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Estimation and control of self-absorption in laser induced breakdown spectroscopy. Application to Stark width measurements

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The curve-of-growth methodology is used to estimate self-absorption in laser induced breakdown spectroscopy experiments. Starting from three plasma parameters (N_e, T, $N'l$), the profiles distorted by self-absorption are calculated providing the area and width of the lines. The variation of the area and width with respect to the optically thin values is studied as a function of the optical depth. The method has been used to control self-absorption and estimate the resulting error in Stark width measurements.

Self-absorption is one of the main systematic errors in diagnostics of laser induced plasmas by emission spectroscopy. The distortion of the line profiles caused by self absorption leads to two effects: the decrease of the line intensity with respect to the optically thin value, which becomes apparent in the saturation of the intensity vs. optical depth curves [1], and the broadening of lines, which acquire an apparently large width [2]. In this work, we present a method useful to estimate these two effects of self-absorption in laser-induced breakdown spectroscopy experiments.

If we consider a simple model of a laser induced plasma in local thermodynamic equilibrium with homogeneous electron density, temperature, and atom and ion densities, the line intensity of a spectral line may be obtained from the integration of a distorted profile $P(\lambda)$ as follows

$$I = \beta L_P(\lambda_0) \int_0^\infty P(\lambda)\, d\lambda \qquad \text{(1a)}$$

$$P(\lambda) = 1 - e^{-k\prime(\lambda) l} \qquad \text{(1b)}$$

where λ_0 is the central wavelength of the emission line, $L_P(\lambda_0)$ is the Planck blackbody distribution, $k'(\lambda)$ is the effective absorption coefficient, l is the length of the plasma along the line-of-sight, and β is a factor including the perpendicular radiating area of the plasma and the system efficiency. If the line shape is described by a Voigt profile $V(\lambda)$, the optical depth may be written as

$$\tau(\lambda) = k'(\lambda) l = \tau_0 V(\lambda) \qquad \text{(2)}$$

where τ_0 may be separated into different factors as follows [3]

$$\tau_0 = 10^{-2} k_t N' l C \qquad \text{(3)}$$

In this equation, C is the concentration of the emitting element in the sample, N' is the the normalized number density, that is, the number density of the emitting species that would be obtained for the sample with 100% concentration. The factor k_t is the part of the optical depth that depends on the transition parameters and the plasma temperature, defined by

$$k_t = \frac{e^2 \lambda_0^2}{4\varepsilon_0 m c^2} f \frac{g_i e^{-\frac{E_i}{kT}}}{U(T)} \left(1 - e^{-\frac{E_j - E_i}{kT}}\right) \qquad \text{(4)}$$

The numerical integration of the profiles $P(\lambda)$ of (1b) provides the curves of growth (COG) – intensity vs. concentration– as described in [3]. The result depends on the Doppler width $\Delta\lambda_D$ and the damping constant $a = (\ln 2)^{1/2} \Delta\lambda_L / \Delta\lambda_D$, where $\Delta\lambda_L$ is the Lorentzian linewidth. If the electron density N_e and temperature T of the plasma are known, by fitting experimental COGs for lines with known oscillator strengths and Stark widths, the parameter $N'l$ may be obtained. The knowledge of $N'l$ completes the characterization of the plasma, allowing the calculation of the COGs of lines of interest to estimate their self-absorption. In Stark width determination, the concentration $C_{10\%}$ for 10 % self-absorption is deduced, and a sample with a similar concentration C is used to measure the line profiles [4,5]. Here, we report the estimation of the errors in the line widths due to self-absorption. Fig. 1 shows the relative variations of the area and the width as a function of the ratio $\tau_0/\Delta\lambda_D$for a range of optical depths τ_0 from 0.01 to 0.5, and different values of the damping constant a.

