ratio of the Fourier transforms of the interferograms shows the absorption spectrum (see also equation (13)). The advantage of the FT spectrometer is the fact that during the experiment the detector is measuring all wavelengths at the same time, and thus the total intensity of the light source (this is called multiplexing), while in the monochromator the detector only measures the intensity at a certain wavelength. Certainly in
the infra-red part of the spectrum, where detectors are less sensitive, this is an important advantage. This is why in the early days FT spectrometers were mainly used to record spectra in the (far-)infra-red. Due to the fact that it is easier to record spectra with a resolution of about 0.1 cm\(^{-1}\) with a FT spectrometer than with a monochromator, FT spectrometers are nowadays also used to record spectra in the visible and even UV-part of the spectrum.

4.1.2. Absorption spectroscopy with a narrow band light source. In case narrow band tunable lasers are used in absorption spectrometers, the laser itself acts as the frequency selective element. In the visible part of the spectrum typical line widths of tunable pulsed dye lasers are in the order of 0.2 cm\(^{-1}\), while in the infrared tunable diode and quantum cascade lasers can easily have line widths two orders of magnitude smaller. An absorption spectrum is recorded by tuning the laser over the absorption feature. The intensity is recorded in front and behind the sample and with equation (13) the absorption can be deduced. If the cross section of the transition is known, the density can directly be determined. This is in sharp contrast to the LIF technique that always needs calibration (see section 4.2).

In figure 3 the transmission spectrum is shown of the exhaust of a DBD reactor operating with CO\(_2\) as input gas and recorded with a quantum cascade laser.

Figure 3. Absorption spectrum of the exhaust of a DBD reactor operating with CO\(_2\) as input gas and recorded with a quantum cascade laser.

(typically a few wavenumbers) by simply changing either the temperature or the current. The radiation emitted by the laser is detected simply with a photodiode (for visible range lasers) or a Mercury–Cadmium–Telluride (MCT) detector (in the infrared). The wavelength range scanned by the laser has to be calibrated using an interferometric element such as a Fabry–Perot. Laser diodes can have a stronger intensity at a given wavelength than broadband sources. This is an advantage to use them as source for cavity based techniques, but this can also induce artefacts in absorption measurements. E.g. if the absorbing level is too much depopulated by the laser, then the absorption coefficient \(k(\nu)\) from equation (15) is not proportional anymore to the density of \(n_j\) because the upper level of the absorption transition is now significantly populated. The spectral resolution of laser diodes (in the order of 300 MHz (10\(^{-2}\) cm\(^{-1}\)) and less) offer also the possibility to resolve the Doppler profile of an absorption line. From the Doppler width the gas temperature, \(T_g\), can be inferred [34, 63].

Absorption spectroscopy has been successfully applied both with continuous wave (cw) as well as pulsed lasers. Tunable cw diode lasers in the 3–30 \(\mu\)m wavelength range, and recently quantum cascade lasers [6], have shown their merits in detecting molecular species in reactive plasmas. Over the years also many different detection techniques have been reported, all aimed at increasing the sensitivity of the absorption technique [64]. One is particularly interesting to mention, since it is very often easy to implement. In that case the intensity of the cw laser is modulated, e.g. by means of a chopper, and the signal is recorded with a lock-in amplifier at the modulation frequency. In this way any background light from the sample (which is not modulated) or electronic signals at other frequencies than the modulation frequency is suppressed, which can lead to a sensitivity increase of an order of magnitude (see e.g. chapter 6 of [5]). Another detection technique uses a tunable pulsed dye laser. And even though pulsed lasers very often suffer from large pulse-to-pulse intensity fluctuations, they can still be used for ultrasensitive absorption measurements in the range between 200 and 800 nm. The basic principle for this ultra-sensitive absorption technique, called cavity ring down(CRD) spectroscopy, was reported in 1988 by O’Keefe and Deacon [65]. This technique is based upon the measurement of the rate of absorption rather than the magnitude of absorption of a light pulse confined in a closed optical cavity with a high \(Q\)-factor. The advantage over normal absorption spectroscopy results from (i) the intrinsic insensitivity of the CRD technique to light source intensity fluctuations, and (ii) the extremely long effective path lengths (many kilometers) that can be realized in stable optical cavities [66]. In Chapter 3 of [64] an overview is given of the sensitivities of the different absorption techniques, assuming a minimal detectable fractional absorbance \((\Delta I/I_0)\) and 1 s integration time. Two examples of minimal detectable molecular densities, \(n_{\text{min}}\), that they report are: 1. for single pass absorption and \(\Delta I/I_0 = 10^{-3}\), \(n_{\text{min}} = 10^{20}\text{m}^{-3}\) and 2. for CRD spectroscopy with a pulsed laser and \(\Delta I/I_0 = 10^{-4}\), \(n_{\text{min}} = 10^{16}\text{m}^{-3}\).
4.2. Laser induced fluorescence spectroscopy

