Chapter 2

ABSTRACT

In general, spectroscopy is concerned with the study of interactions between electromagnetic radiation and matter, while analytical spectroscopy makes use of the exploitation of these interactions for qualitative and quantitative analysis. The interactions studied in atomic spectroscopy involve atoms and the purpose often is to determine the elemental concentration or in some cases simply the presence of the element in the sample. The appropriate energy required to interact with atoms falls within the UV-Visible region. This chapter gives an introduction to plasma spectroscopy with a focus on emission spectroscopy and the underlying principles of atomic and molecular spectroscopy in plasmas. Common diagnostic methods are presented, ready for direct application, to obtain plasma parameters by plasma spectroscopy. The basic theory underlying determination of plasma parameters and selection rules for transitions between atomic and molecular levels leading to spectral emission are briefly discussed.
2.1. INTRODUCTION

Plasma spectroscopy is one of the most established and oldest diagnostic tools in astrophysics and plasma physics (1). Radiating atoms, molecules and their ions provide an insight into plasma processes and plasma parameters and offer the possibility of real-time observation. Emission spectra in the visible spectral range are easy to obtain with a quite simple and robust experimental set-up (2). The method itself is non-invasive, which means that the plasma is not affected. Also the set-up is very simple with a line-of-sight through the plasma. Thus plasma spectroscopy is an indispensable diagnostic technique in plasma processing and technology as well as in fundamental research (2). Although spectra are easily obtained, interpretation can be fairly complex. Principles and fundamental techniques of plasma spectroscopy are very well described in literature (3, 4). Elementary processes that determine the radiation of atoms and molecules in plasmas are discussed in detail in (5). An overview of plasma diagnostic methods for various applications can be found in (6, 7). Applications of plasma spectroscopy for different purposes are described in literature (8-12).

2.2. BASIC THEORY OF_ATOMIC SPECTRA

Atomic spectroscopy can be used for qualitative and quantitative determination of elements (13-17). Sensitivities of atomic methods lie typically in the parts per million to parts per-billion range. Additional advantages of these methods are speed, convenience, unusually high selectivity and moderate instrument costs. Spectroscopic determination of atomic species can conveniently be performed in a gaseous medium in which the individual atoms (or ions, such as Fe\(^+\), Mg\(^+\) or Al\(^+\)) are in the free state as single entities. Consequently the first step in all atomic spectroscopic procedures is atomization, a process in which the sample is volatized and dissociated in such a way as to produce individual atoms. The efficiency and reproducibility of atomization step in large measure determine the method’s sensitivity, precision and accuracy. There are several methods that are used to atomize the sample for atomic spectroscopic studies, like flame atomization and direct plasma atomization in DC/AC arcs, spark discharges, or electrical discharges.
Each element has a characteristic structure with a positively charged nucleus surrounded by electrons in orbital shells to provide neutrality. These electrons occupy discrete energy levels, but it is possible for an electron to be moved from one level to another within the atom by gain or loss energy. This energy may be supplied by collisions with other atoms/electrons with high energies i.e. heating (AES - Atomic Emission Spectroscopy); as photons of light (AAS - Atomic Absorption Spectroscopy and AFS - Atomic Fluorescence Spectroscopy); or by X-rays (XRF – X-ray Fluorescence). Transitions between energy levels occur when the amount of energy transferred is equal to the difference between the two levels involved ($\Delta E$). Uncharged atoms may exist in the lowest energy level or ground state, or at any one of the series of excited states depending on how certain electrons have been moved to higher energy levels. Energy levels and $\Delta E$ associated with electron transitions are unique for each element.

The $\Delta E$ for transitions of outer shell electrons in most elements correspond to the energy equivalent to UV-radiation and these transitions are used for AES, AAS and AFS. The energy of the photon is characterized by $E = h\nu$, where $h$ is the Planck’s constant and $\nu$ is the frequency of radiation corresponding to that photon. Furthermore frequency and wavelength are related as $\nu = \frac{c}{\lambda}$, where $c$ is the velocity of light and $\lambda$ is the wavelength. Therefore, $E = \frac{hc}{\lambda}$

It follows that a specific transition $\Delta E$ is associated with a unique wavelength. Under appropriate conditions, outer shell electrons of vaporized atoms may be excited by thermal energy i.e. collisions with other atoms/electrons. As these electrons return to the more stable ground state or any lower state, the excess energy will be emitted in the form of light, which can be measured with a detector that is AES. When light (radiant energy) of characteristic wavelength enters an analytical system, outer shell electrons of the corresponding atoms will be excited as energy is absorbed. Consequently the amount of light transmitted from the system to the detector will be attenuated; this is AAS. Finally, when radiant energy is absorbed by ground state atoms and they go to excited states, they may return to the ground/lower state,
emitting the excess energy as radiation, termed fluorescence, leading to Atomic Fluorescence Spectroscopy, AFS.

