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Stark broadening measurements in plasmas produced by laser ablation of hydrogen containing compounds☆

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ABSTRACT

We present a method for the measurement of Stark broadening parameters of atomic and ionic spectral lines based on laser ablation of hydrogen containing compounds. Therefore, plume emission spectra, recorded with an echelle spectrometer coupled to a gated detector, were compared to the spectral radiance of a plasma in local thermal equilibrium. Producing material ablation with ultraviolet nanosecond laser pulses in argon at near atmospheric pressure, the recordings take advantage of the spatially uniform distributions of electron density and temperature within the ablated vapor. By changing the delay between laser pulse and detector gate, the electron density could be varied by more than two orders of magnitude while the temperature was altered in the range from 6,000 to 14,000 K. The Stark broadening parameters of transitions were derived from their simultaneous observation with the hydrogen Balmer alpha line. In addition, assuming a linear increase of Stark widths and shifts with electron density for non-hydrogenic lines, our measurements indicate a change of the Stark broadening-dependence of H_α over the considered electron density range. The presented results obtained for hydrated calcium sulfate ($CaSO_4{\cdot}2H_2O$) can be extended to any kind of hydrogen containing compounds.

1. Introduction

Stark broadening of spectral lines is under investigation since the discovery of the effect in 1913. With the diversification of the available plasma sources and the increasing interest for plasma diagnostic tools, the theoretical and experimental studies dedicated to Stark broadening became popular in the 1960s [1,2]. Since that time, several review papers have been published to summarize the results obtained by a large number of research groups all over the world [3–7]. Despite of the numerous efforts in the past decades, precise Stark broadening parameters are still only partially available, even for the most prominent transitions. This is mainly due to the difficulties of calibrating the Stark broadening measurements using an alternative and independent measurement method. Recently, Thomson scattering was applied to measure electron density and temperature in laser-produced plasmas [8,9]. However, the application of this method to high-density thermal plasmas is doubtful due to electron heating by the probe laser radiation. From the theoretical point of view, there does not exist any model that enables accurate calculations of Stark broadening over a large electron density range, as illustrated by Griem for H_α [10].

The lack of accurate Stark broadening data and the need of further developments in appropriate models motivate the related research in different types of plasmas. With respect to arcs, sparks or other electrical discharges, the plasmas produced by pulsed lasers are historically younger. This is mainly due to the technological development of laser sources: reliable pulsed lasers that generate highly reproducible plasmas are available since the last two decades only. In addition, the small size and the fast expansion dynamics present particular difficulties for plasma diagnostics. With the invention of gated detectors and the development of applications such as laser-induced breakdown spectroscopy (LIBS), the investigation of plasmas produced by pulsed laser ablation stimulated a strongly growing interest in the past years. The small size and the large initial density now appear as advantages, since the former property limits the optical thickness of plasma emission, and the latter feature favors the establishment of local thermal equilibrium [11,12].

The expansion dynamics of plasmas produced by laser ablation strongly depend on the irradiation conditions and the surrounding atmosphere. The use of infrared radiation favors the absorption of laser photons by the background gas, leading to an elongated shape of the plasma [13]. This condition enables rapid intermixing of the ablated vapor with the surrounding atmosphere [14]. Contrarily, the use of shorter wavelength radiation increases the laser-material energy coupling. The plasma screening effect [15,16] is reduced, and the plasma is characterized by a hemispherical shape [17]. If, in addition to the use of the short laser wavelength, the ablation process occurs in an argon atmosphere, the ablation plume appears spatially almost uniform.

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This was illustrated by the analysis of the spectral shapes of resonance lines and strongly Stark-shifted transitions [18].

Stark broadening parameters of calcium lines are of interest to laboratory plasma diagnostics, as well as for theoretical modeling. In LIBS plasmas for example, Ca is often present as an impurity. Also, due to its large abundance all over the universe, calcium presents a constituent of many stellar plasmas, and Ca and Ca^+ lines are of a great importance in astrophysics [19]. The most intense lines and in particular the ionic resonance lines were investigated extensively in the past [20–31]. The resonance lines are generally strongly self-absorbed, and their practical usage for plasma diagnostics is often doubtful. Stark broadening calculations, based on the semiclassical perturbation formalism, have been performed for many Ca [19,32] and Ca^+ transitions [33,34]. The correlation of Stark broadening with the energy gap between the upper-level of the transition and the ionization potential was also investigated [35]. However, Stark parameters of many Ca transitions in the visible and UV ranges are still missing in literature.

In the present work, we take advantage of the spatially uniform character of the plasma produced by UV nanosecond laser ablation in argon at near atmospheric pressure. Samples of hydrated calcium sulfate were ablated to obtain spectral line emission from hydrogen, calcium, oxygen and several impurities. Comparing the measured emission spectrum to the spectral radiance computed for a uniform plasma in local thermodynamic equilibrium, we were able to characterize the plasma and to deduce the Stark broadening parameters for many atomic and ionic lines. With respect to the traditional methods based on space-resolved spectroscopic measurements and complex data analysis via Abel inversion [20, 28,36], the presented method appears easier to handle and gives rapid access to a large number of data. Indeed, using an echelle spectrometer of large resolving power, the recording of a few spectra at different delays enables the determination of Stark broadening parameters of a large number of spectral lines.

