Laser-induced breakdown spectroscopy for Stark broadening and shift experiments: Measurement of Fe II and Ni II Stark shifts

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Abstract. We present experimental studies on characterization of laser-induced plasmas relevant for the measurement of Stark widths and shifts by laser-induced breakdown spectroscopy. The selection of samples for plasma generation is investigated. It is shown that fused glass samples provide spectra with much higher line-to-background ratio for many lines of interest, compared to alloys. The influence of self-absorption on the line width is studied as a function of the concentrations of the emitting element in the sample and time of the plasma evolution. New Stark shifts for several Fe II and Ni II are measured.

1. Introduction

Since the advent of laser-induced breakdown spectroscopy (LIBS), an interest has existed in performing Stark broadening and shift experiments for characterization of the electron density of laser-induced plasmas used in different applications [1]. Precise measurement of the electron density relies on the knowledge of accurate data for Stark widths and shifts. However, these parameters are still not available for many transitions of several atoms and ions, so there is a need of new experimental data, which are also useful for the diagnostics of other types of plasmas and to verify the calculations. In the case of Fe II and Ni II, our group has reported recently measurements of Stark widths for a high number of transitions [2-5], which have been compared to the relatively few data found in the literature. Regarding Stark shifts, we have not found previous results for Fe II or Ni II.

Laser-induced plasmas are spectroscopic sources of high electron density which may be obtained in a relatively easy way from gases, liquids and electrically conducting or non-conducting solid samples. Because of these properties, laser-induced plasmas are particularly suitable for the measurement of Stark widths and shifts [6]. However, a detailed characterization of the laser-induced plasma is necessary to obtain precise measurements. The previous step of plasma characterization allows the control of self-absorption, the selection of suitable samples for plasma generation and the estimation of the effect of plasma inhomogeneity.
In this work, we describe experimental work performed by our group in which LIBS is used for characterization of laser-induced plasmas with the purpose of measuring Stark parameters. Also, new data for Fe II and Ni II Stark shifts measured by LIBS are presented.

2. Experiment
The experimental set-up is similar to that used previously [5], so it is only described briefly. The laser-induced plasmas are generated by focusing a Nd:YAG laser (wavelength 1064 nm, pulse width 4.5 ns, repetition rate 20 Hz) onto a sample placed in air at atmospheric pressure. The laser pulse energy has varied depending on the type of sample used: For alloys, the pulse energy was set at 100 mJ by means of an optical attenuator whereas for fused glass samples, a lower pulse energy of 60 mJ has been employed. The focal length of the focusing lens was 128 mm and the lens-to-sample distance was 118 mm and 124 mm for pulse energies of 100 mJ and 60 mJ, respectively. The emission of the plasma is collected and focused by a mirror system onto the entrance slit of a Czerny-Turner spectrometer equipped with a time-resolved intensified CCD (1200 × 256 effective pixels). The grating (3600 and 1200 lines mm⁻¹) and the slit width (20 and 50 µm) are selected according to the spectral resolution needed. In each spectrum measured the emission from 100 laser shots is accumulated while the sample rotates at 100 rev min⁻¹.

3. Results and discussion
3.1. Samples used
Two different types of samples have been used to generate the laser-induced plasmas. Alloy samples have been prepared from the pure metals in powder form by melting in an induction furnace [2-4]. Alloys have the advantage that they can be

Figure 1. Spectra from laser-induced plasmas generated from a Fe-Cu alloy sample (a) and a Fe₂O₃ fused glass sample (b). The iron concentration in both cases is 1.0 at. %.
reused in different measurements by sanding the surface to eliminate the craters formed by the laser ablation. On the other hand, we have prepared fused glass samples from pure oxides in powder form by borate fusion in a fluxer [5]. These samples may be prepared from several types of compounds, including oxides and salts, which allows including non-metallic elements. In figure 1, spectra containing Fe II lines of interest obtained using a Fe-Cu alloy and a Fe₂O₃ fused glass are compared. The iron concentration in the sample is 1.0 at.% in both cases. As can be seen, for the alloy sample, the Cu II lines from the copper matrix overlap with the Fe II lines. Conversely, the absence of lines from the borate matrix in the case of the fused glass, with the exception of a few intense B I lines and weak Li I lines appearing at other spectral regions, allows the measurement of Fe II lines at 2368.60 Å, which may hardly be observed in the alloy spectrum. Furthermore, even lines well resolved from the Cu II line as 2364.83 Å show a higher line-to-background ratio in the case of the fused glass spectrum. This is shown in figure 2, where the line-to-background ratio for this line, obtained as the height of the line divided by the intensity of the background, is plotted as a function of the time of plasma evolution for the two types of samples.