When high energy photons, electrons, or particles strike a solid sample, an electron from the inner shells (K, L or M) of the constituent atoms may be displaced. The resulting orbital vacancy is filled by an outer shell electron, with an accompanying emission of an X-ray photon; its energy is equal to the difference of the energy levels involved. This emission is known as X-ray fluorescence. The energy of emission i.e. the wavelength is characteristic of an atom (element) from which it originated, while the intensity of emission is related to the concentration (number) of the atom in the sample and the wavelengths of the absorbed/emitted energies are unique for a given element. It is this that makes atomic spectroscopic techniques specific, so that one element can be detected even in the presence of an enormous excess of other chemically similar elements.

2.2.1 Quantum numbers of the electrons in an atom

A single electron moving in a spherically symmetrical but non- Coulomb field of force (for example, the emission electron of an alkali) can always be characterized by two quantum numbers, the principal quantum number \( n \) and the azimuthal quantum number \( l \). According to quantum mechanics, \( n \) can be considered as an approximate measure of the extent of the region in which the electron preferably remains.

Different values of \( n \) (1, 2, 3 …) correspond to widely different energy values. \( l \) gives the angular momentum of the electron in its orbit and, for a given value of \( n \), can take all integral values from 0 to \( n-1 \). The energy difference between states with different \( l \) and equal \( n \) is, in general, not as great as that between states with different \( n \). The possible states of an electron can thus be divided into principal groups or levels which differ from one another in their \( n \) values, and into sub-groups or sub-levels which have a given \( n \) but different \( l \) values. Even for given \( n \) and \( l \) values, several different states of an electron are possible: first, due to the various possible
orientations of the vector \( l \) (for example, in a magnetic field), and, second, due to the electron spin \( s = \frac{1}{2} \) which can set parallel or antiparallel to a magnetic field (18).

In an atom with several electrons, the motion of each individual electron can also be regarded, to a first approximation, as a motion in a centrally symmetric but non-Coulomb field of force. This field results from the overlapping of the Coulomb field of the nucleus and the mean field of the other electrons. Therefore, to this approximation a definite value of \( n \) and \( l \) can also be ascribed to each electron in a complicated atom. The approximation will be particularly good when we are considering a single electron with large \( n \), as is usually the case for most of the higher terms of an atom (terms of an emission electron). Then the action of the remaining electrons may really be described, to a close approximation, as due to their mean field. In contrast to this, if we are dealing with a number of electrons which have equal \( n \) and are thus approximately equidistant from the nucleus, taking a mean field give a relatively poor approximation, since the action of the other electrons on a given electron is strongly dependent on their momentary positions. In this case, the field in which the given electron moves can, in general, no longer be considered (even approximately) to be centrally symmetric and the quantum numbers \( n \) and \( l \) have no longer any exactly definable meaning (18).

The normal state of an atom is that state in which all the electrons are in the lowest possible orbits. The lowest possible orbit of a single electron in a centrally symmetric field is the 1s orbit (\( n = 1, \ l = 0 \)), which is also called the K shell. Accordingly, one might perhaps think that, for the normal state of Uranium, all the 92 electrons are in this K shell, and analogously for all other atoms. However, such a conclusion can easily be shown to be incorrect; for, if the electron configuration of the ground state of an atom altered regularly with the atomic number, it would obviously be quite impossible to explain the observed periodicity of the chemical and spectroscopic properties of the elements. Furthermore, according to this assumption, the ground state of any atom would have to be an S state, which is not the case according to the analysis of the different spectra. For example, B and Al have a \( ^2 \)P state for the ground state. We know that, in the case of Li, all three electrons are not in
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the K shell; one (the emission electron) is in a 2s orbit (Li shell, \( n = 2, l = 0 \)), as can be concluded from a comparison of the Li spectrum with those of Li-like ions (18).

