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Method for measurement of transition probabilities by laser-induced breakdown spectroscopy based on CSigma graphs–Application to Ca II spectral lines

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ABSTRACT

We propose a method for determination of transition probabilities by laser-induced breakdown spectroscopy that avoids the error due to self-absorption. The method relies on CSigma graphs, a generalization of curves of growth which allows including several lines of various elements in the same ionization state. CSigma graphs are constructed including reference lines of an emitting species with well-known transition probabilities, together with the lines of interest, both in the same ionization state. The samples are fused glass disks prepared from small concentrations of compounds. When the method is applied, the concentration of the element of interest in the sample must be controlled to avoid the failure of the homogeneous plasma model. To test the method, the transition probabilities of 9 Ca II lines arising from the 4d, 5s, 5d and 6s configurations are measured using Fe II reference lines. The data for 5 of the studied lines, mainly from the 5d and 6s configurations, had not been measured previously.

1. Introduction

Accurate data for transition probabilities of spectral lines of neutral and ionized atoms are necessary for the diagnostics of different types of plasmas, including astrophysical, laboratory, fusion and industrial plasmas. From a theoretical point of view, transition probability calculations are very sensitive to the interaction schemes used, so experimental data allow testing the validity of the atomic structure models. However, for many atoms and ions, the available data are scarce or suffer from high uncertainty.

Ionized calcium has been used in astrophysical observations from galaxies, interstellar gas clouds, stars [1,2] and meteors [3], mainly the relevant H and K lines. Laboratory experiments involving transitions between the low energy levels of the Ca II have been recently used to study the optical frequency standard and quantum information processing [4,5]. Previous values of transition probabilities of Ca II were firstly obtained by Gallagher [6] for three spectral lines arising from the 4p level introducing atomic vapours into an argon discharge. Branching ratios precision measurements were performed for the same lines by Gerritsma et al. [7] with a single calcium ion suspended in a linear Paul trap. The only experimental measurements found in the literature for other lines were carried out by Andersen et al. [8] using the beam-foil technique to obtain oscillator strengths including 4d, 5s and 5d levels in the Ca

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II spectrum. Although there is a shortage of experimental data, theoretical calculation of transition probabilities of Ca II has received a considerable effort due to its quasi-hydrogenic nature. There is good agreement between works only related to the lower levels [9,10] whilst several theoretical approaches have been used with different agreement for calculations including higher energy levels. Biemont [11] obtained new oscillator strengths for the potassium isoelectronic sequence by Hartree–Fock wavefunctions. A relativistic pseudopotential approach was employed by Hafner and Schwarz [12] whereas a core polarization potential was tested by Laughlin [13]. Meléndez et al. [14] concluded, by using the Thomas–Fermi–Dirac central potential method, that polarization interaction can affect the oscillator strength by up 12%. Mitroy and Zhang [15] employed the semiempirical approach whilst a systematic study of the ionized calcium was carried out by Safronova and Safronova [16] using a relativistic high order method. In order to test the different theoretical methods used, a lack of experimental measurements remains, where self-absorption is one of the most important sources of error.

Laser-induced breakdown spectroscopy (LIBS) has been increasingly accepted as a technique suitable for the measurement of atomic data, including transition probabilities [17] and Stark broadening and shift parameters [18]. Two approaches were used in early works for the determination of transition probabilities by LIBS [17]. One of them was based on the measurement of branching ratios from the relative intensities in the LIBS spectra. The absolute transition probabilities were then obtained using experimental lifetimes and line-strength sum rules. In the second approach, a Boltzmann plot is constructed using lines with known transition probabilities from the literature. Then, the absolute transition probabilities of the lines of interest are deduced from the Boltzmann plot and the measurement of the corresponding line intensity. This method relies on the existence of local thermodynamic equilibrium in the plasma, whose excitation temperature is determined. The two methods described require that the lines used are emitted in optically thin conditions. Generally, this requirement is not easily accomplished in laser-induced plasmas, which are sources characterized by a high density. The usual method to ensure optically thin conditions consists in reducing the concentration of the emitting element in the sample and performing an estimation of self-absorption. However, the suitable concentration is different for each of the lines of interest, as self-absorption depends on the line intensity and line width. In previous works [19,20], our group has determined transition probabilities by LIBS using a method that avoids self-absorption, based on the measurement and calculation of curves of growth. This method requires the knowledge of transition probabilities and Stark widths for a group of lines of the atom or ion investigated. From the curves of growth of these lines, the plasma is characterized by a small set of parameters and then the oscillator strengths of the lines of interest are determined by fitting their experimental curves of growth. A disadvantage of this method is the need for a relatively wide set of samples of known concentrations. Also, characterization is performed from several curves of growth of different lines, which implies a certain complexity in the fitting process.

In a recent work [21], our group has introduced $C\sigma$ graphs as generalized curves of growth, which allow including several lines of various elements in the same ionization state at different concentrations. In [21], $C\sigma$ graphs are proposed as a new approach for plasma characterization in LIBS. In the present work, we describe a method for measurement of transition probabilities based on $C\sigma$ graphs. This method aims at avoiding self-absorption in the measurement and overcoming the drawbacks of our previous approach based on conventional curves of growth. To test the method, transition probabilities of Ca II lines are measured and the results are compared to available values in the literature.

2. Measurement procedure

2.1. *Cσ graphs*

The method for plasma characterization based on $C\sigma$ graphs was described in detail in our previous work [21], so only the main definitions and equations are recalled here. By integrating the radiative transfer equation for a homogeneous plasma in local thermodynamic equilibrium, the following expression is obtained for the wavelength-integrated line intensity

$$I = \beta A L_P \int_{\text{line}} \left(1 - e^{-\tau(\lambda)}\right) d\lambda = \beta A L_P \int_{\text{line}} \left(1 - e^{-k'(\lambda) l}\right) d\lambda, \quad (1)$$

where A is the transverse area of the region of the plasma whose emission is detected, β is the instrumental factor of the system, $L_P = L_P(\lambda_0, T)$ is the Planck radiance of a blackbody, considered constant in the integration over the line profile and calculated at the plasma temperature T and at the central wavelength λ_0 of the transition, $\tau(\lambda)$ is the optical depth, $k'(\lambda)$ is the effective absorption coefficient and l is the length of the plasma along the line-of-sight. Two assumptions are made at this point: the laser-induced plasma is formed only by neutral atoms and singly-charged ions and the stoichiometry in the ablation process is maintained. With these assumptions, the optical depth may be factorized as follows

$$\tau(\lambda) = C\, Nl\, k_t r_i\, V(\lambda) \quad (2)$$

where C is the concentration of the emitting element in the sample expressed as atomic fraction (at/at), N is the total density in the plasma and $V(\lambda)$ is the line profile, which is described by Voigt profile. The remaining two factors in Eq. (2) have been defined as follows. On one side, the coefficient $k_t(T)$ for a transition, dependent on the atomic data of the transition and the temperature, is defined by

$$k_t = \frac{e^2 \lambda_0^2}{4\varepsilon_0 m c^2} f \frac{g_i e^{-\frac{E_i}{kT}}}{U_\alpha^z(T)} \left(1 - e^{-\frac{E_k - E_i}{kT}}\right), \quad (3)$$

where e is the elementary charge, ε_0 is the permittivity of free space, m is the electron mass, c is the speed of light in vacuum, f is the transition oscillator strength, g_i is the degeneracy of the lower energy level, E_i, E_k are the energies of the lower and upper energy levels respectively, k is the