During a LIF experiment a light source, very often a laser, is used to excite species to an excited state and the fluorescence emitted by the excited state is detected. The number of photons, \( N_p \), emitted at a wavelength \( \lambda_j \) from a volume \( V \) after excitation of atoms or molecules from an initial state \( i \) to a final state \( j \) with a laser with intensity \( I_L \), is given by (see figure 4):

\[
N_p(\lambda_j) = \sigma_j I_L n_i V \frac{A_{jk}}{A_j + R}
\]  

(17)

Here, \( \sigma_j I_L n_i \) is the amount of photons absorbed per unit volume and time, with \( \sigma_j \) the cross section for absorption from state \( i \) to state \( j \). \( A_{jk} \) is the Einstein coefficient for the transition from state \( j \) to \( k \), which is responsible for the emitted fluorescence at \( \lambda_k \). \( A_j \) is determined by the fluorescence lifetime \( \tau_j \) of state \( j \), i.e. \( A_j = 1/\tau_j \). \( R \) is the total loss rate due to other processes than fluorescence. At low pressures this loss process can usually be neglected. During any experiment only part of the total emitted fluorescence can be collected. The measured LIF signal, \( S_p \), is then written as:

\[
S_p = N_p \frac{\Omega}{3\pi} Q
\]  

(18)

with \( \Omega \) the solid angle over which the fluorescence is detected. \( Q \) incorporates all losses due to the optics between the imaged LIF volume and the detector used to measure the LIF signal and the quantum efficiency of the detector [67]. Equations (17) and (18) show that the LIF signal is proportional to the density of the atoms or molecules in the lower state \( i \). The sensitivity of the technique stems from the fact that the detector recording the LIF signal is not detecting any LIF signal when the laser is not on resonance with a transition of the species under investigation; this is a so-called zero-background measurement technique. Also, the detection can be performed on a different wavelength as the excitation wavelength, i.e. off-resonant detection. In this way spurious scatter from optics in the beam path can be blocked by means of optical filters. Like in Thomson–Rayleigh scattering experiments (vide infra), also here the emission of the plasma detected during the experiment can be reduced by gated detection, i.e. the detector only looks at the plasma when species, which were excited by the light source, fluoresce. For an absolute density measurement a calibration is necessary to determine e.g. \( V, Q \) and \( \Omega \) [68]. This is one of the main drawbacks of this technique. Next to that, also the total loss rate \( R \) should be determined (see equation (17)). However, if one is working in an environment in which the composition of the sampled gas changes during the experiment, \( R \) is changing during the experiment. Only when the time dependence of the LIF signal can be recorded accurately enough and with enough time resolution, \( R \) can be determined, and subsequently an absolute determination of the excited species is possible [69, 70]. This very often means that the excitation source should deliver pulses with sub-nanosecond duration.

In order to be able to detect a molecule by means of laser induced fluorescence, the molecule should possess at least an excited state that is preferably single-photon accessible and is at an energy that corresponds to a wavelength that can be produced with the help of a dye laser. Roughly speaking, this means between 200 and 800 nm. Nd:YAG pumped tunable dye lasers readily deliver light at wavelengths with which ground state densities of molecular radicals can be determined. Also, the fluorescence lifetime of the upper state should not be too long, since otherwise the excited particle might have moved out of the detection volume or de-excited via collisions. For the detection of the ground state of several atoms and small molecules the first prerequisite is not fulfilled e.g. in case atomic ground state densities have to be determined, the wavelength for excitation is very often in the vacuum ultra-violet (VUV) region of the spectrum, and other excitation schemes have to be used. One of the schemes that have been successfully applied in determining ground state densities of atomic hydrogen, nitrogen and oxygen is two-photon absorption laser induced fluorescence (TALIF) [51, 71–75]. Recently this has also been reported with femtosecond time resolution and 2D-imaging of the fluorescence signal of atomic oxygen on an ICCD-camera [76] and on a molecular species, i.e. carbon monoxide, produced in a glow discharge operating on CO2 [77]. The excitation from the ground state is performed with two photons in the UV, and the fluorescence is detected in the (infra-)red. The detected fluorescence is proportional to the ground state density, like in the normal LIF detection scheme, but the dependence on laser intensity is quadratic. This makes calibration a tedious exercise.
For the detection of molecular hydrogen in the different ro-vibrational states in its electronic ground state LIF in the VUV has been successfully applied [78]. Rotational density distributions in vibrational states with $v > 3$ were recorded. Both excitation and fluorescence were in the VUV, which made a more elaborate experimental setup necessary [79].