2. Method and calculation details

2.1. Principle of Stark broadening measurements

The method for the measurement of Stark broadening parameters consists of the following three successive steps: (i) the plasma temperature T, the electron density n_e, and the relative fractions of elements C were deduced for spectra recorded at different times (delay between laser pulse and detector gate) using the iterative procedure described in Ref. [37]. Here, n_e is deduced from H_α for which accurate electron density measurements are expected for n_e-values of the order of 10^{17} cm^{-3} [10]; (ii) Once the plasma is characterized, the Stark widths and shifts of non-hydrogenic lines are deduced from best agreement between measured and computed spectra. The plasma being characterized previously, the calculation of the line profiles accounts for Doppler- and resonance broadening; and (iii) The Stark broadening parameters w and d of the non-hydrogenic lines were deduced from the linear increase of Stark width and shift with n_e.

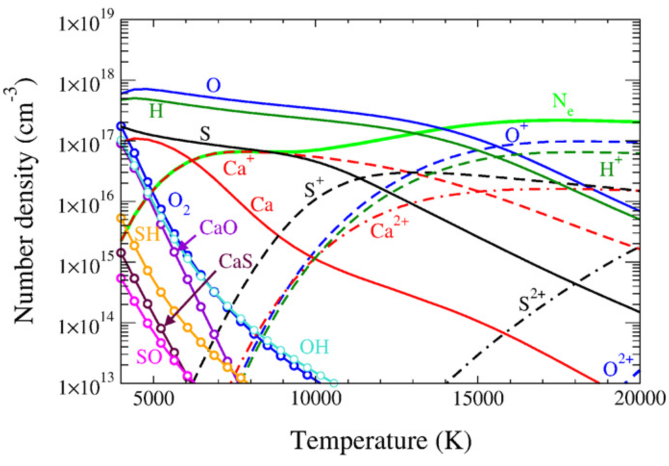

Fig. 1. Number densities of species versus temperature computed for a $CaSO_4 \cdot 2H_2O$ plasma in LTE at atmospheric pressure.

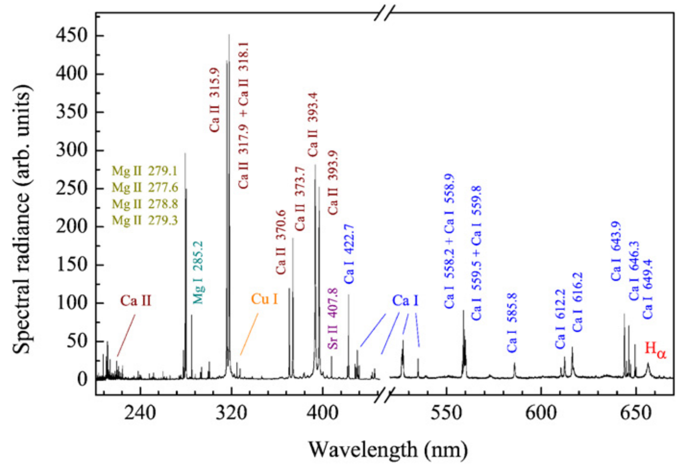

Fig. 2. Spectrum recorded during ablation of hydrated calcium sulfate for $t = (475 \pm 75)$ ns.

2.2. Calculation details

Material ablation with pulsed lasers in a background gas at near atmospheric pressure leads to almost hemispherical expansion if the interaction of the laser beam with the gas is negligible, and the laser spot diameter is small compared to the plasma radius. In that case, the blast wave model may be applied to describe the plume expansion dynamics. The conditions are fulfilled for ultraviolet nanosecond laser pulses [13,17]. If argon is used as a buffer gas, the spatial distributions of electron density and temperature within the ablated vapor are almost uniform and the spectral radiance of the plasma can be calculated using [37]

$$I_\lambda = U_\lambda (1 - e^{-\alpha L}), \quad (1)$$

where U_λ is the black-body spectral radiance, L is the plasma diameter along the observation direction, and α is the absorption coefficient given by [1]

$$\alpha(\lambda) = \pi r_0 \lambda^2 f_{lu} n_l P(\lambda) \left(1 - e^{-hc/\lambda kT}\right). \quad (2)$$

Here, r_0 is the classical electron radius, λ is the wavelength, h is the Planck constant, c is the vacuum light velocity, k is the Boltzmann constant, f_{lu} and n_l are the absorption oscillator strength and the lower

Table 1
Atomic fractions of the constituents of the hydrated calcium sulphate pellet deduced from the LIBS spectra C_{LIBS}. The reference values C_{ref} correspond to the chemical formula $CaSO_4 \cdot 2H_2O$.

Elmnt.	C_{LIBS}(%)	C_{ref}(%)
Ca	9.1	8.3
S	8.3	8.3
O	47	50.0
H	35	33.3
Cu	0.04	–
Fe	0.014	–
Li	0.017	–
Mg	0.4	–
Si	0.08	–
Sr	0.012	–