The state of each electron in an atom is defined by its orbital quantum number \( (n = 0, 1, 2 \text{ etc}) \), orbital angular momentum value \( (l = 0, 1, 2 \text{ … respectively designated as } s, p, d, \text{ etc}) \), the spin \( s = \pm \frac{1}{2} \), and the total angular momentum, \( j = l \pm s \). The final state of the atom with many electrons is defined by these parameters, vectorially added over all electrons, giving us the corresponding quantities for the whole atom, values \( L, S, \) and \( J \); for example, like \( ^2P_{3/2} \), the superscript indicating the multiplicity \( (2 S+1) \), where \( S = \frac{1}{2} \) is the total spin quantum number here, the symbol \( P \) indicating the total orbital angular momentum quantum number \( L \) (1 in this case), and the subscript indicating the total angular momentum \( J (= L + S, \text{ here}) \). Though, as stated above, the electrons in the higher energy levels return to lower levels with emission of radiation, these transitions cannot take place from any level to any other level. They are governed by what are known as selection rules. Transitions between energy levels are allowed only for \( \Delta S = 0; \Delta L = \pm 1; \) and \( \Delta J = 0, \pm 1 \) (19, 20).

2.3 SOURCES OF ATOMIC SPECTRA

2.3.1 Absorption Spectra

The above concepts can be illustrated with Sodium atom as an example. Sodium (Atomic Number 11) has the electronic configuration 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^1\), giving a ground state \(^2S_{1/2}\). The absorption of radiation of 285, 330 and 590nm excites the single 3s\(^1\) outer electron to 3p, 4p, 5p orbitals, respectively (Figure 2.1). These excited states are designated by their quantum numbers; \( S = \frac{1}{2}, 2S+1=2 \) giving doublets; \( L = 1, \) namely \( P \); and \( J= L \pm S = 3/2 \) and 1/2. The excited states are thus \(^2P_{3/2}\) and \(^2P_{1/2}\). After a few nanoseconds, the excited atoms relax to their ground state by transferring their excess energy to other atoms or molecules in the medium.

The absorption and emission spectra for sodium are relatively simple. For elements that have several outer electrons that can be excited, the spectra might be much more complex and may consist of hundreds of lines.
2.3.2 Emission Spectra

Figure 2.2 shows the transitions associated with three of the most prominent emission lines in Sodium. These lines can be observed by heating gaseous sodium to 2000°C to 3000°C in a flame, or exciting some compound of Sodium like NaCl, in an electrical discharge. The heat promotes the single outer electron of the atoms from their ground state 3s to 3p, 4p, or 5p excited state orbitals. After a very short time (nanoseconds) the excited atoms relax to the ground state, giving up their energy as photons of visible or ultraviolet radiation. As shown in the figure the wavelengths of the emitted radiations for sodium are 590, 330, and 285nm for these three transitions, each of which gives a doublet.

Each of the excited level is a doublet, arising from $L+S = 3/2$ and $L - S = 1/2$, Sodium gives doublets, eg. from 3p- D2 589.0 and D1 589.6nm. For both $\Delta S = 0$; $\Delta L = -1$; for D1 $\Delta J=0$, and for D2 $\Delta J = \pm1$.

2.4 MOLECULAR EMISSION SPECTRA IN LASER INDUCED PLASMA

At the very high temperatures of the laser-produced plasma, it may be thought that there may not be any molecular species present in the plasma, this is not so.
Emission spectra of diatomic molecules are observed in the early stages of the plasma. Since such spectra can give important information, this is briefly discussed here.

![Energy level diagram for emission](image)

**Fig 2.2** Energy level diagram for emission

When two atoms are brought close to each other, for example, through a collision, there will be a mutual attraction due to the interaction of the nuclei and electrons, and also a mutual repulsion between the two positively charged nuclei. The net result is often, under appropriate conditions, a chemical bonding leading to molecule formation, its energy determined by the electron configuration, masses and attractive forces of the constituent atoms, and other possible nuclear motions. Because of the combination of repulsive and attractive forces, the molecule will not be rigid, but will vibrate about its equilibrium state, with certain energies. These vibrational energies are quantized, and the vibrational states are defined by the vibrational quantum numbers $v = 0, 1, 2 \ldots$ with corresponding energies $(v + \frac{1}{2}) \nu$, where $\nu$ can be regarded, to a very good approximation, as the frequency of a harmonic oscillator,