4.3. Thomson, Rayleigh and Raman scattering

The most important parameter that characterizes the plasma is the electron density. It determines the conductivity of the plasma, the excitation and light emission, the production of radicals and thus the chemical reactivity. Another important parameter is the electron temperature.

As we already discussed in section 3, several optical techniques are available to determine both the electron density and temperature, i.e. Stark broadening, actinometry, and line and continuum emission [4, 80], to just name a few. All have their advantages and disadvantages. Stark broadening, actinometry, and line and continuum emission measurements are all non-intrusive, but, as they are all line-of-sight measurements, a reconstruction technique, like e.g. Abel inversion, has to be applied to the line-of-sight integrated data to obtain spatial resolution. Thomson scattering is a non-intrusive optical diagnostic with which spatially resolved electron densities and temperatures can be readily obtained. Thomson scattering is based on the elastic scattering of light from free electrons [81, 82]. The amount of scattered photons is linear proportional to the electron density and laser power. Due to the movement of the electrons, the scattered light is Doppler broadened with respect to the line width of the excitation source. As the electrons have a much higher velocity than the heavy particles, the light that scatters off the free electrons shows a much broader scattering feature than the scattering originating from the bound electrons of the heavy particles i.e. the Rayleigh scattering feature [83]. Although the electron scattering cross-section is much smaller than the heavy particle scattering cross-section and the density of the heavy particles is usually much higher than the electron density, the large difference between the Doppler broadening allows distinguishing between the electron and heavy particle scattered signal in frequency space. Interpolation of the Thomson scattering feature in the central part of the spectrum allows for the determination of the Rayleigh scattering signal. Next to the Thomson and Rayleigh scattering component, a third component is always present, i.e. the stray light component arising from windows and surfaces of the chamber. The width is determined by the laser line width. The basic components of a Thomson–Rayleigh setup are shown in figure 5(a).

The total Thomson scattered light intensity is directly proportional to the electron density. This means that if the sensitivity of the system is calibrated, the electron density can be determined from the area under the Thomson spectrum. The calibration can easily be performed by measuring the Rayleigh scattered signal from a known amount of gas in the plasma chamber [84]. The electron temperature can be determined from the Doppler width of the Thomson scattered spectrum. The width is determined by the velocity distribution function of the scattering electrons. It should be mentioned that the velocity distribution function that is actually measured, is the one-dimensional velocity distribution function in a direction determined by the relative directions of the incident laser and detection axes. When the distribution function is Maxwellian, the electron temperature, $T_e$ in eV, is determined by:

$$T_e = \left( \frac{\Delta \nu_{\text{Th}}}{4 \sqrt{\ln 2} \nu_0 \sin(\theta/2)} \right)^2 \times \frac{m_e c^2}{e}. \quad (19)$$

Here, $\Delta \nu_{\text{Th}}$ is the full width at half maximum of the Thomson scattering spectrum, $\nu_0$ the laser frequency, $\theta$ the angle between the incoming laser beam and scattered light, and $m_e$, $e$ and $c$ are the electron mass, the electron charge and the speed of light, respectively. As the Thomson scattering signal is proportional to the laser power, high-power, and often pulsed, lasers are used in these experiments. The advantage of a pulsed laser in combination with gated detection of the scattered signal is that the measured emission of the plasma can be decreased relatively with respect to the measured scattered radiation. However, care has to be taken not to use too high powers for the radiation, since that can lead to excitation and/or dissociation of the gasses in the plasma, and thus disturbing the system under investigation, rendering it intrusive.
The elastic scattering from the heavy particles in the plasma, i.e. the Rayleigh scattering, is almost always the most intense feature in the measured spectrum. The height of the signal is proportional to the total density of the heavy particles in the plasma [85]. From this scattering signal no direct information can be obtained about the kind of species present in the plasma. However, under some circumstances from the ratio of the polarized and depolarized Rayleigh scattering, one can get more information about the species in the scattering medium [86].

Thomson and Rayleigh scattering are elastic scattering processes. Inelastic scattering, that only occurs at molecular species (in contrast to Rayleigh scattering, which occurs at all heavy particles), is called Raman scattering [14, 87]. In a Raman scattering process the molecule ends up after the scattering process in a different energy state than before the process. When the molecule is after the scattering process in a higher (lower) state, i.e. the scattered light has a longer (shorter) wavelength, the scattering is called (anti-)Stokes Raman scattering (see figure 5(a)). This technique has not often been employed in the study of plasma, because of the small cross section for Raman scattering. However, the advantage is that every molecule has a Raman spectrum, and can thus in principle be detected. This is especially interesting for homonuclear diatomic species like H$_2$, N$_2$ and O$_2$, which are very difficult to detect otherwise. As in the case of Thomson–Rayleigh scattering, a laser is used as a light source. As the Raman scattering cross-section becomes bigger at shorter wavelength, light in the blue part of the spectrum is preferably used. A laser that is very often used in these studies is the Ar-ion laser, which has strong emissions at 488 and 514 nm. As previously mentioned, pulsed Nd:YAG lasers are commonly used for Thomson scattering experiments. As a consequence, nowadays, also Raman scattering in plasmas is conducted with Nd:YAG lasers [31, 88, 89].