![Figure 2](image_url)

**Figure 2.** Line-to-background ratio for the Fe II line at 2364.83 Å as a function of the time of plasma evolution for alloy samples (open squares) and fused glass samples.

As can be seen, the line-to-background ratio increases monotonously with time, a behavior expected from the decrease of the continuum emitted by the plasma and the reduction of the line width due to the decrease of the electron density, which makes that the line intensity, in spite of suffering also a decrease, is distributed among a narrower wavelength range. For the purpose of measuring Stark widths and shifts, however, only spectra at initial times may be used, as the electron density must be high enough so that the Stark width is significantly higher than the instrumental width. In the case of lines with relatively low Stark widths and shifts, such as the Fe II lines, for our instrumental width of 0.135 Å, the useful time interval goes from around 0.5 µs to 3.5 µs. We may observe in figure 2 that, at this time interval, the line-to-background ratio is significantly higher for fused glass samples than for alloy samples.
3.2. Investigation of self-absorption

Self-absorption is one of the main causes of systematic error in the measurement of Stark widths by LIBS, as it distorts the line profiles, leading to an increase of the line width [7]. However, the possibility of LIBS for varying the concentration of the emitting element in the sample allows controlling this effect. We have studied the influence of self-absorption on the line width using fused glass samples prepared from iron oxide having Fe concentrations in the range 0.1-0.8 at.%. As self-absorption depends also strongly on the time of plasma evolution, the investigation has also included the dependence on this parameter. Figure 3 shows the ratio of the line width (FWHM) \( w \) to the electron density \( N_e \) for the intense Fe II line at 2599.40 Å plotted as a function of the Fe concentration in the sample, for different instants of the plasma evolution. The electron density of the plasma at each instant has been measured as described in previous works [4,8].

![Figure 3](image)

**Figure 3.** Ratio between the line width \( w \) (FWHM) and the electron density \( N_e \) for the Fe II line at 2599.40 Å as a function of the Fe concentration in the sample for different instants of the plasma lifetime.

As can be seen in figure 3, the ratio \( w/N_e \), which should be approximately constant in the absence of self-absorption, increases with the concentration in the sample, the increase being steeper for higher delay from the laser pulse. This figure shows the importance of controlling self-absorption to obtain an accurate measurement of the Stark width. For the concentration 0.1 at.% finally used in the measurement, the values of \( w/N_e \) at different instants converge to a single value within the experimental error, so the effect of self-absorption on the Stark width is small, leading to an error which is estimated as lower than 10% for the ensemble of Fe II lines investigated.

3.3. Measurement of Stark shifts

Figure 4 shows a typical measurement of the profile of a Fe II line at different instants of the plasma evolution. The spectra have been measured at six time windows having different delays from the laser pulse, centred at instants of the plasma lifetime ranging from 0.6 to 3.4 µs. The width of the time windows increases with the delay from 0.06 to 0.6 µs. In these plots, the intensity is normalized to the
width of the time window used in each case. As the delay from the laser pulse increases, a decrease of the line width and a decreasing red shift are observed, both related to the temporal decay of the electron density. The wavelength of the unshifted profile, indicated by the dashed line, is obtained from the spectrum at 10-µs delay, when the Stark shift is negligible. To obtain the shifts, the position of the maximum is determined by fitting the line profiles to Voigt profiles. The electron density of the plasma at each time window is determined from the Stark broadening of the H\textsubscript{α} line [4,8].

![Figure 4](image_url)

**Figure 4.** Spectra of the Fe II line at 2368.60 Å obtained at different time windows from 0.4 µs to 3.4 µs. The dashed line indicates the wavelength of the unshifted profile.