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}},$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass of the system, and $k$ a constant for a given bond, called the force constant. The diatomic molecule can also rotate about the two axes perpendicular to the inter-nuclear axis with certain energy. The rotational energies are, again, quantized, and are given (in cm$^{-1}$) by $BJ(J+1)$. The
rotational quantum numbers can take values $J = 0, 1, 2 \ldots B$, the rotational constant, is related to the moment of inertia $I$ by the equation, 

$$B = \frac{\hbar}{8\pi^2 cl}$$

The total energy of a molecule is thus the sum of the rotational, vibrational, and electronic energies. Just as in the case of atoms, the electronic energies are determined by their quantum states, defined by the total spin quantum number $S$ giving an electronic state with multiplicity of $(2S+1)$ given by ($\Sigma = S, S-1, S-2 \ldots$ -$S$), the angular momentum quantum number (representing the component of the electronic orbital angular momentum along the inter nuclear axis, $\Delta = 0, 1, 2 \ldots$, designated as $\Sigma, \Pi, \Delta \ldots$ states), and the total angular momentum $\Omega = | \Sigma \pm \Delta \ldots |$. Thus, a $^3 \Delta$ state, ($\Delta = 2, S=1$), will have 3 component levels $^3 \Delta_3, ^3 \Delta_2, \text{and } ^3 \Delta_1$. In addition to these, for homonuclear diatomic molecules the levels are also labeled according to their symmetry for inversion at the center, as $g$ or $u$ i.e. $g$ symmetric, and $u$ anti-symmetric. Again, as in the atomic transitions, there are selection rules governing the transitions between the molecular energy levels. These are slightly more complex than the atomic case. For example, under certain conditions we have:

$\Delta J = 0, \pm 1$ - Rotational;

$\Delta V = 0, \pm 1$ - Vibrational;

$\Delta = 0, \pm 1$ - Orbital angular momentum;

$\Delta S = 0$ - Spin;

$\Delta \Sigma = 0$, Total angular momentum; however, these rules have to be modified further, depending on the electronic states (20).

In general thus, the total energy of the molecule is the sum of the potential and kinetic energies of the electrons, and the potential and kinetic energies of the nuclei (vibration and rotation). If, at any time, we regard the nuclei as fixed in space, then the electronic energy will depend on the inter-nuclear distance. During the nuclear vibration, the electrons, because of their very low mass, will instantaneously move, changing their energy as per the new inter-nuclear distance. That is to say that, the
electronic energy and coulomb potential of the nuclei acts as a potential energy under which the vibrational motions occur. In other words, we have a Potential Energy (PE) curve for a given electronic state, which is a plot of the energy of the electronic state as a function of inter-nuclear distance (vibrational energy).

An understanding of the process of formation of molecules in the plasma can be obtained from their potential energy curves. Figure 2.3 shows the potential energy curves for a simple molecule which is often observed in flames, namely, C₂ (20).

![Potential Energy Curves](image)

**Fig 2.3** The potential energy curves for a simple molecule

The short lines in each curve correspond to the vibrational levels in that state. Each vibrational level has several closely spaced rotational levels (not shown). The ground electronic state is a $^3\Pi_u$ state, (formed from two ground state $^3\text{P}$ carbon atoms) and some of the higher electronic states correspond to $^1\Sigma_g$, $^1\Pi_u$, $^3\Pi_g$ and so on (for example, one ground state $^3\text{P}$ and one excited state $^1\text{D}$ carbon atoms give the $^3\Pi_g$ excited state). As the vibrational energy in any of these levels is increased, the molecule is excited to higher and higher vibrational levels, with corresponding
increase in the average inter-nuclear distance. Eventually, with sufficient energy, the molecule dissociates into the ground or excited atomic states, as shown to the right of the figure.

The Carbon atom with an electron configuration \(1s^2\ 2s^2\ 2p^2\) has two outermost equivalent p electrons, which give rise to the states \(^3P\), \(^1D\), and \(^1S\). The ground state is \(^3P_0\). Excitation of the \(2s/2p\) electrons of carbon atom to higher states gives higher energy levels of the atom, as shown below. These are also produced on dissociation of the higher molecular electronic levels as shown in the potential energy curves.

