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Experimental Stark widths and shifts of Nb II spectral lines

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ABSTRACT

Stark widths and shifts of Nb II spectral lines have been measured by laser-induced breakdown spectroscopy (LIBS). The experimental line profiles are obtained from spectra of the emission of laser-induced plasmas generated with samples prepared by borate fusion with small niobium concentrations, selected to minimize self-absorption. Using different time delays in the detection of the emission, electron densities ranging from 0.81×10^{17} cm^{-3} to 6.7×10^{17} cm^{-3} and temperatures in the interval 10,100–16,700 K are employed in each measurement. The 26 Stark widths and 22 Stark shifts determined include spectral lines from transitions between 10 multiplets and 3 configurations. To our knowledge, only two experimental data for Nb II Stark widths were available previously in the literature.

1. Introduction

Measurements of Stark broadening parameters are needed in order to validate atomic structure calculations and for analyzing astrophysical data and laboratory plasmas. Theoretical Stark calculations increase their complexity with partly filled subshell configurations, and Nb II is a clear example with its open $4d^4$ ground configuration. Lakićević [1,2] estimated the Stark widths and shifts of the 2721.6 and 3225.5 Å Nb II spectral lines employing ionization potential regularities for ions with atomic number from 21 to 89. Hermann et al. [3] reported measurements of the Stark widths of the Nb II lines at 3194.970 Å and 3225.475 Å. To our knowledge, there are no theoretical data for Nb II Stark widths or shifts in the literature.

Despite the scarce existing data, niobium ions are of great interest in astrophysical data, because spectral lines of rare earth elements (REE) are observed in spectra of white dwarfs and chemically peculiar (CP) stars. For the singly charged ion Nb II, spectral lines have been reported in the spectra of Ap star γ Equulei [4] and CP star H465 [5], where abundance determination and opacity calculations have been performed. Simić et al. [6], studying the importance of Stark broadening in stellar atmospheres with Nb III, obtained this as the dominant effect in comparison to thermal Doppler in DB white dwarf atmospheres, whilst not negligible in A type hot stars. Nilsson et al. [7], used the Nb II transition data to obtain abundances in the solar photosphere and five metal-poor stars. Also, niobium plays an important role to understand the slow neutron capture process (the s-process), which is produced during the ”asymptotic giant branch” part of the life in the star [6]. Furthermore, in modern industrial areas the Nb content is a key parameter. For example, its magnetic properties are essential for superconductors and magnetic resonance imaging devices [8]. Also, the addition of niobium enhances the properties of metal alloys, and Zr-Nb alloys become structural materials of the nuclear reactors [9], while Nb dopped Ti-Al alloys are widely employed for the aerospace field [10]. Recently, the Nb content in high entropy alloys has emerged as a key parameter for next generation batteries [11].

Laser-induced breakdown spectroscopy (LIBS) is being used as a convenient technique for measurement of Stark broadening parameters (as examples, see references [12] and [13]). Our group has been using the CSigma-LIBS methodology [14] to limit self-absorption so that its effect in the measurements is low, which allows to determine parameters from weak and strong lines simultaneously. Our aim here is to provide accurate experimental measurements of Stark widths and shifts for Nb II spectral lines involving transitions between $4d^4$, $4d^3 5s$ and $4d^3 5p$ configurations.

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2. Experiment

The LIBS equipment employed for the measurement of Stark broadening and shift parameters has been used previously [15], so only a brief description is given here. A Q–switched Nd:YAG laser (wavelength 1064 nm, pulse width 4.5 ns, pulse energy 60 mJ, repetition rate 20 Hz) was focused at right angles to the sample surface to generate the plasmas in air at atmospheric pressure. The focusing lens (126 mm focal length) was placed at 122 mm from the sample surface. During the measurements, the samples rotated at 100 rev min^{-1} to avoid the formation of a deep crater by the ablation process, thus improving the reproducibility. The samples employed in this study were five fused glass disks prepared by fusion in lithium borates of pure (99.9985 %) Nb_2O_5 in powder form, with corresponding Nb atomic concentrations of 0.02, 0.04, 0.08, 0.15, 0.25, and 0.4 at. per cent. A trace amount of $CaCO_3$ (corresponding Ca concentration of 0.008 at. per cent.) was added for electron density measurement by using the Ca II line at 3968.469 Å (see Section 3).

