MERLIN, AN RT-LTE SOFTWARE SUPPORTING THE DIAGNOSTIC APPLICATION OF LIBS TO H-ISOTOPE MEASUREMENTS

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1. INTRODUCTION

Laser-induced plasmas can be used to determine the multi-elemental composition of solid, liquid or gaseous samples. Using a pulsed laser beam focused on the sample, the resulting absorption leads to a temperature increase of several 10,000 K [Morel 2016], therefore to a neutral phase to plasma transition. During the relaxation phase over which the recombination takes place, a continuum then lines radiation is emitted. Its analysis based on Optical Emission Spectroscopy (OES) may lead to the composition of the plasma if fundamental assumptions are fulfilled [Morel 2015]. The most restrictive one is the achievement of the Local Thermodynamic Equilibrium (LTE). The characterization of LTE is therefore one of the key points of this analysis method, also known as Laser-Induced Breakdown Spectroscopy (LIBS) [Mizolek 2006].

A high electron density n_e in the plasma ensures an important collision frequency which permits a satisfactory coupling between electrons and heavy particles. LTE is then achieved which allows a synthetic spectrum computation. The composition is then derived from the comparison between the computed and experimental spectra by an iterative procedure. The reliability of such a determination is directly linked to the quality of experimental data but also to the computational process itself (broadening effect and/or homogeneity).

MERLIN (MultiElemental Radiative equiLibrIum emissioN) has been developed to support OES interpretation and more particularly laser-induced experiments. This software computes equilibrium composition to generate the corresponding emission spectrum of any input mixture through a radiative transfer (RT) calculation. The user has a large set of input possibilities such as choosing input species, enabling different physical broadening effects or even choosing the spectral database used for computation. For this communication, a specific application of MERLIN devoted to LIBS H-isotopes measurements in gaseous, porous and metallic media is presented.

2. DESCRIPTION OF MERLIN

The computation of equilibrium composition is based on a fictitious chemical kinetics (for which the detailed balance principle is assumed). The final result is derived from solving a coupled system of differential equations obtained from equilibrium laws (mass action, Saha for ionization and Guldberg & Waage for dissociation). The system is bounded by user inputs: ionization degree and species length have to be given. The software automatically requests necessary data (ionization, dissociation potentials and partition function) online. A temperature looped computation enables the obtention of the mixture composition at fixed pressure.

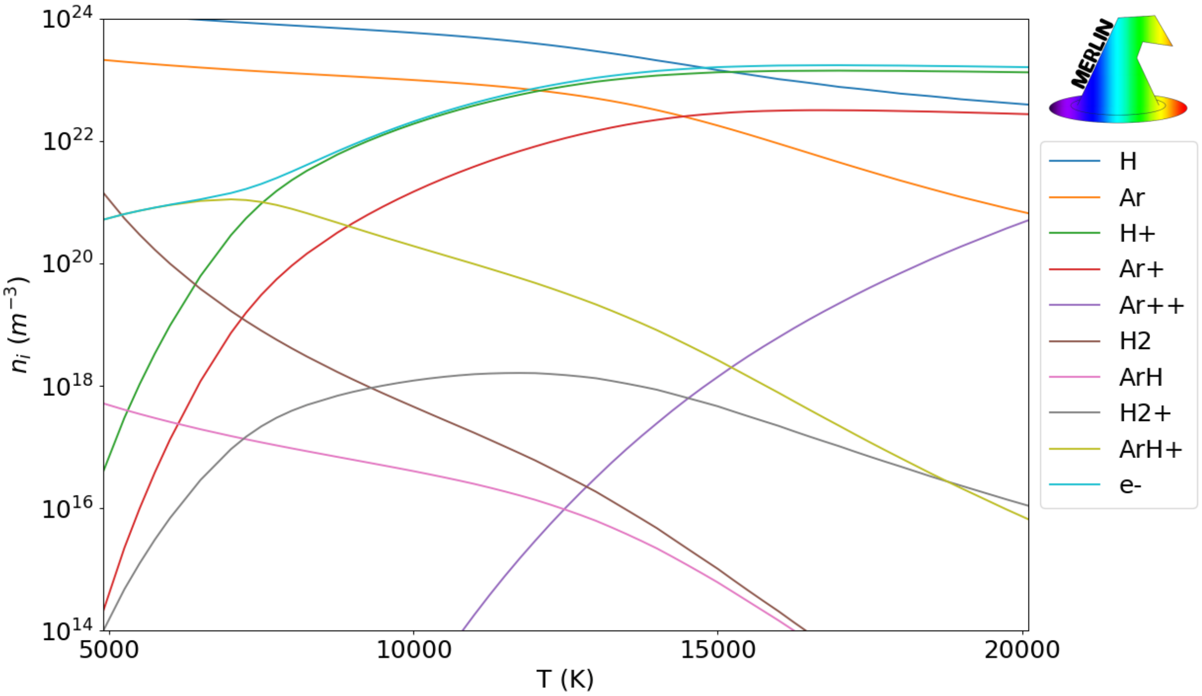

Figure 1. Composition of 0.25Ar - 0.75H_2 (expressed in mole fractions) mixture at equilibrium versus temperature at atmospheric pressure.

