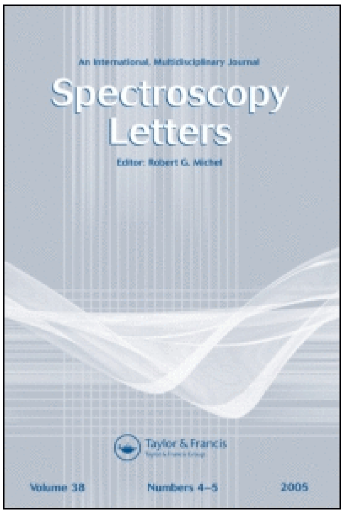

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Measurement of the Stark Broadening of Atomic Emission Lines in Non-Optically Thin Plasmas by Laser-Induced Breakdown Spectroscopy

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Measurement of the Stark Broadening of Atomic Emission Lines in Non–Optically Thin Plasmas by Laser-Induced Breakdown Spectroscopy

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Abstract: We propose a new method for determining the Stark broadening of atomic emission lines using laser-induced breakdown spectroscopy. The method allows the determination of the Stark broadening in non–optically thin plasmas, through the introduction of a correction for self-absorption. Couples of lines of the same species are considered. If one of the Stark broadenings is known, the determination of the other does not require the measurement of the electron density of the plasma. Examples are given for the application of the proposed method to the measurement

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of the Stark broadening of several aluminum emission lines (Al I at 308.2 nm, Al I at 394.4 nm, and Al I at 396.2 nm).

Keywords: Aluminum alloys, double pulse, LIBS, self-absorption, stark broadening

INTRODUCTION

The knowledge of the Stark broadening parameters of atomic emission lines is extremely important in a number of applications, ranging from astrophysics to analytical chemistry.[1–4] However, accurate measurement of Stark broadening poses serious experimental difficulties; a fact that explains why these parameters are available only for a limited subset of the emission lines usually visible in standard atomic spectroscopy experiments.[5–10] Among the most serious problems affecting the direct measurements of the Stark broadening from the emission of plasmas, plasma inhomogeneity and the occurrence of self-absorption effects are considered dominant. In a recent paper,[11] Bengoechea et al. proposed a method for measuring the Stark broadening from laser induced breakdown spectroscopy (LIBS) plasmas, demonstrating that an accuracy of the order 7% can be obtained on the determined Stark broadening; for achieving this level of accuracy, the authors had to make sure that self-absorption effects were indeed negligible in their experimental conditions.To that purpose, they made several measurements on different samples, in order to build curves-of-growth for the line on which the Stark broadening parameter was to be measured, and then they chose the sample for the actual measurement, while being sure that the concentration of the element is in the linear zone of the curve-of-growth, where the self-absorption effects are negligible. This procedure is in fact very effective, but it calls for several different measurements on samples of known concentration; moreover, for most of the lines of interest, the linear zone of the curve-of-growth is limited to concentrations of a few percent. The LIBS signal at such low concentrations may be too low for acquisition of reliable and reproducible information on the Stark broadening. Moreover, the effect of self-absorption depends strongly on the experimental conditions (laser energy, focusing on the surface) and on the physical properties of the reference samples used (surface reflectivity, heat conductivity, etc.), which should not vary during the construction of the curve-of-growth.

However, because values of the Stark broadenings are affected by uncertainty of the order 40–50%,[5–10] an alternative method may be useful for quickly obtaining an evaluation of the Stark broadenings. Such a method may be less accurate than the procedure proposed by Bengoechea et al., but would still guarantee an accuracy comparable with other results available in the literature, with the benefit of a much more direct procedure.

Therefore, the purpose of this paper is the definition of a procedure for a quick estimation of the Stark broadenings of atomic emission lines that could be effective even in the presence of self-absorption. In the following section, the basis of the method will be described within the framework of the general theory of self-absorption in laser-induced plasmas.

SELF-ABSORPTION IN LASER-INDUCED PLASMAS

The theoretical model used is similar to the one introduced by Amamou et al.[12] for the determination of the ratio of atomic transition probabilities from emission spectra in a plasma at local thermal equilibrium and in the presence of self-absorption.