The laser-induced plasma was imaged 1:1 onto the entrance of a Czerny–Turner spectrometer (focal length 0.75 m, grating of 3600 lines mm^{-1}, slit width 20 μm) by using a pair of flat and concave (focal length 125 mm) mirrors. The detector was an intensified charge–coupled device (ICCD, 1024 × 1024 pixels). The experimental setup had a good spectral resolution (15 pm at 3000 Å) providing an instrumental broadening comparable to or less than the experimental line widths, which allowed the detailed measurement of the true line profiles.

The LIBS spectra were acquired with temporal resolution using suitable gate widths (0.06–1.60 μs) and delay times (0.57–6.20 μs). As the plasma electron density decreases for increasing delay time, the variation of this parameter allows the measurement of the Stark widths for different electron densities. An additional spectrum was also measured with a late time window (width 10 μs, delay 20 μs) where the electron density has decreased to a negligible value. This spectrum was used as a reference for Stark width and shift determination. To reduce the statistical error and to improve the signal–to–noise ratio, each measurement was replicated at 5 different positions in the samples and further averaged. On each position, the recorded spectrum was the result of the in–software accumulation of individual spectra generated from 100 consecutive laser shots after discarding 100 previous cleaning shots.

3. Results and discussion

The laser–induced plasma was characterized at the different time windows through the calculation of the electron density and the temperature. The plasma electron density was obtained from the Stark width of the Ca II line at 3968.469 Å by using the values reported in a previous study by our group [12] for the Stark width of this line. The use of the Ca II line is convenient for electron density determination for various reasons: (1) As the Nb II emission, the Ca II emission comes from the sample, contrary to the widely used H_α line, whose emission arises from the water content of air, and therefore may have a different distribution in the plasma. (2) The calcium spectrum has relatively few lines which do not overlap with the Nb II lines of interest, (3) The Ca II and Nb II lines are detected using the same spectrometer grating, which avoids experimental errors due to grating movement, (4) For the trace Ca content in the samples (i.e., 0.008 at. per cent), self-absorption of the Ca II line is negligible. The plasma temperature was obtained from the Boltzmann two–line method applied to the well-known Nb II lines at 3076.857 Å [16] and 3080.343 Å [7]. Under this approach, the resulting electron density decreased from 6.7×10^{17} cm^{-3} at 0.6 μs down to 0.81 $\times 10^{17}$ cm^{-3} at 3.4 μs, whereas the temperature decreased from 16,700 K at 0.6 μs down to 10,100 K at 3.4 μs. The temperature and electron density values obtained for the different samples were the same within the experimental error; hence, matrix effects were negligible in our experiment.

Self–absorption of the investigated Nb II spectral lines, which affects the emission line shapes from laser-induced plasmas, was minimized by preparing the samples with suitable low Nb concentrations in such a way that the effect of self–absorption on the total line width was less than 10 % for each analytical line. The CSigma-LIBS method [14] was used to determine the concentration required to avoid self-absorption of each line. Then, the Stark widths and shifts of the Nb II spectral lines were determined through the study of the temporal evolution of their emission line profiles. The Nb II emission spectra were measured at seven time windows centered at 0.60, 0.74, 1.00, 1.30, 1.80, 3.40, and 7.00 μs. In Fig. 1, the spectra of two Nb II spectral lines at 2697.062 Å (Fig. 1a) and at 3194.972 Å (Fig. 1b) are shown for some representative instants of the plasma evolution. It can be seen that the experimental widths (FWHM) of the lines present a decreasing trend suggesting a corresponding decrease of their Stark widths due to the fast decay of the electron density in time. Different shifts are observed for the two lines of Fig. 1. While a large red shift that decreases with time is observed for the 2697.062 Å Nb II line (Fig. 1a), a small blue shift is noticed for the 3194.972 Å Nb II line (Fig. 1b). These line shifts are also related to the fast variation of the electron density with time.

To determine the Stark widths, the experimental lines have been fitted to Voigt profiles, as done in previous works [17]. However, for the Nb II lines studied here, a difference has been introduced at the time of obtaining the Gaussian component of the Voigt profile. In the measurements of previous works, a fixed Gaussian component was used, associated to the combination of both the instrumental and Doppler widths, which was common for all the measured lines. This Gaussian component was obtained using a late time window, as explained in the experimental section. The Lorentzian component, resulting from the fitting of the profile at a certain delay, is related to the Stark width to be determined. However, for Nb II, the lines show at the late time window an additional broadening to the instrumental and Doppler widths. Moreover, this extra broadening depends on the concrete line measured. We attribute this extra broadening to the hyperfine structure (hfs),