Just as the molecule, when given sufficient energy, dissociates into the atoms in appropriate electronic levels, the reverse can also happen under suitable conditions. When atoms in various states approach each other, with sufficiently high kinetic energy which will enable them to overcome the repulsive forces, resulting in a direct interaction. As the distances reduce to those corresponding to the dissociation limits (~2-3 Å), they follow through into the potential energy valley, ending up in the various vibrational levels of the particular electronic state of the molecule. In the case of the \(C_2\) molecule, for example, atoms in the \(^3P\) ground state will lead to the \(^3\Pi_u\) state of the molecule, atoms in the excited states like \(^1D\), \(^1S\), and \(^3P\) (see Table 2), will give rise to formation of the molecule in the excited electronic states. These excited molecules relax to the lower states giving rise to the molecular emission spectra.

The laser plasma, immediately after formation, has the elements in highly excited atomic/ionic states. In the initial hundred nano-seconds or so, before the plasma expands, the number densities (number/unit volume) of these particles are very high (for example, since the plasma as a whole is neutral, the number of ions is equal to the electron number, which can be easily measured -Chapter V- which is very high). With their high energy, they undergo collisions with each other and finally end up in appropriate excited electronic levels of the molecule. The relaxation of these into lower levels gives rise to the molecular spectra. At the resolutions normally employed for quantitative elemental analysis, the rotational structure is not resolved and we get a spectrum with appearance of bands, which can be easily recognized.
Figure 2.4 shows typical spectra of Copper plasma as function of delay from laser pulse. The molecular bands are clearly seen in the beginning, and they disappear leaving the atomic lines, at later times.

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**Fig 2.4 Temporal evolution of copper plasma**

Molecular emission from laser plasma is of great importance for several reasons. As discussed above, the analysis of these spectra give detailed information on the dynamics of the plasma. These include information on the states of atoms and ions produced initially, their collisional interactions, formation of selected states of excited atoms through the dissociation of the excited molecular species etc.

LIBS is now being well recognized as a suitable technique for remote planetary surface exploration. ("Curiosity", the current Mars Rover, is carrying an LIBS system). The surface soil in these planetary surfaces contain mainly silicates, but other species like carbonates, sulphates, nitrates etc are also likely to be present. While the analysis of metallic elements like alkali and alkaline earth elements and transition metals are easily analyzed by LIBS atomic emission, analyses of carbon, sulfur, nitrogen etc are difficult since their strong lines are seen in the vacuum UV (The allowed transitions, 1P to 1S or 1D, for the C atom are below 200nm; see
energy levels). But these elements easily form molecular species like CO, NO, SO, etc, whose extensive electronic spectra fall into the UV region and are thus easily identified.

**Table 2** National Institute of Standards and Technology (NIST) atomic spectra database levels data for carbon atom (21)

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Term</th>
<th>J</th>
<th>Level (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s²2p²</td>
<td>⁴P</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>16.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>43.40</td>
</tr>
<tr>
<td>2s²2p²</td>
<td>⁴D</td>
<td>2</td>
<td>10 192.63</td>
</tr>
<tr>
<td>2s²2p²</td>
<td>⁴S</td>
<td>0</td>
<td>21 648.01</td>
</tr>
<tr>
<td>2s²p³</td>
<td>⁵S₀</td>
<td>2</td>
<td>33 735.20</td>
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<td>2s²p³</td>
<td>⁴P₀</td>
<td>0</td>
<td>60 333.43</td>
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<tr>
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<td></td>
<td>1</td>
<td>60 352.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>60 393.14</td>
</tr>
<tr>
<td>2s²p³</td>
<td>⁴P₀</td>
<td>1</td>
<td>61 981.82</td>
</tr>
</tbody>
</table>

Isotopic composition is of great importance in planetary sample analysis, because it can give information on the origin and history of these samples. They thus provide important details about planetary samples. While isotopic composition can also be obtained from atomic spectra, atomic isotope shifts are extremely small (fraction of a cm⁻¹), and require high resolution, necessitating use of bulky spectrographs for separation of isotopic lines. Vibrational isotope shifts of diatomic molecules are fairly high, (several tens of cm⁻¹), and can be easily observed with normal spectrographs. In the present work we have attempted to investigate some of the molecular emission bands and the results are presented in later chapters.

**2.5 LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)**

The AAS method discussed above requires the sample to be in solution so that it can be aspirated into the flame. For samples in the solid or powder form, we can use
instead of the electrical discharge (D.C. Arc), the technique based on laser ablation of the sample, known as Laser Induced breakdown Spectroscopy.