An example of this procedure is given for a 0.25Ar - 0.75H_2 mixture in **Figure 1.** [Liu 2009, Stancil 1994, Maltsev 2019, Capitelli 2012]. MERLIN shows a satisfactory agreement with similar published compositions computed by Fauchais *et al.* [Fauchais 1994]. This explains why neutral species remain dominant for T < 12 000 K. Also, for higher temperature the ionization degree increases, which leads to H^+, Ar^+ and Ar^{2+} formation. A competition between ionization and dissociation for H_2^+ is observed through a non-monotonic evolution with temperature.

3. RESULTS AND DISCUSSION

Nowadays research and environmental politics agree to say that hydrogen is an element of interest for the future of humankind for many reasons. First, hydrogen isotopes are nuclear fusion reaction fuels which can be considered as tomorrow's energy. Second, it allows a carbon and NOx free combustion. In addition to this, hydrogen is often used for instance in industrial processes such as plasma vapor deposition, ceramic treatment or even fundamental research studies. We propose here to describe its emission into plasmas obtained from gas, porous substrates or even metallic samples.

Every spectrum presented below have been computed considering no Van Der Waals or Doppler broadenings. Also, the apparatus function has been fixed to a nominal lorentzian distribution with 0.0145 nm as FWHM (Full Width at Half Maximum), which corresponds to our experimental conditions. Concerning the Stark broadening, the FWHM are fixed as follows (respectively Mijatovic *et al.* [Mijatovic 2020], Fantoni *et al.* [Fantoni 2017]):

$$\Delta_{H-Stark}^{Lorentz} = 1.098 \left(\frac{n_e\ (\mathrm{m}^{-3})}{10^{23}} \right)^{0.67965} \quad \mathrm{nm}$$

$$\Delta_{other-Stark}^{Lorentz} = 2\ \omega_S(T)\ \frac{n_e\ (\mathrm{m}^{-3})}{n_{e,ref}}\ \mathrm{nm}$$

$$\omega_S(T) = 4.8767 \times 10^{-4} + 1.6385 \times 10^{-8} T - 1.8473 \times 10^{-13} T^2$$

Of course, this default correlation can reveal unsubstantial compared to published electron impact parameters and it can be mandatory to inject measured values to obtain realistic Stark broadenings. But this communication only aims to claim the purpose of numerical tools to support experimental LIBS measurements.

3.1. Gas mixture: H mole fraction influence in Ar-H_2 mixture

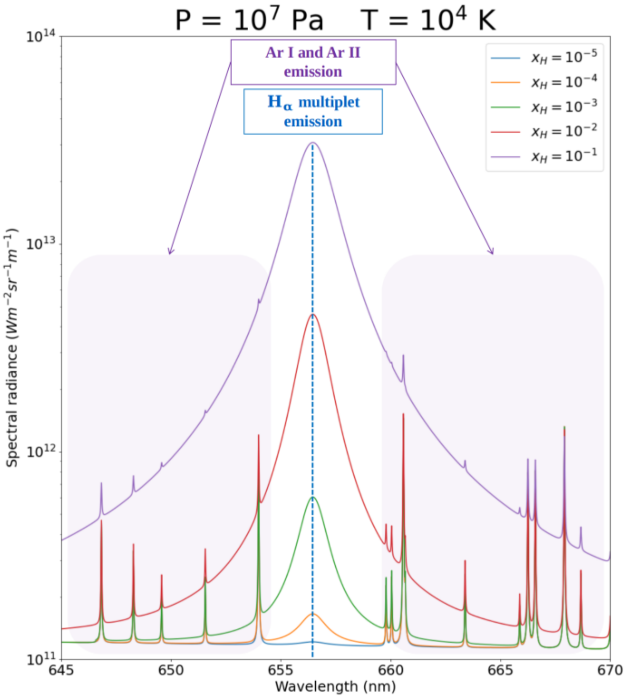

Figure 2. Equilibrium emission spectrum of an Ar - H_2 mixture diluted at X_H mole fraction of hydrogen.