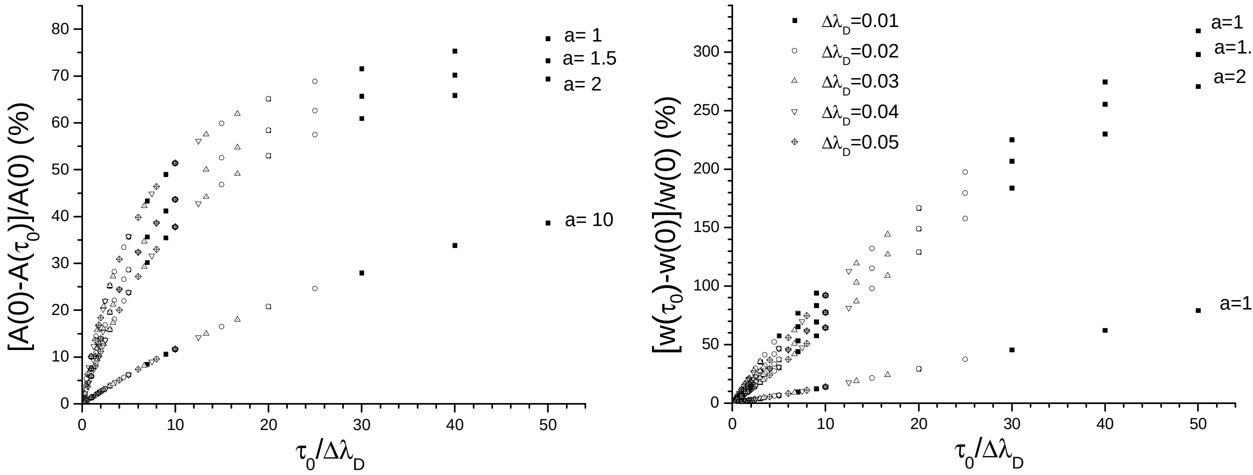
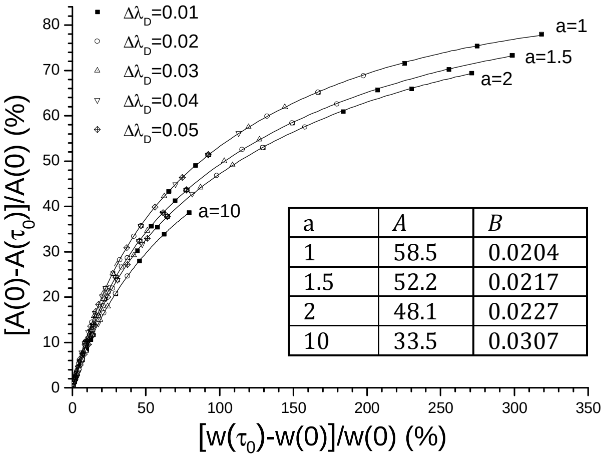


Fig. 1: Relative variations of the area and the width of the line due to self-absorption

In Fig. 2, the variation of the area is plotted against the variation of the width. For small optical depth, both variationa are similar, whereas at high τ_0, the variation of the area shows a significant saturation. The curves in Fig. 2 can been fitted for $\tau_0/\Delta\lambda_0<10$ to the function $y = A(1-\exp(-Bx))$; the fitting parameters A, B are indicated in the figure. These curves are useful to deduce the error in the line width due to self-absoption from the variation of the area, which can be estimated more easily.



a	A	B
1	58.5	0.0204
1.5	52.2	0.0217
2	48.1	0.0227
10	33.5	0.0307

As an example, the table shows the variation of the area and width due to self-absorption for two Fe II lines of different intensities in the conditions for Stark width measurements, reported in [4].

Line	k_t (14500 K) (10^{-30} m^3)	$C_{10\%}$ (%)	C (%)	τ_0	$\Delta A/A$ (%)	$\Delta w/w$ (%)
2743.20 Fe II	2.44	0.73	0.5	0.08	7.6	8.4
2739.55 Fe II	5.96	0.29	0.5	0.2	15	17

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