It can be demonstrated[12] that the photons flux [i.e., the number of photons emitted per unit time, unit surface, and unit wavelength (s^{-1} cm^{-3})] emitted by a homogeneous plasma rod of length l is

$$n_p(\lambda, l) = \frac{\varepsilon(\lambda)}{\kappa(\lambda)}\left(1 - e^{-\kappa(\lambda)l}\right), \tag{1}$$

where

$$\varepsilon(\lambda) \equiv \frac{1}{4\pi} A_{ki} n_k L(\lambda) \tag{2}$$

and

$$\kappa(\lambda) = \frac{\lambda_0^4}{8\pi c} A_{ki} g_k \frac{n_i}{g_i}\left(1 - \frac{n_k g_i}{g_k n_i}\right) L(\lambda). \tag{3}$$

In the previous expressions, c is the speed of light (cm s^{-1}), λ_0 is the central wavelength of the transition (cm), A_{ki} represents the transition probability between the upper level k and the lower level i (s^{-1}), n_k is the population (cm^{-3}) of the upper level, g_k and g_i are the degeneracies of the upper and lower level (dimensionless), respectively, n_i is the population (cm^{-3}) of the lower level, and $L(\lambda)$ is the spectral emission profile (cm^{-1}).

Because the Stark broadening of the line is usually considered the dominant effect and the Gaussian Doppler broadening of the line is neglected, we assume that the emission lineshape $L(\lambda)$ has a pure Lorentzian shape, that is,

$$L(\lambda) = \frac{\Delta\lambda_0}{4(\lambda - \lambda_0)^2 + \Delta\lambda_0^2}, \tag{4}$$

where $\Delta\lambda_0$ represents the full width at half maximum (FWHM) of the line. The use of Lorentzian lineshape is appropriate when any asymmetry in the profile is not detectable (i.e., when the ion static contribution to the Stark broadening is negligible).[13] In this case, the linewidth $\Delta\lambda_0$ is approximately proportional to the plasma electron density n_e (cm^{-3}) through the temperature-dependent Stark broadening parameter w_s (cm^4).[14]

$$\Delta\lambda_0 \approx 2w_s(T)n_e \tag{5}$$

Other broadening effects might be present in the laser-plasma, such as resonance broadening and Van der Waals broadening. For a discussion of these effects, see for example Ref. 4.

In order to investigate the effect of self-absorption on the shape and intensity of a given emission line, in a previous paper[15] we introduced the self-absorption coefficient SA, defined as the ratio of the observed emission line intensity (in counts per seconds) at its maximum over the intensity calculated from the linear extrapolation of the low self-absorption part ($\kappa\ (\lambda_0)l \ll 1$) of the curve-of-growth of the line considered

$$\mathrm{SA} = \frac{n_p(\lambda_0)}{n_{p_0}(\lambda_0)} = \frac{(1 - e^{-\kappa(\lambda_0)l})}{\kappa(\lambda_0)l}. \tag{6}$$

It was demonstrated[15] that the ratio of the integral intensity of the self-absorbed emission line over the non–self-absorbed one scales as

$$\frac{N_p}{N_{p_0}} = \frac{\int n_p(\lambda)d\lambda}{\int n_{p_0}(\lambda)d\lambda} = (\mathrm{SA})^\beta, \tag{7}$$

with $\beta = 0.44$, while the FWHM of the measured emission lines becomes

$$\Delta\lambda = \Delta\lambda_0(\mathrm{SA})^\alpha, \tag{8}$$

with $\alpha = \beta - 1 = -0.56$.

EVALUATION OF THE STARK BROADENINGS OF SELF-ABSORBED LINES

In view of the above-presented results, we can outline the general procedure we propose for a quick evaluation of the Stark broadening of a given emission line by LIBS, even in the presence of self-absorption. The procedure is applicable whenever two emission lines of the same species are observed.

According to Eqs. (7) and (8), considering that

$$\frac{(N_{p_0})_2}{(N_{p_0})_1} = \frac{(g_k A_{ki} e^{-E_k/k_B T})_2}{(g_k A_{ki} e^{-E_k/k_B T})_1} \tag{9}$$

and taking into account the definition of SA coefficient (Eq. (6)), the ratio of the Lorentzian linewidths for the two lines considered can be written as:

$$\frac{(\Delta\lambda_0)_2}{(\Delta\lambda_0)_1} = \frac{(\Delta\lambda)_2}{(\Delta\lambda)_1}\left[\frac{(N_p)_2}{(N_p)_1}\right]^{-\alpha/\beta}\left[\frac{(g_k A_{ki} e^{-E_k/k_B T})_2}{(g_k A_{ki} e^{-E_k/k_B T})_1}\right]^{\alpha/\beta}, \tag{10}$$

where the subscripts refer to line 1 and 2, respectively.