A main drawback of the spontaneous scattering processes on molecules, i.e. Raman scattering, discussed above, is the fact that the scattered light in the plane of the laser beam and perpendicular to the polarization of the laser, is homogeneously emitted in all directions, which makes it very often difficult to detect in environments that strongly radiate. A technique in which the signal is created in a laser-like beam is the so-called Coherent Anti-Stokes Raman Scattering (CARS) technique [90]. During a CARS experiment two collinear laser beams with frequencies $\omega_1$ and $\omega_2$ ($\omega_1 > \omega_2$) are focussed into the sample. The two waves are mixed via the nonlinear polarization of the sample. When $\omega_1 - \omega_2$ equals the frequency of a Raman active transition of the medium, an anti-Stokes(s) and Stokes(s) wave at the frequencies $\omega_{s,h} = 2\omega_1 - \omega_2$ and $\omega_{s,h} = 2\omega_2 - \omega_1$ is generated. Spatial filtering allows for very efficient reduction of the background radiation without loss of CARS signal. Already from this short description of the CARS technique it will be clear that this is an experimentally much more elaborate technique than spontaneous Raman scattering [91]. This technique is presently also being explored to measure electric fields in plasma [92, 93].

In [88] the authors measure the scattering of Nd:YAG laser light from a microwave surfatron plasma jet with a triple grating spectrometer. Depending on the radial and axial position in the jet, the recorded scattering spectra show mainly Raman scattering (close to the exit of the source and away from the expansion axis), mainly Thomson scattering (close to the exit of the source and on the expansion axis) and a combination of both (a few millimeters downstream recording the Thomson and Raman scattering spectra). The spectrometer is equipped with a mask between the first and second grating, to block the much intenser Rayleigh signal and stray light (the green crosses in figure 19). A result of a measurement which only shows Thomson scattering is depicted in figure 6. This spectrum is recorded in the centre of the plasma jet and 1 mm downstream from the source exit. The center part is blocked by the mask to avoid spilling over of charge from the overexposed pixels by the strong Rayleigh scattering signal in the center of the CCD-camera, when no mask would be present. From these kind of measurements the authors derive electron density and temperature, rotational temperature, partial ($N_2+O_2$)-pressure and the $N_2/O_2$ ratio. From the Thomson fit, i.e. the line in the graph, and using equation (19), the electron temperature can be deduced. To do this, it is convenient to rewrite equation (19) to:

$$T_e = \frac{m_e c^2}{16 \ln 2} e \left( \frac{\Delta \lambda_{Th}}{\lambda_0} \right)^2 = 4.61 \times 10^4 \times \left( \frac{\Delta \lambda_{Th}}{\lambda_0} \right)^2,$$

(20)

where we have used that the scattering was recorded with $\theta = 90^\circ$. Measuring the full width at half maximum of the dashed curve ($\Delta \lambda_{Th}$), taking the laser wavelength as the centre wavelength ($\lambda_0$) and using equation (20), an electron temperature of 1.5 eV is obtained (in accordance with what is reported in [88]). To absolutely calibrate the intensity axis, the authors used the rotational Raman scattering spectrum of one atmosphere of air [94]. This spectrum can be measured at a position on the CCD chip different from the simultaneously recorded Thomson scattering spectrum. An electron density of $4.6 \times 10^{20}$ m$^{-3}$ is deduced from the Thomson scattered signal in figure 6. Recently, a similar technique has been applied in an
atmospheric-pressure plasma jet [14]. Here, the Rayleigh signal was filtered out with a Bragg grating, which is experimentally less complicated than using a triple grating setup.

5. Conclusions

In this paper we have given an introduction in some of the optical diagnostic techniques that are nowadays commonly used in the study of low-temperature plasmas. The focus has been on optical diagnostics that can be used to study the plasma phase. Diagnostics like spectroscopic ellipsometry, sum frequency and second harmonic generation and attenuated total reflection spectroscopy, which are used to study plasma-surface interactions, have not been discussed. This paper is meant for scientists new in the field of plasma diagnostics and should serve as a starting point to explore further. It is not a review, but much more a description of the basic principles of some of the commonly used plasma diagnostics. Many references are given to books where these principles are further clarified and to papers in which these diagnostics are successfully applied in the study of plasma.

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