Spectroscopic analysis of coal plasma emission produced by laser ablation

Análisis espectroscópico de un plasma de carbón producido por ablación láser

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ABSTRACT: An analysis of plasma produced by laser ablation using 1,064 nm of laser radiation from a Q-switched Nd:YAG on coal mineral samples under air ambient, was performed. The emission of molecular band systems such as C_2 Swan System $(d^3 \prod_g \rightarrow a^3 \prod_u)$, the First Negative System N_2 (Band head at 501.53 nm) and different emission lines were investigated using the optical emission spectroscopy technique. The C_2 molecular spectra (Swan band) were analyzed to determine vibrational temperature (0.62 eV). The density and electron temperature of the plasma have been evaluated using Stark broadening and the intensity of the nitrogen emission lines (N II). Values of 1.2 eV of electron temperature and 1.82×10^{19} cm^{-3} of electron density were found.

RESUMEN: Se presenta un análisis espectroscópico en aire del plasma producido por la ablación de un láser infrarrojo Nd: YAG con $\lambda = 1.064$ nm sobre carbones provenientes de tres diferentes minas naturales (Santander, Norte de Santander y Cesar) en Colombia. El estudio de la emisión de los sistemas de bandas moleculares como Sistema Swan $C_2 (d^3 \prod_g \rightarrow a^3 \prod_u)$, primer Sistema Negativo N_2 (alrededor de 501,53 nm) y diferentes líneas de emisión atómicas fueron investigados utilizando la técnica de espectroscopia de emisión óptica. Los espectros moleculares C_2 (conocida como banda Swan) se analizaron para determinar la temperatura de vibración (0.62 eV). La temperatura de la densidad de electrones y del plasma han sido evaluadas utilizando el ensanchamiento Stark y la intensidad de las líneas de emisión de nitrógeno (N II). Se encontraron valores de 1,2 eV de temperatura electrónica y $1,82 \times 10^{19}$ cm^{-3} de electrones densidad.

1. Introduction

Laser-produced plasmas are a topic of interest in different fields of science with applications in medicine, astrophysics and synthesis of new materials [1]. In the case of plasmas produced by laser ablation, light energy is used to remove a portion of a sample by melting, fusion, sublimation, ionization, erosion and/or explosion. Several laser ablation-based methods have been implemented such as *laser-induced plasma spectroscopy* (LIPS), *pulsed laser deposition* (PLD) [1]. In laser ablation, most of these molecules are formed in their excited states so that spectroscopic measurements offer an excellent mean to investigate their evolution and dynamics [2].

Optical emission spectroscopy (OES) is a technique where light emitted from the plasma by electronically excited species, is collected and transmitted to a grating spectrometer. This technique allows species identification and as a consequence gives information about the elemental composition of the sample. Carbon molecules are very interesting for their unique and fascinating structural and spectroscopic properties. These molecules are very important in astrophysical processes as well as in combustion and soot formation [3].

Research on coals minerals using technologies based in laser [4, 5] is carried on in order to determine their elemental composition. Therefore, plasma diagnostics of coal mineral can provide valuable information about the reaction mechanisms that are involved in combustion and gasification processes [6]. Otherwise, studies of the influence of sample morphology on laser ablation of coal, comparing both temperature and electron density of the coal plasma with the different particle size have been done [7]. Moreover, morphological changes of pulverized coal have been analyzed in [8]. The authors found that volatile components are increasing as a consequence of the temperature and also due to volatilization time.

The experiment carried out with different mineral coals under laser ablation technique and their corresponding plasma diagnostic, is a new approach to study the processes that are present when coal is pulverized by laser. Besides, the implementation of a cheaper and easier technology

for characterization of the plasma radiation-that is due to carbon-laser interaction is the main contribution of this work. Hence, the importance of the OES technique that was used in the experimental work has been demonstrated. Then, Colombian coal samples were ablated to produce plasma at environmental conditions. The spectra were analyzed to determine both temperature and electron density and also the vibrational temperature.

2. Experimental Setup

Laser ablation was done with a Nd: YAG laser (λ=1,064 nm) with a pulse duration of 9 ns and repetition rate of 10 Hz. The laser beam was focused using glass lens with f = 0.23 m on the target and the laser energy fluence was 7 Jcm^{-2} during 10 min. Experimental targets were coal samples from mines located in Santander, Norte de Santander and Cesar, Colombia. All samples were irradiated in atmospheric air (26 °C and 55% relative humidity). The plume is generated by the laser impact of coal samples as is shown in Figure 1; the detection of plasma emission was performed by means of an optical fiber, which carries the radiation to the spectrometer. The plasma characterization was performed by *optical emission spectroscopy* (OES) using a spectrometer model *Jobin Yvon Triax 550* of 0.55m, f = 6.4 equipped with two gratings of 1200 *l/mm* and 150 *l/mm*, coupled to a model 3000 CCD camera cooled air multi-channel and 512×512 pixels. Calibration measurements were done with the fundamental harmonic of laser. Instrumental resolution of equipment is 0.025 nm and the uncertainty values were taken into account for the analysis.
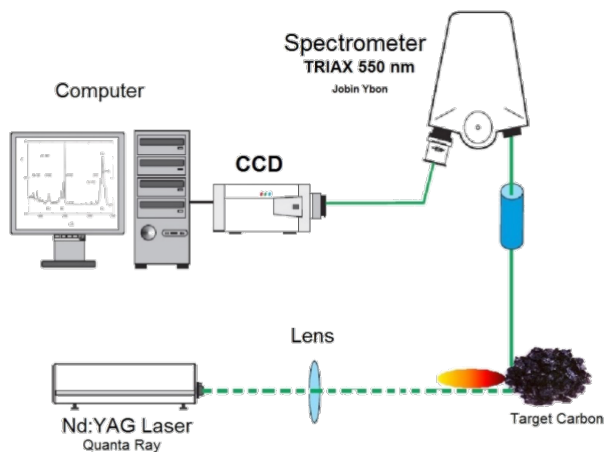