All the ratios in the right term of Eq. (10) are either experimentally measured or known from the spectral databases.[16,17]

At this point, the simplest eventuality is that the Stark broadening of one of the lines is known. According to Eq. (5), the ratio of the Lorentzian widths of the two lines considered in Eq. (10) is

$$\frac{(\Delta\lambda_0)_2}{(\Delta\lambda_0)_1} = \frac{(w_s(T))_2}{(w_s(T))_1}, \tag{11}$$

from which the Stark broadening of the other line is immediately calculated.

On the other hand, if both the Stark broadenings of the two lines are unknown, we can have recourse to eq. (7), which gives the relation

$$\frac{(N_p/N_{p_0})_2}{(N_p/N_{p_0})_1} = \left[\frac{(\mathrm{SA})_2}{(\mathrm{SA})_1}\right]^{\beta} = \left[\frac{\kappa(\lambda_0)_1}{\kappa(\lambda_0)_2}\frac{(1-e^{-\kappa(\lambda_0)l})_2}{(1-e^{-\kappa(\lambda_0)l})_1}\right]^{\beta}. \tag{12}$$

Substituting the expression for the κ (λ_0) absorption coefficient Eq. (3) in Eq. (12), we obtain

$$\frac{\left(\frac{N_p}{N_{p_0}}\right)_2}{\left(\frac{N_p}{N_{p_0}}\right)_1} = \left[\frac{\frac{\left(\lambda_0^4 A_{ki} g_k e^{-\frac{E_i}{k_B T}}\right)_1}{\left(\lambda_0^4 A_{ki} g_k e^{-\frac{E_i}{k_B T}}\right)_2}\left(\frac{(\Delta\lambda_0)_2}{(\Delta\lambda_0)_1}\right)(1-e^{-\kappa(\lambda_0)_2 l})}{\left(1-e^{\frac{\left(\lambda_0^4 A_{ki} g_k e^{-\frac{E_i}{k_B T}}\right)_1}{\left(\lambda_0^4 A_{ki} g_k e^{-\frac{E_i}{k_B T}}\right)_2}\left(\frac{(\Delta\lambda_0)_2}{(\Delta\lambda_0)_1}\right)\kappa(\lambda_0)_2 l}\right)}\right]^{\beta} \tag{13}$$

Equation (13) can be solved numerically for the opacity κ $(\lambda_0)_2$ l of line 2, from the experimentally measured intensity ratio $(N_p)_2/(N_p)_1$ of the two lines and the $(\Delta\lambda_0)_2/(\Delta\lambda_0)_1$ parameter obtained from Eq. (10), assuming the temperature T of the plasma is known.

This value can now be substituted in Eq. (6) for obtaining $(\mathrm{SA})_2$; again substitution of this parameter in Eq. (8) allows the determination of $(\Delta\lambda_0)_2$ from the measured FWHM of the line $(\Delta\lambda)_2$. The determination of $(\Delta\lambda_0)_1$ immediately follows from Eq. (10).

Assuming that the plasma electron density is known by independent measurements, the Stark broadening for each of the two lines can be finally derived from Eq. (5).

EXPERIMENTAL RESULTS

In order to check the reliability of the above-presented method, some measurements were performed on pure aluminum samples at the Applied Laser Spectroscopy (ALS) Laboratory in Pisa and at Cairo Laboratories. The measurements at ALS Lab were done using Modì (MObile Dual-pulse Instrument), a double-pulse mobile LIBS system realized by the Applied Laser Spectroscopy group in collaboration with Marwan Technology s.r.l. (Pisa).[18] Modì uses a Nd-YAG Laser emitting two collinear pulses (with a reciprocal delay variable from 0 to 50 μs) at 1064 nm with 80 mJ energy per pulse and 12-ns FWHM, coupled with an Echelle spectrometer (with spectral resolving power $\lambda/\Delta\lambda = 7500$) equipped with an intensified CCD (iCCD) for time-resolved LIBS measurements. The measurements were performed both in single pulse, at 160 mJ energy, and double-pulse regime ($80 + 80$ mJ with an interpulse delay of 2 μs). The LIBS measurements were performed as a function of the delay after the (second) laser pulse, to explore different plasma conditions (particle density, temperature and electron density). The measurements performed at Cairo Laboratory used the experimental setup described in Ref. 15. A high-power Nd-YAG laser (Brilliant B, Quantel, France), delivering up to 800 mJ in 6-ns FWHM at 1064 nm was focused through a 10-cm focal length lens on a plane solid target in air. The spectra were collected through an optical fiber coupled to a SE200 Echelle spectrograph (Catalina Scientific Corp., AZ, USA) with spectral resolving power $\lambda/\Delta\lambda = 4500$, equipped with a time-gated iCCD (iStar DH734-18F, Andor Technology, UK). The time delay after the laser pulse ranged between 1.5 and 5 μs. In both the experiments, the spectra were acquired using a gate time of 1 μs, which provided a good signal-to-noise ratio, necessary for a precise measurement of the spectral linewidths, at the same time guaranteeing, at least at relatively long delays, that the plasma parameters (particle density, temperature and electron density) would remain quasi-stationary during the measurement time window.