Experimentally, argon is often used as surrounding gas for LIBS experiments because of its spectral data in addition to its high confinement capacity resulting from its atomic mass. As gaseous H-retention, we have chosen to present the emission of an Ar-H_2 mixture with variable H dilution (see **Figure 2.**).

These results are obtained by fixing the plasma pressure at $P = 10^7$ Pa and the temperature at $T = 10^4$ K. Namely, H dilution leads to a stronger H_α emission. Diluting also appears to lead to greater n_e values characterized by a strong Stark broadening.

3.2. Porous substrate: temperature influence in zeolite-like structure

Zeolites are crystal lattices which are mainly composed of gaps. This results to a porous material able to capture light species like hydrogen. Several studies are linked to hydrogen retention in those materials which appear to be a reliable solution to hydrogen storage. The LIBS hydrogen probing in such matrices can be used to estimate the capture efficiency. Different computations for a special zeolitic structure have been made at atmospheric pressure (see **Figure 3.**).

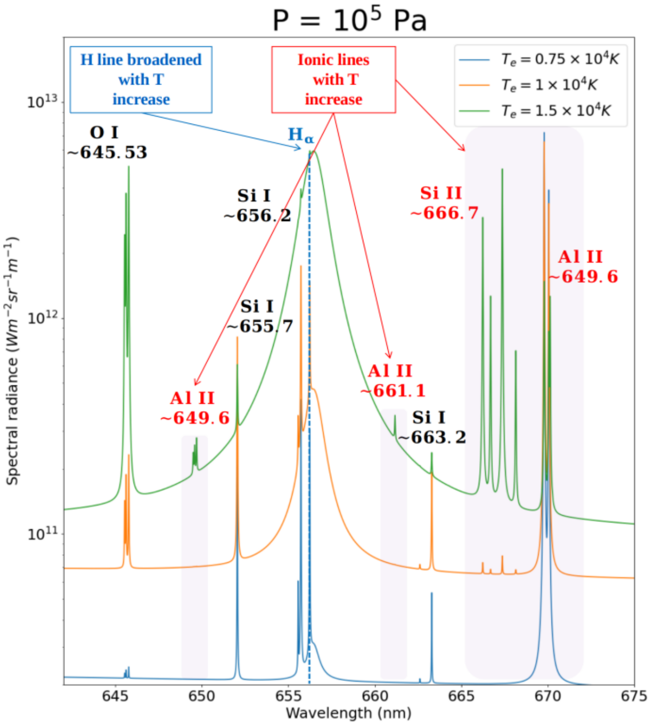

Figure 3. Equilibrium emission spectrum of zeolite-like (0.087H / 0.087Al / 0.217Si / 0.609O) structure versus plasma temperature.

The studied zeolite composition is 0.087H / 0.087Al / 0.217Si / 0.609O without any retention. A temperature increase leads to a higher ionization degree: this is directly observable through the appearance of Al II (around 649.6 nm, 661.1 nm and 649.6 nm) and Si II (around 666.7 nm) lines. In terms of composition, a significative n_H decrease is noticed. In addition, at low temperature, the hydrogen LIBS diagnostic is perturbed by

S I lines around 656.2 nm: probing another Balmer line is therefore requested if the diagnostic is performed in the visible spectral range.

3.3. Metallic samples: H/D mole fraction ratio influence in bulk tungsten

Hydrogen isotopes are used as fuels in nuclear fusion reaction. In a tokamak, a strong magnetic field is used to avoid a contact between the fusion plasma and machine walls (the term «magnetic confinement» is commonly used). The lower part of the tokamak, also named divertor, is more exposed to radiation and high flux density. Divertors are made in tungsten due to its high fusion temperature and its mechanical properties. The LIBS detection of hydrogen and/or deuterium retention in metallic heavy matrix such as tungsten is challenging: since low permeation factor and screening effect due to mass difference increase the limit of detection. We have performed calculations of the resulting emission of a 0.99 W / 0. 01(H-D) plasma with variable light elemental mole ratio (see **Figure 4.**).