Figure 1 Experimental Setup [9]

3. Results and discussion

Spectral measurements were performed in coal plasma, the electron temperature was evaluated using the relative intensities of the N II, and electron density of plasma with Stark broadening method, and the parameters are available in the literature [10, 11]. Electron temperature determination is shown in Figure 2.
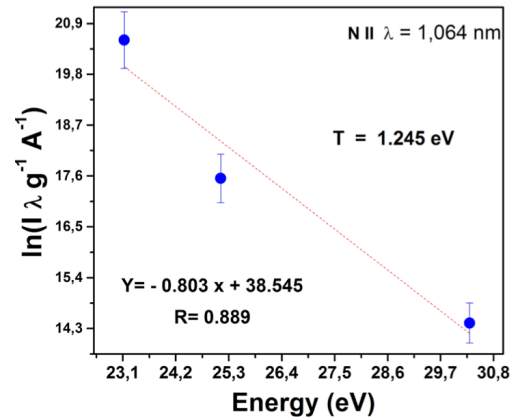

Figure 2 Fitting of data of Table 1 assuming LTE to determine the electron temperature

3.1. Temperature and electron density

Spectroscopic measurements of plasmas produced by ionization in air at atmospheric pressure using nanosecond laser pulses are reported. The measures are consistent with the features observed in nanosecond lasers. The value of electron temperature was 1.2 eV assuming the *local thermal equilibrium* (LTE) – Eq. (1) [10].

$$\ln\left(\frac{I_{mn}\lambda_{mn}}{A_{mn}g_{mn}}\right) = ln\left(\frac{N}{Z}\right) - \left(\frac{E_m}{kT_e}\right) \tag{1}$$

I_{mn} is the intensity of transition line observed. λ_{mn} is the wavelength of transition. A_{mn} is the probability of transition. The degeneracy of upper states is g_{mn}. E_m is the emission of upper level energies. Boltzmann constant k and T_e are the electron temperature. The slope of Eq. (1) [(1) $(kT_e)^{-1}$] is compared with the slope obtained at the graphs and the T_e can be calculated.

The Table 1 has the values that were used to determine this temperature. Experimental values of λ are compared with NIST database values [12]. $A_{mn}g_{mn}$ is taken from NIST data.

LTE is valid if collisional processes are more important than radioactive decay. In dense plasmas Ne ≥ 10^{16} cm^{-3} and temperature $kT ≤ 5$ eV, the velocity distribution of free electrons is almost always Maxwellian [13]. We estimate the electron density in the plasma by measuring the width of the individual nitrogen line. The electron density is related to the line broadening, and for highly ionized and high density plasma, the collisions with charged particles present a strong electric field that produced a broadening of the transitions between the split atomic levels. These micro electric fields are associated with Stark broadening [14].

Electron density must be enough high in order to fulfill the criterion for LTE. This high density is a necessary condition although no sufficient [15]. The relation between electron density and electron temperature is presented in Eq. (2).

$$n_e \geq 1.4x10^{14}T_e{}^{12}(\Delta E_{mn})^3 cm^{-3} \tag{2}$$

Table 1 N II lines used to determine the electron temperature in plasmas produced by 1064 nm of laser irradiation in Norte de Santander samples

Wavelength-NIST λ (nm)	Wavelength-Experimental λ (nm)	Intensity Observed I (u.a)	$\ln\left(\dfrac{I_{mn}\lambda_{mn}}{A_{mn}g_{mn}}\right)$	Energy E_m(eV)
628.57	628.51	10,197.97	20.54	23.13
654.42	653.38	6,868.76	17.55	25.13
685.70	685.65	2,029.19	14.42	30.30

Substituting values for T_e and ΔE in (2) the value obtained is 9.57×10^{15} cm^{-3}. The result implies that LTE approximation used in this analysis is valid. An electron density of 1.82×10^{19} cm^{-3} using Stark broadening has been calculated. In Figure 3 is shown how the Lorentz function fits the line of the spectra obtained.
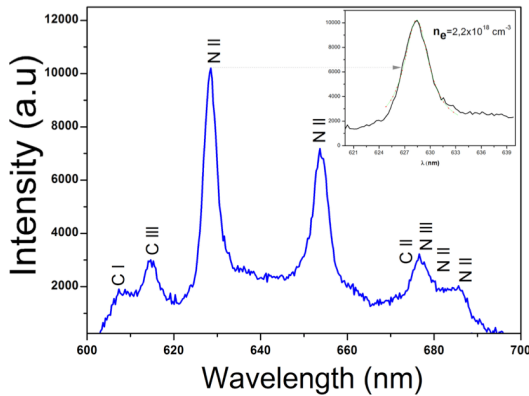