The measurements of the linewidths were performed through a Voigt fitting of the line profile; the Gaussian contribution to the measured FWHM due to the instrumental broadening was then subtracted in order to obtain only the Lorentzian contribution associated to the Stark effect (Fig. 1). The instrumental broadening was determined by measuring the FWHM of the Hg lines emitted by a standard low-pressure Hg lamp.

The evaluation of n_e, reported in Fig. 2 as a function of the acquisition delay for both the Cairo and Pisa experiments (in single- and double-pulse configuration), was performed by measuring the Stark broadening of

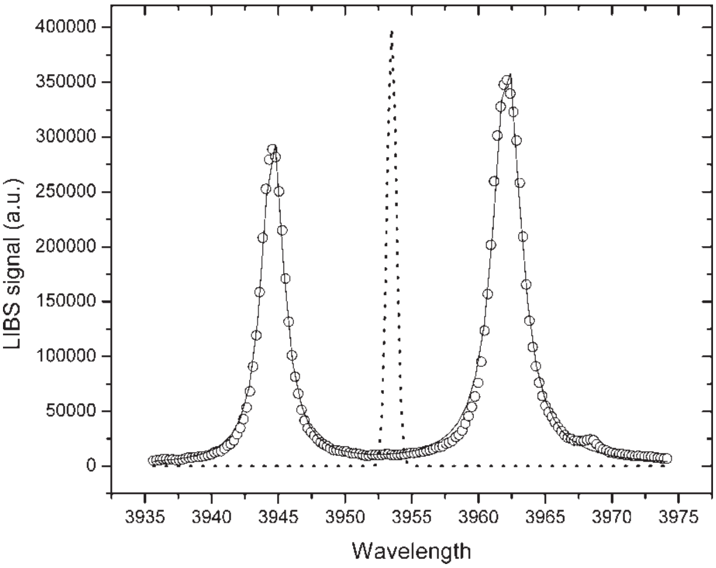

Figure 1. Portion of the LIBS spectrum showing the two Al I lines at 394.4 nm and 396.2 nm. Circles, experimental points; continuous line, Voigt best fit of the emission lines; dotted line, instrumental broadening in the spectral region considered (Gaussian profile).

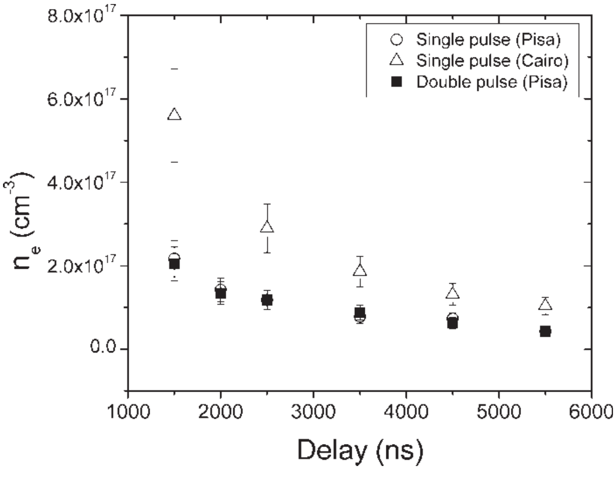

Figure 2. Measured electron density, as a function of the acquisition time delay, in single pulse at 160 mJ (open circles, Pisa experiment), single pulse at 800 mJ (open triangles, Cairo experiment), and double pulse at $80 + 80$ mJ with 2-μs interpulse delay (solid squares, Pisa experiment) configurations. The acquisition gate is 1 μs in all the configurations; the acquisition delay, in double-pulse measurements, is considered after the second pulse.

the H_α line at 656.27 nm, according to the relation[19]

$$n_e(\mathrm{cm}^{-3}) = C(\lambda, T)(\Delta\lambda_{1/2})^{3/2}, \tag{14}$$

where $\Delta\lambda_{1/2}$ is the measured FWHM of the H_α line in angstroms and $C(\lambda, \mathrm{T})$ is a coefficient, weakly depending on electron density and temperature, tabulated by Griem.[14]