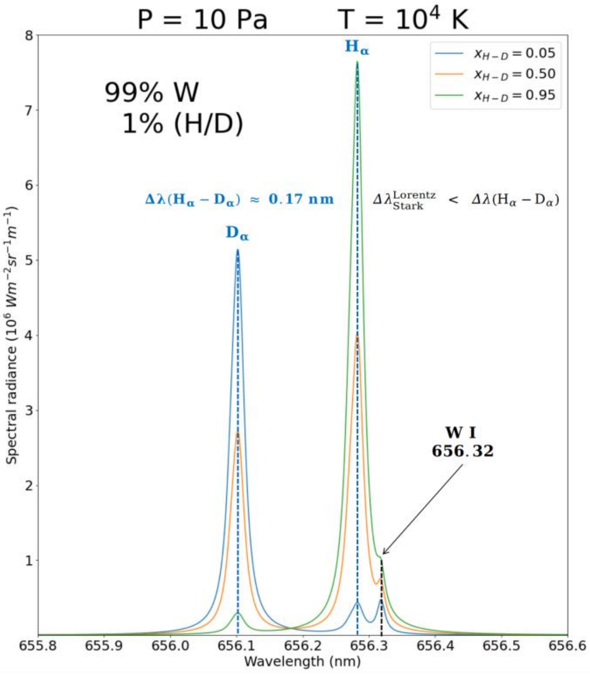

Figure 4. Equilibrium emission spectrum of H/D retention in bulk W (0.99 W / 0. 01(H-D).

A particular attention has to be paid to the spectral scale. In fact, the isotopic shifting of H and D Balmer-α lines is about 0.17 nm. Experimentally, it does not appear to be a limitation as long focal or high gratings spectrometers allow such a resolution with no particular problem. The main issue is residing in broadening which can hardly be as weak as shown on **Figure 4**. Indeed, inner plasma pressure cannot be as low as 10 Pa. Another limitation is due to the perturbation of a W I line emitting at 656.32 nm. In addition to this, a major probing issue is linked to light element concentration profile which is particularly low (the per cent is the order of magnitude) in surface and becomes tinier in a volumic point of view. All of those make the H_α and D_α tricky to detect in a bulk W matrix. Fortunately, many alternatives can be explored to probe light element in a heavy matrix (VUV H-isotopes Lyman series, stronger H/D concentrations or even implantation in another matrix such as Al with no line around 656.3 nm).

4. CONCLUSIONS

MERLIN has been presented as a relevant tool in support of experimental laser-induced spectral emission data. The software is able to compute a synthetic equilibrium emission spectrum of any kind of mixture from a known spectroscopic setup (apparatus broadening) in known thermodynamic conditions like (P,T) or (n_i, T), with *i* a user chosen mixture species. This is a valuable indicator concerning the power of resolution or even the observability of a probed species in known plasma conditions.

Different applications of H and its isotopes retention have been developed to show the predictive capabilities of the software. Stark broadening for non-H species has been generalized for the simplicity of presentation but must be precised for a fine spectroscopic analysis or a crossed n_e determination. Such a numerical approach allows to observe a competition between apparatus and Stark broadenings when probing near range lines. It is also indicating the necessary conditions to observe ionic emission of a given species.

The upgrade of MERLIN is planned and includes many incoming features to enhance its prediction quality by implementing potential lowerings, resonant and Zeeman broadenings, non-homogeneous emitting media, better molecular emission support or even multi-temperature support.

5. REFERENCES

[Morel 2016]	V. Morel B. Pérès, A. Bultel, A. Hideur, C. Grisolia, *Phys. Scr.*, T 167 (2016) 014016.
[Morel 2015]	V. Morel, A. Bultel, J. Annaloro, C. Chambrelan, G. Edouard, C. Grisolia, *Spectrochim. Acta B*, 103-104 (2015) 112.
[Mizolek 2006]	A. W. Miziolek V. Palleschi, I. Schechter: Laser-induced breakdown spectroscopy, Fundamentals and Applications, *Cambridge University Press*, 2006.
[Liu 2009]	J. Liu E. J. Salumbides, U. Hollenstein, J. C. J. Koelemeij, K. S. E. Eikema, W. Ubachs, F. Merkt, *J. Chem. Phys., 130 (2009) 174306*.
[Stancil 1994]	P. Stancil, *Astrophys. J., 430 (1994) 360*.
[Maltsev 2019]	M. A. Maltsev, I. V. Morozov, E. L. Osina, *TVT,* 57 (2019) 367.
[Capitelli 2012]	M. Capitelli G. Colonna, A. D'Angola: Fundamental aspects of plasma chemical physics, *Springer*, 2012.

[Fauchais 1994] M. I. Boulos, P. Fauchais, E. Pfender: Thermal plasmas - Fundamentals and applications, *Springer*, 1994.

[Mijatovic 2020] Z. Mijatovic, S. Djurovic, L. Gavanski, T. Gajo, A. Favre, V. Morel, A. Bultel, *Spectrochim. Acta B*, 166 (2020) 105821.

[Fantoni 2017] R. Fantoni, S. Almaviva, L. Caneve, F. Colao, G. Maddaluno, P. Gasior, M. Kubkowska, *Spectrochim. Acta B*, 129 (2017) 8.