LIBS technique is based on the analysis of atomic lines generated close to the surface of the sample by generating plasma. The atomic lines are generated by focusing on the surface an intense laser beam. When the beam is focused on the sample it initiates an ablation/evaporation process and an avalanche ionization of the sample elements giving rise to the breakdown effect leading to plasma formation. The spectral and time resolved analysis of this emission is suitable to identify the atomic species originally present in the sample surface. Initially, in the first few hundred nanoseconds or even longer, the plasma gives rise to continuum emission, due to deceleration of the charged particles, ion-electron recombination etc. LIBS atomic spectra can be detected once the plasma continuum emission is reduced. Time resolved capability is thus necessary to discriminate the late atomic lines from the early plasma continuum. High resolution spectral analysis also is required to isolate single emission lines that are the spectral signatures of each element, from the dense atomic line emissions from several higher populated levels. The atomic lines and in some cases ionic lines once assigned to specific transitions allow for qualitative identification of the species present in the plasma. Their relative intensities can be used for the quantitative determination of the corresponding elements.

The LIBS analysis system comprises typically of three major component units namely,

i. Laser Source

ii. Sample holder

iii. The system for spectral analysis

The lasers used for plasma generation are usually the pulsed type. Pulsed laser systems are preferred over continuous wave lasers because of their grater peak power. Because of the high power available, Nd-YAG lasers are mostly preferred for Laser Induced Breakdown Spectroscopy.
2.6 LIBS PLASMA

A local assembly of atoms, ions and free electrons, overall electrically neutral, in which the charged species often act collectively, is called plasma. It is characterized by a variety of parameters, like plasma temperature, electron density and the degree of ionization. A weakly ionized plasma is one in which the ratio of electrons to other species is less than 10% whereas, highly ionized plasmas may have atoms stripped of many of their electrons, resulting in very high electron to atom/ion ratios. LIBS plasmas are generally considered as weakly ionized plasmas. A schematic overview of the temporal history of LIBS plasma initiated by a single laser pulse is shown in Figure 2.5. At early times, ionization is very high. As electron-ion recombination proceeds, neutral atoms, and then molecules form. Throughout there is a background continuum that decays with time more rapidly than the spectral lines. The continuum is mainly due to bremsstrahlung (free–free) and recombination (free–bound) events. In the bremsstrahlung process photons are emitted by electrons accelerated or decelerated in collisions. A recombination occurs when a free electron is captured into an ionic or atomic energy level and gives up its excess kinetic energy in the form of a photon. Time resolution of the plasma light in LIBS allows for discrimination in favor of the region where the signals of interest predominate (22).

The characterization of laser-induced plasmas (LIPs) through the determination of their temperature and electron density is essential and has gained considerable interest in recent years for the understanding and use of these complex and versatile spectroscopic sources. The plasma characteristics are dependent on laser irradiance, wavelength, pulse duration, target material, atmospheric conditions, space and time. The characterization of LIP is of importance as it is required to be optically thin as well as in local thermodynamic equilibrium (LTE) for the applicability of optical emissions to the elemental analysis using LIBS (22).
Under the conditions of LTE in the plasma, the excitation temperature governing the distribution of energy level excitation through the Boltzmann equation and the ionization temperature governing the ionization equilibrium through the Saha equation are equal to the electronic temperature describing the Maxwell distribution of electron velocities (3). Thus, one describes the plasma in LTE by a common temperature $T$, called the plasma temperature. Optical emission spectroscopy has recently attracted a lot of attention for characterizing a LIP. The most widely used spectroscopic method for the determination of $T$ is the Boltzmann plot method (3) which employs the ratio of integrated line intensities for two or more atomic lines. Among several diagnostic methods for measuring the plasma electron density $n_e$, plasma spectroscopy based on either Stark broadening of spectral lines or the Saha-Boltzmann equation is considered as the simplest method (3).

2.7 THEORETICAL DESCRIPTION

For the interpretation of spectroscopic data, one requires a plasma ionization model to describe the ionization state and atom/ion energy level populations in terms
of plasma temperature $T$ and electron density $n_e$. We present below the methods for determining these LIP parameters for optically thin plasmas under LTE condition.

### 2.7.1. Boltzmann plot method for $T$

For plasma in LTE, the populations of the various energy levels of a given species are given by the Boltzmann distribution law (3),

$$
\frac{n_{k,Z}}{n_Z} = \frac{g_{k,Z}}{P_Z} \exp\left(-\frac{E_{k,Z}}{k_BT}\right)
$$

(1)

Here, the index $Z$ refers to the ionization stage of the species ($Z=0$ and $Z=1$ corresponding to the neutral and singly ionized atoms respectively), $k_B$ is the Boltzmann constant, $T$ is the plasma temperature, $n_{k,Z}$, $E_{k,Z}$ and $g_{k,Z}$ are the population, energy and degeneracy of the upper energy level $k$ respectively, $n_Z$ is the number density and $P_Z$ is the partition function of the species in ionization stage $Z$.