Hydrogen emission is always present in the LIBS spectra taken in ambient air, because of the water vapor due to the natural humidity of the air. [20] The use of the H_α line for the measurement of the electron density has the definite advantage of providing a result that is not affected by self-absorption, unless the sample itself would contain high levels of hydrogen. Moreover, the linear Stark effect acting on the hydrogen atoms results in a large broadening of the lines, which reduces the relative uncertainty of the measurement compared with the case of lines emitted by other elements.[13]

The electron density measured in the Cairo experiment is about three times higher than the one measured in Pisa, due to the higher laser intensity used in that experiment. The plasma temperature was also measured, as a function of the acquisition delay time, using the Saha–Boltzmann plot method (Fig. 3). The Saha–Boltzmann plot is a generalization of the Boltzmann plot method, which allows using lines coming from different ionization stages of the same element for the determination of plasma temperature, given the knowledge of the plasma electron density (see Ref. 21 for more details). In this technique, because of the larger maximum difference of the upper level energies of the transitions considered, a considerable reduction of the fitting

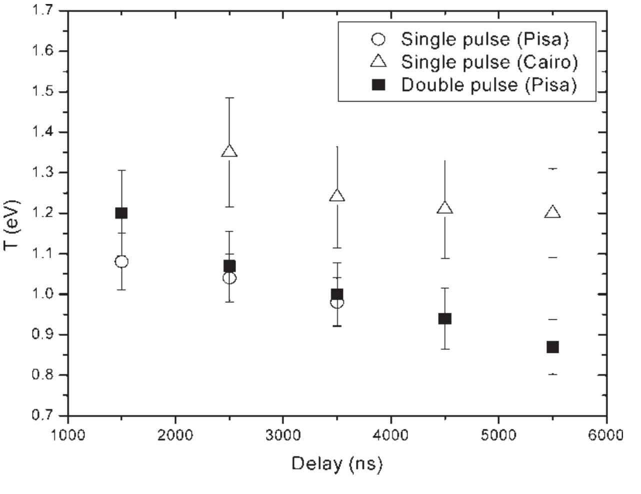

Figure 3. Measured plasma temperature, as a function of the acquisition time delay, in single-pulse (opens circles and triangles) and double-pulse (solid squares) configurations. The experimental conditions are the same as in Fig. 2.

Table 1. Al emission lines used for electron temperature determination

Species	Wavelength (nm)	g_k	g_i	E_k (cm^{-1})	E_i (cm^{-1})	A_{ki} (s^{-1})
Al I	308.2	4	2	3.24×10^4	0	6.3×10^7
Al I	309.3	6	4	3.24×10^4	1.12×10^2	7.4×10^7
Al I	394.4	2	2	2.53×10^4	0	4.9×10^7
Al I	396.2	2	4	2.53×10^4	1.12×10^2	9.8×10^7
Al II	281.6	1	3	9.54×10^4	5.99×10^4	3.8×10^8
Al II	358.6	9	7	1.23×10^5	9.55×10^4	2.5×10^8
Al II	466.3	3	5	1.07×10^5	8.55×10^4	5.3×10^7

error is easily obtained with respect to the usual Boltzmann plot method. For the measurements here considered, the Al emission lines reported in Table 1 were used. All the emission lines intensities were corrected for self-absorption, using a recursive algorithm: the self-absorption coefficients of the lines were calculated first on the basis of the temperature measured using the non–self-absorption corrected data; then, the self-absorption corrected intensities were used for a more precise calculation of the temperature. The procedure is repeated until convergence is achieved. In general, a couple of iterations is enough for stabilizing the value of plasma temperature. The experimental errors on temperature calculation are of the order 5%, coming mainly from the uncertainties of the electron density and the fitting of the line profile.

For illustrating the application of the method here proposed for the calculation of the Stark broadening parameters, we will first consider the two Al I lines at 396.2 nm and 308.2 nm, whose Stark broadenings are known in the literature.[7] Their spectral parameters are reported in Table 2.

The ratio of the lines intensities and the FWHM widths of the two lines here considered is shown in Figs. 4 and 5 for both the Cairo and Pisa experiments, as a function of the time delay after the laser pulse (the second in double-pulse configuration).