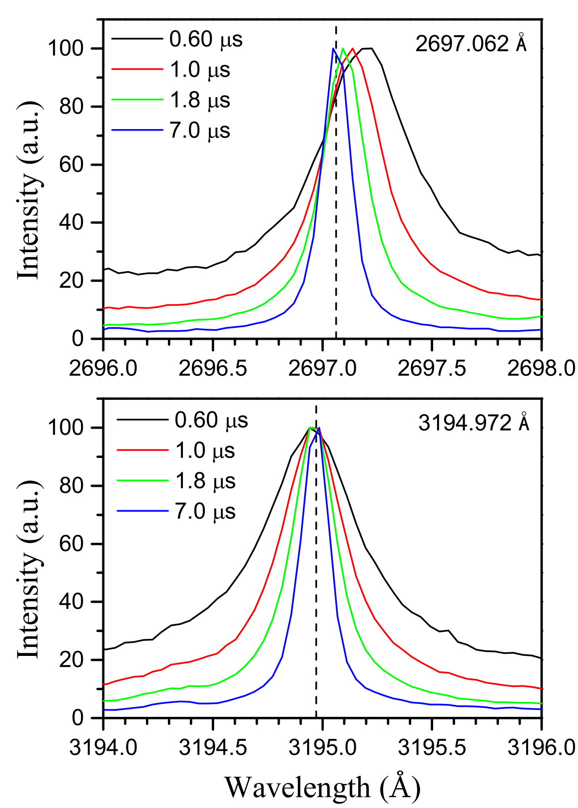

Fig. 1. Spectra of the Nb II lines at 2697.062 Å (a) and 3194.972 Å (b), measured at different time windows centered at the indicated times.

which was observed and quantified for Nb II lines by Nilsson and Ivarsson [16]. The nuclear spin of niobium is $I = 9/2$ and, as a result, many Nb II lines show line profiles broadened by hfs. We have performed an estimation of the hfs width by comparing the Gaussian components obtained at the late time window for the lines of Nb II at 3094.170 Å and Ti II at 3088.026 Å. According to the $I = 0$ nuclear spin of titanium, we neglect the hfs of Ti II, and the corresponding width for the Nb II line is obtained by quadratically subtracting the Ti II Gaussian width from that of Nb II. The resulting hfs width for the Nb II line at 3094.170 Å is 12 pm, which agrees approximately with the width of almost 20 pm reported in reference [16]. Due to the non-negligible broadening by hfs in Nb II, instead of a fixed Gaussian width, in the present experiment we discount a variable Gaussian width, measured at the late time window for each concrete Nb II line, which accounts for the instrumental, Doppler, and hfs widths. On the other side, for shift measurements, the wavelength of the line peak at the late time window was taken as reference.

Self–absorption entails a reduction of the observed line intensities together with a broadening of the lines. The latter is illustrated in Fig. 2 for the most intense Nb II line measured (3094.170 Å). In fact, it is observed that, for the different times of measurement, the line FWHM divided by the electron density increases with the Nb concentration due to the additional broadening of the line profiles with respect to the optically thin case. Self–absorption is more noticeable at the latest time, a behavior resulting from the combination of two effects: On one side, the drop of the electron density leads to a consequent lower Lorentzian width, resulting in higher self–absorption. On the other side, the ion number density decreases with time, which favors a lower self-absorption. In Fig. 2, we see that, for Nb concentrations equal or less than 0.08 at. per cent, the ratios for the different time windows have the same value within the experimental error, which indicates that the effect of self–absorption on the line shape is minimized.

Figs. 3 and 4 show, as an example, the results obtained for the Stark widths (FWHM) and shifts, respectively, as a function of the electron density, for the Nb II lines at 2697.062 Å and 3194.972 Å, the same whose line profiles are shown in Fig. 1. In both plots, a proportionality relationship between the line width/shift and the electron density was found, as well as for all the investigated Nb II lines. Thus, the known relationship between temperature and Stark broadening is not observed for our experimental temperature range. Therefore, the final results for the Stark widths and shifts are given by the corresponding slopes of the linear fittings of the experimental data at a reference electron density of 10^{17} cm^{-3}.