The integrated intensity $I_Z$ of a spectral line occurring between the upper energy level $k$ and the lower energy level $i$ of the species in ionization stage $Z$ in optically thin plasma, i.e. plasma in which only very little radiation is absorbed, is given as

$$
I_Z = \frac{hc}{4\pi\lambda_{ki,Z}} A_{ki,Z} n_{k,Z} L
$$

(2)

where $h$ is the Planck constant, $c$ is the speed of light, $L$ is the characteristic length of the plasma, $A_{ki,Z}$ is the transition probability and $\lambda_{ki,Z}$ is the transition line wavelength. Using Eq. (1), Eq. (2) can be rewritten as

$$
I_Z = \frac{hc}{4\pi\lambda_{ki,Z}} A_{ki,Z} L \frac{n_Z}{P_Z} g_{k,Z} \exp\left(-\frac{E_{k,Z}}{k_BT}\right)
$$

(3)

By taking the natural logarithm, Eq. (3) can be rewritten as
\[ \ln \left( \frac{I^*_Z \lambda_{ki,Z}}{g_{ki,Z} A_{ki,Z}} \right) = -\frac{1}{k_B T} E_{k,Z} + \ln \left( \frac{hcL_n Z}{4\pi P_z} \right), \]  
\tag{4} 

This yields a linear plot (the so-called Boltzmann plot) if one represents the magnitude on the left-hand side for several transitions against the energy of the upper level of the species in ionization stage \( Z \). The value of \( T \) is deduced from the slope of the Boltzmann plot. As Eq. (4) is obtained under the assumption of plasma being optically thin as well as in LTE, the applicability of this equation is limited to LTE and optically thin plasmas.

### 2.7.2 Saha-Boltzmann equation method for \( n_e \)

The electron density using atom and ion spectral lines emitted from the plasma is determined from the Saha-Boltzmann equation as \( (3, 23) \)

\[ n_e = \frac{I^*_Z}{I_{Z+1}} \times 6.04 \times 10^{21} (T)^{3/2} \times \exp(\frac{(-E_{k,Z+1} + E_{k,Z} - \chi_Z)}{k_B T}) \text{ cm}^{-3}, \]  
\tag{5} 

where \( I^*_Z = \frac{I_Z \lambda_{ki,Z}}{g_{ki,Z} A_{ki,Z}} \) and \( \chi_Z \) is the ionization energy of the species in the ionization stage \( Z \). The lowering of the ionization energy due to interactions in the plasma is negligibly small which has been omitted in Eq. (5).

### 2.7.3 Optically thin plasma

The elemental composition analysis from the line intensities in a LIBS experiment becomes simple if the plasma is optically thin and is in LTE. It is thus necessary to know the time window for time-evolving plasma like LIPS where the plasma is optically thin as well as in LTE. Using Eq. (3), the intensity ratio of two lines of the same species of ionization stage \( Z \) is expressed as

\[ \frac{I_1}{I_2} = \frac{\lambda_{nm,Z}}{\lambda_{ki,Z}} \left( \frac{A_{nm,Z}}{A_{ki,Z}} \right) \left( \frac{g_{nm,Z}}{g_{ki,Z}} \right) \exp\left( -\frac{E_{k,Z} - E_{n,Z}}{k_B T} \right) \]  
\tag{6} 

where \( I_1 \) is the line intensity from the \( k-i \) transition and \( I_2 \) is that from the \( n-m \) transition. If we consider two emission lines having the same upper level or as close as possible, the temperature effect of the Boltzmann factor on the reproducibility of the line intensity ratio is minimized and at the same time the consideration of the efficiency factor of the collecting system is avoided. Neglecting the exponential factor in that condition, one can find out the theoretical value of the intensity ratio of the two lines by using the atomic parameters of the transitions. By matching this ratio with the measured values at different delay times, one finds out the time window where the plasma is optically thin.

The results of applying the above theoretical considerations to the LIBS plasmas in our work are discussed in detail in the respective chapters.

2.8 REFERENCES