A typical plot of the line shift vs. the electron density is shown in figure 5. As can be seen, a proportionality relation is obtained, which means that the weak dependence of the Stark shift on temperature has not been observed. Therefore, the final results are obtained as the slopes of the linear fittings of these plots with zero intercept, this value corresponding to the Stark shift at an electron density of 10^{17} cm^{-3}.

![Figure 5](image_url)

**Figure 5.** Line shift of the Fe II line at 2368.60 Å as a function of the electron density.
The results for the Stark shifts of Fe II and Ni II lines are presented in tables 1 and 2, respectively. The experimental relative error of the Stark shifts is mainly due to the uncertainty of the electron density, which has been estimated as 11%. However, the minimum absolute error due to resolution is 0.1 pm. To our knowledge, these are the first experimental results for the Stark shifts of these lines and no previous theoretical results have been reported.

Table 1. Stark shift at electron density $N_e = 10^{17}$ cm$^{-3}$ of Fe II spectral lines.

| Transition | Multiplet | $\lambda$ (Å) | $d^a$ (pm) |
|------------|-----------|----------------|------------|
| $3p^63d^7 - 3d^6(^3D)4p$ | $a^4F - z^4F^o$ | 2331.307 | 2.06 |
| | $a^4F - z^4D^o$ | 2368.596 | 1.96 |
| $3d(^3D)4s - 3d(^1D)4p$ | $a^4D - z^4P^o$ | 2591.543 | 0.48 |
| | $a^3H - z^3H^o$ | 2233.917 | 1.73 |

Temperature range: 12000-17600 K. The relative error of $d$ is 11%, with a minimum absolute error of 0.1 pm.

Table 2. Stark shift at electron density $N_e = 10^{17}$ cm$^{-3}$ of Ni II spectral lines.

| Transition | Multiplet | $\lambda$ (Å) | $d^a$ (pm) |
|------------|-----------|----------------|------------|
| $3d(^3F)4s - 3d(^1F)4p$ | $^4F - ^4G^o$ | 2216.477 | 0.51 |
| | $^4F - ^4F^o$ | 2138.582 | 0.48 |
| | | 2210.379 | 0.48 |
| | $^2F - ^2D^o$ | 2356.403 | 0.48 |
| $3d(^3P)4s - 3d(^1D)4p$ | $^4P - ^2F^o$ | 2220.399 | 0.47 |
| | $^2D - ^2P^o$ | 2213.195 | 0.40 |
| $3d(^1G)4s - 3d(^1G)4p$ | $^2G - ^2G^o$ | 2107.953 | 0.74 |
| | | 2113.518 | 0.70 |

Temperature range: 12000-17600 K. The relative error of $d$ is 11%, with a minimum absolute error of 0.1 pm.

4. Conclusions
Laser-induced plasmas are spectroscopic sources suitable for measurement of Stark widths and shifts. Generation of the plasmas from fused glass samples allows obtaining spectra from many atoms and ions showing higher line-to-background ratios compared to spectra obtained from alloy plasmas. The selection of the concentration of the emitting element in the sample allows controlling the effect of self-absorption on the line width.

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References
[1] Radziemski L J, Loree T R, Cremers D A, Hoffman N M 1983 Anal. Chem. 55 1246
[2] Aragón C, Vega P, Aguilera J A 2011 J. Phys B: At Mol Opt Phys. 44 055002
[3] Aguilera J A, Manrique J, Aragón C, 2011 J. Phys B: At Mol Opt Phys. 44 245701
[4] Aguilera J A, Aragón C, Manrique J. 2013 JQSRT 114 151
[5] Aragón C, Aguilera J A, Manrique J. 2014 JQSRT 134 39
[6] Colón C, Hatem G, Verdugo E, Ruiz P, Campos J 1993 J. Appl. Phys. 73 4752
[7] Konjević N, Ivković M, Jovičević S 2010 Spectrochim. Acta Part B 65 593
[8] Aragón C, Aguilera J A 2010 Spectrochim. Acta Part B 65 395