Note that, for a precise determination of the Stark broadening of the lines considered, their true linewidths should be much larger than the instrumental broadening. If this condition is not realized, the error on the determination of

Table 2. Spectral parameters of the Al lines considered in this paper

Species	Wavelength (nm)	g_k	g_i	E_k (cm^{-1})	E_i (cm^{-1})	A_{ki} (s^{-1})
Al I	308.2	4	2	3.24×10^4	0	6.0×10^7
Al I	309.3	6	4	3.24×10^4	1.12×10^2	7.4×10^7
Al I	394.4	2	2	2.53×10^4	0	4.9×10^7
Al I	396.2	2	4	2.53×10^4	1.12×10^2	9.8×10^7

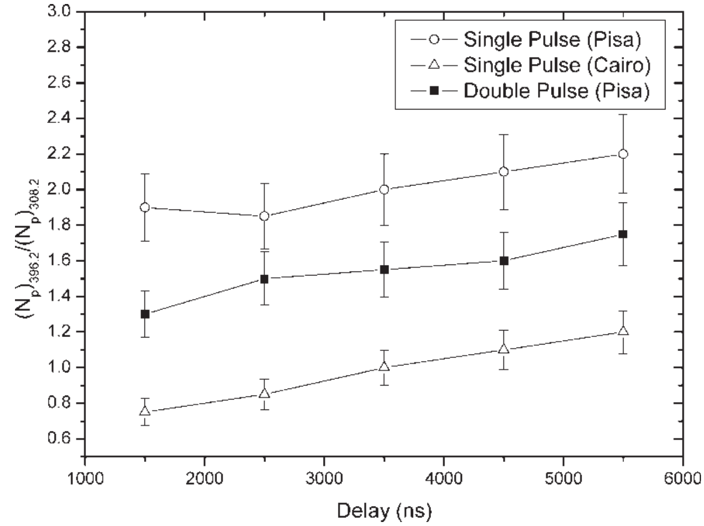

Figure 4. Intensity ratio of the two Al I lines at 396.2 nm and 308.2 nm, as a function of the acquisition time delay, in single-pulse (open circles and triangles) and double-pulse (solid squares) configuration.

the emission lines FWHM increases dramatically, and the method here proposed becomes unreliable.

From the experimental values of the ratios obtained in the Pisa and Cairo experiment, using the measured values of the electron temperature in Fig. 2 and the spectral parameters reported in Table 2, we can derive the $(\Delta\lambda_0)_2/(\Delta\lambda_0)_1$ ratio, according to Eq. (10).

The uncertainty of $(\Delta\lambda_0)_2/(\Delta\lambda_0)_1$, on which will depend the final accuracy of Stark broadening calculation, results from the contributions of the errors on the measured linewidths and intensities, on the transition probabilities, and on the plasma temperature. In this case, considering that the errors are statistically independent, we estimated an uncertainty of $\sim$30–35% on the calculated ratios, which is mainly caused by the uncertainty on the A_{ki} values. Considering that the uncertainty of the A_{ki} ratio of lines coming from the same species can be markedly lower than that calculated by the error propagation from the single A_{ki} errors, it is reasonable to consider the above-calculated uncertainty as a pessimistic estimate. The approximation of homogenous plasma, which typically produces an error around 5–7% on the Stark broadening determination,[11] does not bring relevant variations of the uncertainty calculated (because it is statistically independent from other error sources), and it can be made much lower considering emission lines with comparable upper energy levels. Similar results are reported by Colon and Alonso-Medina[22] in a recent paper on LIBS determination of Stark widths of singly ionized lead lines.

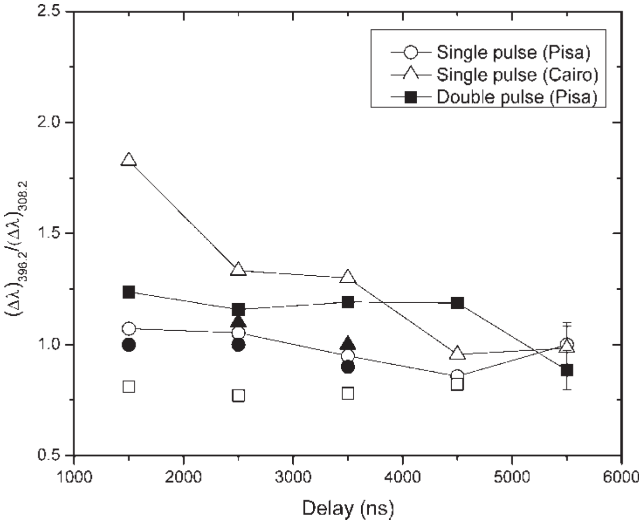

Figure 5. Ratio of the linewidths of the two Al I lines at 396.2 nm and 308.2 nm, as a function of the acquisition time delay, in single-pulse (open circles and triangles) and double-pulse (solid squares) configuration. For comparison, the prediction of Eq. (10) for $(\Delta\lambda_0)_2/(\Delta\lambda_0)_1$ is also reported. The solid circles and triangles correspond with single-pulse conditions, and open squares correspond with double-pulse configuration. The error bar is reported only on the last point for the sake of readability.

