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Review

Spectroscopic diagnostics of laser-induced plasmas ☆

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ABSTRACT

An overview of spectroscopic diagnostics techniques for low temperature plasmas is presented with an emphasis to electron number density — N_e measurement. Stark broadening of non-hydrogenic atom and positive ion spectral lines is given. The attention is drawn to experimental techniques used for line intensity and line profile measurement. Self-absorption test, importance of Abel inversion, deconvolution of experimental line profiles and measurement of line asymmetry are treated in some detail in order to improve N_e measurements. Finally the sources of theoretical and experimental Stark broadening data are reviewed and some details discussed.

Contents

1. Introduction

The understanding of physical processes and their interrelation in the laser-induced plasma referred in literature as Laser Induced Breakdown Spectroscopy (LIBS) is of basic importance for its analytical application. Most information from the LIBS comes through the measurement of atomic line radiation, which can be analyzed and used for plasma diagnostic purposes. This is made possible only through knowledge of the principles of plasma spectroscopy, whose origin can be traced back to astrophysics. In the past fifty years the applications of plasma spectroscopy for

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diagnostics were widespread from micro-discharges to fusion plasmas. The principles of plasma spectroscopy are well established and only the question of which physical processes are predominant distinguishes the diagnostics of one plasma source from another. Although examples are presented to illustrate diagnostic techniques and difficulties related to LIBS and its analytical applications the conclusions and suggestions are of general importance and may be applied to other plasma sources as well.

The difficulty in application and spectroscopic diagnostics of LIBS comes from plasma spatial inhomogeneity, time variation of plasma shape, which is simultaneously followed by the change of plasma parameters and emission of ablated material in plasma plume. Here, one can include the influence of matrix effect to plasma radiation and radiative transfer, which may cause variable line self-absorption during plasma evolution and decay. All these processes influence spectral line intensity, which is basis for both, analytical application and plasma diagnostics. Thus, one can conclude that LIBS is a very complex system, which requires knowledge of several plasma parameters simultaneously for reliable analytical application.

A typical analytical LIBS has a relatively short lifetime of several microseconds, and, over the times of interest, a plasma electron number density, N_e, in the range of $10^{16}<N_e<10^{17}\ \mathrm{cm}^{-3}$, together with an excitation electron temperature, $kT_e \approx 1$ eV. Here, the emphases will be on monitoring, measurement and correction of spectral line emission intensities for self-absorption. This is essential for both analytical applications and diagnostic purposes. Pressure line broadening of spectral lines and, in particular, Stark broadening of non-hydrogenic atom and singly charged positive ion lines, will be discussed in some detail. The deconvolution of symmetric and asymmetric line profiles will be considered. Sources of theoretical and experimental data required for these diagnostics will be discussed, together with their typical uncertainties. Future needs for atomic spectroscopic data will also be considered.

2. Broadening and shifting of spectral lines

The theory of line broadening is described in a number of textbooks, monographs and articles, see e.g. Ref. [1] and references therein. Recently simple approximate formulae for all types of pressure broadening (resonance, Van der Waals and Stark) and Doppler broadening were given and their application discussed [2]. This is followed with relevant literature. Thus, only minimum details about Stark broadening required for explanation of atomic line asymmetry, experimental profile deconvolution and data requirements will be given here. The details about measurements of line shapes and shifts are described elsewhere, see e.g. [3], and therefore, only details not described in full length elsewhere are given here. Further, it is important to note that all theoretical profiles and their parameters described under pressure broadening [2,3] below are related to spectral line shapes observed under optically thin conditions. This is also valid when discussing Doppler and instrumental broadening. The convolution and deconvolution of line profiles is also dealing with optically thin profiles. Thus the experimental profile has to be corrected first to the optically thin case. The correction for self-absorption is possible if absorption is not too large, see below, and then the line shape is analyzed and results used for plasma diagnostic purposes.