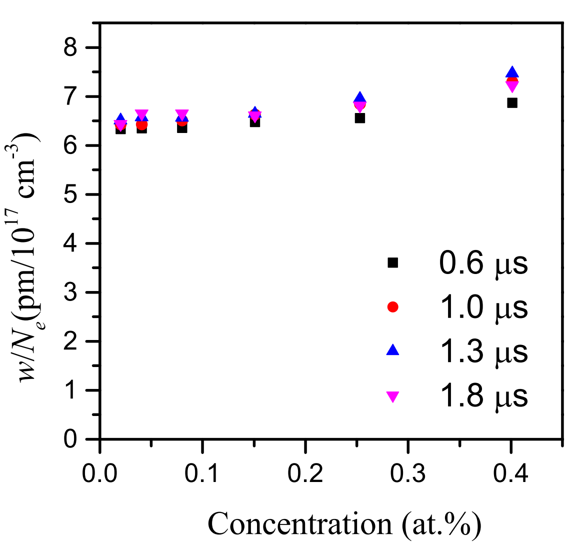

Fig. 2. Ratio of the line width to the electron density as a function of niobium concentration for the Nb II line at 3094.170 Å measured at different time windows centered at the indicated times.

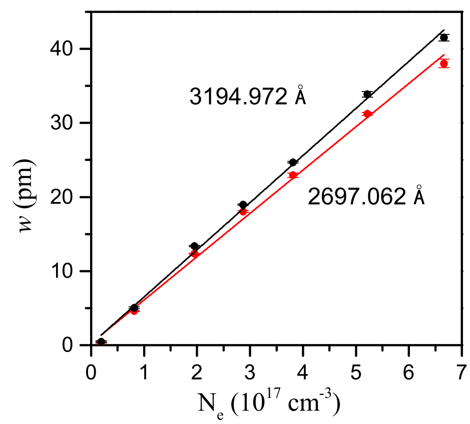

Fig. 3. Line width (FWHM) vs. electron density for Nb II lines. The error bars represent the standard deviation of the average for five repeated measurements. The Stark widths are determined as the slopes of the linear plots.

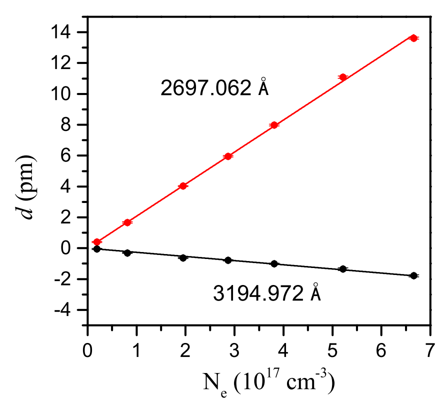

Fig. 4. Line shift vs. electron density for Nb II lines. The error bars represent the standard deviation of the average for five repeated measurements. The Stark shifts are determined as the slopes of the linear plots.

The experimental Stark widths and shifts measured in this work are reported in Table 1, where 26 and 22 parameters, respectively, are ordered by transition. For those lines for which the Stark shift is not provided, the absolute value of d is lower than 0.05 pm. Table 2 has been added to provide fast track of the lines. These results include spectral lines from transitions between 10 multiplets and 3 configurations, with upper energy levels in the range 4.3–5.9 eV and lower energy levels in 0–2.5 eV. This implies strong and weak lines, measured with negligible self-absorption. The obtained values have variations lower than 10 % between transitions from the same multiplets. Our results for the Stark widths of the lines at 3194.970 Å and 3225.475 agree with those reported by Hermann et al. [3] within the experimental errors. To our knowledge, there are no theoretical data in the literature to be compared to our results. The width estimated by Lakićević [2] is higher than our measurement by a factor of 3. No comparison is made for shift as only an absolute value was estimated by this author.

The experimental error of w and d, indicated in Table 1, has been obtained as the quadratic composition of the uncertainty in the measurement of the electron density (11 %), the error due to the remaining self-absorption (10 %), the error due to the inhomogeneity of the plasma (3 %), and the statistical error. The latter is estimated as the standard deviation (SD) of the slope of the linear fitting which provides the parameter. For w, the SD is small, in the range 1–5 %, which leads to a common total error of about 15 % for all reported w data. In the case of d, self-absorption is not included in error estimation, as it does not cause additional shift of the lines. A minimum absolute error of 0.05 pm is

Table 1
Stark widths and shifts (pm) of Nb II spectral lines at electron density 10^{17} cm^{-3}. Temperature ranged from 10,100 to 16,700 K. The estimated errors are indicated. The minimum absolute error for shifts is 0.05 pm.