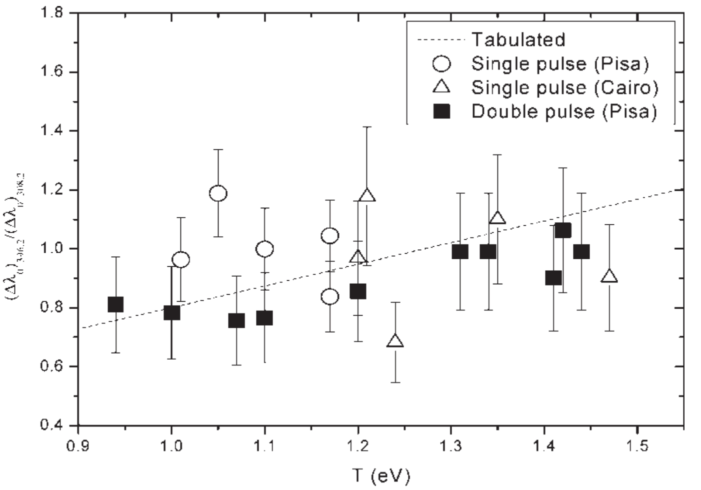

Figure 6. Ratio of the Lorentzian widths (corresponding with the ratio of the Stark broadenings) of the two Al I lines at 396.2 nm and 308.2 nm, as a function of plasma temperature, in single-pulse (open circles and triangles) and double-pulse (solid squares) configuration. The dashed line corresponds with the ratio of the Stark broadenings reported in Ref. 7.

The calculated values of $(\Delta\lambda_0)_2/(\Delta\lambda_0)_1$in single- (Pisa and Cairo experiments) and double-pulse configuration (Pisa experiment) are plotted in Fig. 6 for the Al I couple of lines at 396.2 nm and 308.2 nm, as a function of the plasma temperature, and compared with the ratio of the corresponding Stark broadenings as reported in Ref. 7. The same calculation can be performed considering the other couple of Al I lines at 394.4 nm and 308.2 nm. The results are reported in Fig. 7. For both the couples of lines here considered, the agreement between the tabulated and predicted ratios is remarkable, considering the experimental errors. It is worth noticing that the scattering between theoretical and experimental values is for almost all the points lower than the 30–35% uncertainty estimated above. Moreover, the results obtained in the Pisa and Cairo experimental configurations are consistent, despite the very different plasma parameters. It is clear, then, that supposing that the Stark parameters of only one line is known, the other could be determined with a comparable precision according to the procedure here suggested. Note also that both the lines considered for the current example are strongly self-absorbed, and nevertheless the result obtained is still significant.

The "blind" determination of both the Stark broadenings of the couple of lines considered is clearly more difficult and is based on the numerical solution of Eq. (13) for obtaining the absolute value of the opacity of one of the lines. Although the treatment of self-absorption effects here presented is quite general, under the hypotheses of plasma homogeneity and local thermal

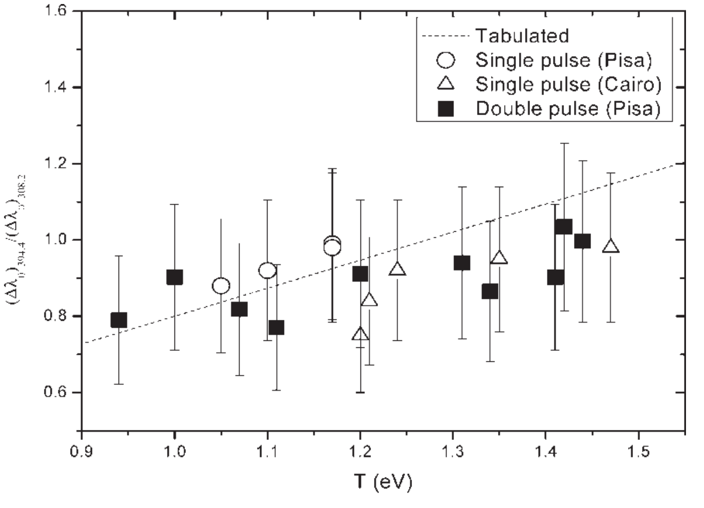

Figure 7. Ratio of the Lorentzian widths (corresponding with the ratio of the Stark broadenings) of the two Al I lines at 394.4 nm and 308.2 nm, as a function of plasma temperature, in single-pulse (open circles and triangles) and double-pulse (solid squares) configuration. The dashed line corresponds with the ratio of the Stark broadenings reported in Ref. 7.