2.1. Stark broadening

2.1.1. Stark broadening of neutral atom lines

According to Stark broadening theory [1] the shape and shift of plasma-broadened isolated non-hydrogenic lines are mainly determined by electron impacts with the radiating atom and a smaller contribution from the electric microfields generated by essentially static plasma ions. The quadratic Stark effect due to the quasistatic field of ions shifts the energy of the upper and lower level by an amount which depends on the instantaneous local field strength. The distribution of fields in the plasma smears out these shifts and the neutral atom line is asymmetrically broadened. The parameter A (in earlier literature designated as α), tabulated by Griem [1] is a measure of the effect of ion broadening on the line width in comparison to the electron impact width. Extensive numerical calculations by Griem et al. [1] show quantitatively that electron impact broadening is the dominant contribution to the broadening for neutral atoms while ion broadening contributes typically about 10 percent of the total line width.

The shape of the neutral atom line in quasistatic approximation for ions is described by the following expression [4]:

$$j_{A,R}(x) = \frac{1}{\pi} \cdot \int_0^\infty \frac{H(\beta) d\beta}{1 + \left(x - A^{4/3} \cdot \beta^2\right)^2} \tag{1}$$

where $H(\beta)$ is ion microfield distribution [5,6], and x is described by $x = (\lambda - \lambda_0 - d_e)/w_e$, where λ_0 is the wavelength of the center of the unperturbed line, d_e is the electron shift, d_t is the total shift and w_e is the electron impact half–halfwidth.

From a large number of generated profiles Griem [7] found that total Stark (full widths at half maximum FWHM) — w_t of line profiles can be expressed within the quasistatic ion approximation as a function of w_e, A and R. Thus

$$w_t(N_e, T_e) \cong 2 w_e(T_e)[1 + gDA_N(T_e)] N_e \left[\mathrm{cm}^{-3}\right] 10^{-16} \tag{2}$$

$$d_t(N_e, T_e) \cong [d_e(T_e) \pm 2.0\ g_1 A_N(T_e) w_e(T_e)] N_e 10^{-16} \tag{3}$$

where $g = 1.75(1 - 0.75R)$, $g_1 = g/1.75$, $A_N(T_e) = A(T_e) N_e^{1/4} 10^{-4}$ and

$$R = 8.99 \times 10^{-2} N_e \left[\mathrm{cm}^{-3}\right]^{1/6} T_e[\mathrm{K}]^{-1/2} \leq 0.8 \tag{4}$$

$$0.05 \leq A(T_e)\ N_e \left[\mathrm{cm}^{-3}\right]^{1/4} 10^{-4} \leq 0.5 \tag{5}$$

where $w_e(T_e)$, $d_e(T_e)$ and $A(T_e)$ are values of electron impact half–half width, electron shift and ion broadening parameter at electron density $10^{16}\ \mathrm{cm}^{-3}$ tabulated in [1] and D — ion dynamic parameter ($D \approx 1$) in case of heavy elements. For more details about simultaneous determination of $w_e(T_e)$, $d_e(T_e)$, $A(T_e)$ and D see e.g. [8].

The Debye shielding parameter, R, is defined as a ratio of the mean inter-ion distance ρ_0 to the Debye radius ρ_D. For values of A larger than 0.5 the forbidden component begins to significantly overlap, and the linear Stark effect becomes important, while for $A<0.05$ quadrupole interaction must be taken into account. Other considerations, such as Debye shielding affecting line shapes, widths and shifts are covered in detail in [1].

Apart from extensive set of Stark broadening data for light elements He through Ca and Cs, see Appendix IV in [1] and some lines of other heavy elements Zn, Ge, Br, Rb, Cd, Sn, Pb and Hg [9] calculated using same semiclassical code [1], large number of theoretical results evaluated from another semiclassical approach [10] are also available. A more detailed list of these results can be found in [11,12] and references therein.

In the case when w_e, d_e and A data are not available simple formulas developed in [13,14] for their estimation may be used. Experimental determination of these parameters and testing of their values obtained by different theories or approximate formulas will be analyzed later on in Section 5.