No	Transition[a]	Multiplet[a]	λ(Å)[a]	*w*	*d*	*w*[c]	*w*[d]	*d*[d]
1	$4d^4$ – $4d^3(^4F)$ 5p	^5D -$^3D^o$	2768.124	5.5 ± 0.9	1.99 ± 0.21			
2		^5D -$^5D^o$	2697.062	5.8 ± 0.9	2.08 ± 0.24			
3	$4d^3(^4F)$ 5 s - $4d^3(^4F)$ 5p	^5F -$^5G^o$	3094.170	6.5 ± 1.0	0.20 ± 0.02			
			3130.780[b]	6.5 ± 1.0				
			3163.398	6.4 ± 1.0	−0.16 ± 0.02			
			3194.970	6.4 ± 1.0	−0.27 ± 0.03	7		
			3225.475	6.6 ± 1.0	−0.22 ± 0.03	7	20	4
			3215.591	6.9 ± 1.0	−0.07 ± 0.01			
			3254.065	7.2 ± 1.1	−0.24 ± 0.03			
4		^5F -$^3D^o$	3028.433	6.4 ± 1.0	−0.23 ± 0.03			
5		^5F - $^5F^o$	2950.878	5.9 ± 0.9	0.17 ± 0.02			
			2941.537	5.5 ± 0.9	0.18 ± 0.02			
			2910.581	6.2 ± 0.9	0.29 ± 0.04			
			2911.738[b]	6.3 ± 1.0				
			2899.229	5.8 ± 0.9	0.12 ± 0.02			
			2897.801	6.1 ± 0.9	0.24 ± 0.03			
6		^5F -$^5D^o$	2927.808[b]	6.0 ± 0.9				
			2883.170[b]	5.9 ± 0.9				
			2875.387	5.9 ± 0.9	0.11 ± 0.02			
			2868.519	5.9 ± 0.9	0.10 ± 0.02			
7	$4d^4$ – $4d^3(^4F)$ 5p	$^3F2$ -$^3G^o$	3145.404	7.3 ± 1.1	1.62 ± 0.19			
			3180.283	8.3 ± 1.3	1.40 ± 0.16			
			3206.342	7.6 ± 1.2	1.42 ± 0.16			
8	$4d^4$ – $4d^3(^2H)$ 5p	^3H - $^3H^o$	2590.940	5.1 ± 0.9	1.81 ± 0.21			
9	$4d^3(^4P)$ 5 s - $4d^3(^4P)$ 5p	^5P -$^5D^o$	2972.564	6.1 ± 1.0	0.43 ± 0.05			
10		^5P - $^5P^o$	2990.282	6.7 ± 1.0	0.08 ± 0.02			

[a] Data from Kurucz and Bell [18].
[b] The absolute value of the Stark shift for these lines is lower than 0.05 pm.
[c] Hermann et al. [3].
[d] Lakicević [2]. Values normalized to an electron temperature of 20,000 K. Absolute value for the shift data.

Table 2
List of lines with reported Stark width or shift, ordered by wavelength and with multiplet number for faster location in Table 1.

λ (Å)	No
2590.940	8
2697.062	2
2768.124	1
2868.519	6
2875.387	6
2883.170	6
2897.801	5
2899.229	5
2910.581	5
2911.738	5
2927.808	6
2941.537	5
2950.878	5
2972.564	9
2990.282	10
3028.433	4
3094.170	3
3130.780	3
3145.404	7
3163.398	3
3180.283	7
3194.970	3
3206.342	7
3215.591	3
3225.475	3
3254.065	3

considered for *d*, due to the resolution of the measurement of the central wavelength. The SD for *d* has a wide variation from 0.5 % to 25 % depending on the line considered, the higher standard deviations corresponding to the very small shifts which could be measured.

4. Conclusions

We provide experimental Stark widths and shifts for Nb II lines, which have been measured by LIBS using samples prepared by lithium borate fusion. The small concentrations of niobium in the samples, determined by the CSigma-LIBS methodology, has allowed to minimize the systematic error due to self-absorption. The spectral resolution of the system has been enough to observe a non-negligible broadening due to the hyperfine structure, which has been discounted in the measurements.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sab.2025.107337.

CRediT authorship contribution statement

J. Manrique: Writing – original draft, Methodology, Investigation, Formal analysis. **D.M. Díaz Pace:** Writing – original draft, Methodology, Investigation, Formal analysis. **J.A. Aguilera:** Writing – original draft, Software, Methodology, Investigation, Formal analysis. **C. Aragón:** Writing – original draft, Software, Methodology, Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

In this work, we report measurements of Stark widths and shifts of Nd II spectral lines, performed by laser-induced breakdown spectroscopy. The results obtained are new and have not been published previously.

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Data availability

Data will be made available on request.

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