Figure 3 N II emission line at 628.45 nm to calculate electron density by means Stark Broadening

3.2. Vibrational temperature

The *Swan bands* of C$_2$ emission intensities to calculate vibrational temperatures were used. The strongest band of the well-known *Swan* system is emitting in the green of the electromagnetic spectrum. This has a special interest since it provides an estimation of the plume temperature and it is very important in fields as astrophysics. These bands have been observed in the emission spectra of comets and also in the absorption spectra of stellar atmospheres [16]. The Swan systems arise from transitions between the $(d^3\prod_g \rightarrow a^3\prod_u)$ electronic states of the C$_2$ molecules. The band heads $\Delta v = 0$ (Figure 4). The band emission at 510 nm, 515 nm and 520 nm can be utilized to determine the vibrational temperature. These emissions correspond to (0,0), (1,1), (2,2) bands [17]. Boltzmann distribution used for calculation is shown in Eq. (3) [10].

$$ln\sum_{v''}(\lambda^4 I_{v'v''}) = C - G(v')\frac{\hbar c}{kT_{vib}}$$

(3)

λ is the wavelength that corresponds to the emission of headband and I is his corresponding intensity. c is a constant. $G(v')$is a expression for the vibrational energy

level at the upper electronic state. Planck constant is $\hbar$, light velocity is c and Boltzmann constant is k. Finally, T_{vib} is the vibrational temperature. The emission of nitrogen molecule (Figure 4), which emits in the ultraviolet, visible and infrared electromagnetic ranges, was in this case emitting in the visible range.
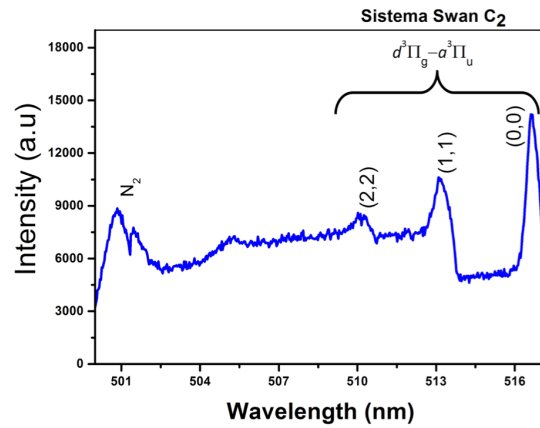

Figure 4 Swan Band of C2, band heads $\Delta v = 0$

The first negative system attributed to $(B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+)$ that according with literature [18], occurs easily in a plasma at moderate pressure, was observed with band head at 501.53 nm compared with 428.5 nm of band head observed in [18]. Boltzmann distribution values that were used to determine vibrational temperature are presented in Table 2 according with Swan Band of C$_2$ in Figure 4. The value of T_{vib} is 0.62 eV (Figure 5) with a high correlation value of 0.99.
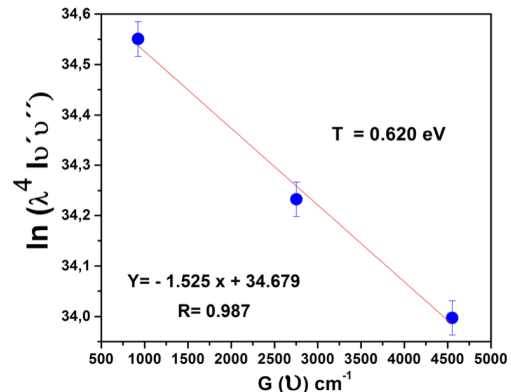

Figure 5 Fitting of Boltzmann distribution values of Table 2. Vibrational temperature is determined with Swan System of C2

Table 2 Emission peaks corresponding to C2 system to determine the vibrational temperature on carbon plasma with 1,064 nm of laser irradiation

Band head λ (nm)	Wavelength Experimental λ (nm)	Intensity Observed I (u.a)	$ln \sum_{v''} (\lambda^4 I_{v'v''})$	G(υ') (cm^{-1})
509.77	510.02	8,599.83	34.00	4,553.40
512.93	513.09	10,622.51	34.23	2,752.05
516.52	516.61	14,206.42	34.55	924.02

4. Conclusions

Analysis of coal plasma emission by means of *Optical Emission Spectroscopic* (OES), the determination of electron temperature, electron density and vibrational temperature and their corresponding ionization states are very interesting research topics. OES technique is relatively easy to implement and the information that can be obtained with spectroscopy study is very useful to characterize the plasma sample, that in the case of coal mineral can give important information of the performance of coal under plasma ablation. This can provide information about the transition and the excited species, incandescence of the carbon particles, recombination processes and fragmentation.

5. References

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