Table 3. Experimentally determined Stark coefficients for the two Al I lines at 394.4 nm and 396.2 nm, at different temperatures, in Pisa single-pulse (SP) and double-pulse (DP) experimental configurations, compared with the values of the same coefficients as reported in Ref. 7, extrapolated at the same temperature (the opacities and the SA coefficients of the lines are also reported)

Species	Wavelength (nm)	Experimental condition	Temperature (eV)	$\kappa\ (\lambda_0)l$	SA	w_s (nm/10^{17}cm^{-3}) measured)	w_s (nm/10^{17}cm^{-3}) (tabulated)
Al I	394.4	Pisa SP	1.10	0.9	0.7	0.028	0.020
Al I	396.2	Pisa SP	1.10	2.3	0.4	0.022	0.020
Al I	394.4	Pisa SP	1.12	0.7	0.7	0.027	0.020
Al I	396.2	Pisa SP	1.12	1.4	0.5	0.025	0.020
Al I	394.4	Pisa DP	1.34	1.6	0.5	0.027	0.023
Al I	396.2	Pisa DP	1.34	3.7	0.3	0.024	0.023
Al I	394.4	Pisa DP	1.40	1.5	0.5	0.025	0.024
Al I	396.2	Pisa DP	1.40	3.3	0.3	0.024	0.024

equilibrium, from an experimental point of view for obtaining a meaningful estimate of the line opacities, the dependence of the right side of Eq. (14) on the $\kappa\,(\lambda_0)_2 l$ parameter should be strong enough for making the comparison with the experimental determined value of the line intensity ratio $(N_p)_2/(N_p)_1$ meaningful. However, in the limit $\kappa\,(\lambda_0)_2 l \gg 1$, Eq. (13) becomes

$$\frac{(N_p/N_{p_0})_2}{(N_p/N_{p_0})_1} = \left[\frac{(\lambda_0^4 A_{ki} g_k e^{-E_i/k_B T})_1}{(\lambda_0^4 A_{ki} g_k e^{-E_i/k_B T})_2} \left(\frac{(\Delta\lambda_0)_2}{(\Delta\lambda_0)_1}\right)\right]^{\beta} \quad \kappa(\lambda_0)_2 l \gg 1, \qquad (15)$$

where, of course, every dependence on the line opacity is lost. Therefore, a meaningful estimation of the $\kappa\,(\lambda_0)_2 l$ parameter can be obtained only in the limit of small to moderate self-absorption ($\kappa\,(\lambda_0)_2 l \leq 1$). This condition can be checked *a posteriori* after the numerical solution of Eq. (13). As an example, in Table 3 are reported the Stark broadenings of the Al I lines at 396.2 and 394.4 nm, measured in the different experimental conditions and at an experimental acquisition delay chosen as to guarantee relatively low values of the line opacity $\kappa\,(\lambda_0) l$. We can observe that the estimation of the Stark broadenings for all the lines here considered is in a very good agreement with the values reported in Ref. 7, despite the fact that the measured values of the $\kappa\,(\lambda_0) l$ parameter are often definitely larger than 1.

In the Cairo data, even at the condition of lower self-absorption, the $\kappa\,(\lambda_0)\,l$ parameter is always larger than 10, thus making impossible a meaningful estimation of the Stark broadenings using Eqs. (13) and (14). In all the other cases when the calculation of the Stark broadenings is possible, the maximum discrepancy between the measured and tabulated values is of the order 30%, which has to be considered a reasonable figure, also considering the indetermination on the data of Ref. 7 and the uncertainty on the measured electron densities, which reflects proportionally on the indetermination of the Stark broadenings in case of "blind" calculations.

CONCLUSIONS

In this paper, we have presented a simple and fast method for evaluating the Stark broadenings from LIBS measurements. The method is based on the estimation of the self-absorption effects on a couple of emission lines of the same species and the following rescaling of the measured linewidths in order to compensate for these effects. When the Stark broadening of one of the lines is known, the method yields the value of the other broadening without need of knowing the plasma electron density; on the other hand, if both the Stark broadenings are unknown, it is still possible to evaluate them, provided the opacities of the two lines are moderate and the electron density is known. The examples presented demonstrate that the method gives reasonable estimates of the Stark broadenings (with maximum discrepancies of the order 30%) in the typical conditions of LIBS experiments.

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