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Electron number density measurements using laser-induced breakdown spectroscopy of ionized nitrogen spectral lines

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ABSTRACT

Spectrally broadened, singly ionized nitrogen emission lines are monitored to determine electron number densities in laser-induced plasma from aluminum, nano- and bulk-zinc monoxide, as well as hydrogen-rich plastic and wood targets. The optical emission spectra for N II at the average wavelength of 500.33 nm are recorded in standard ambient temperature and pressure environments. For time delays of 25 to 450 ns from the onset of the 1064-nm Nd:YAG radiation induced optical breakdown, the electron number densities in the range of $5.1 \pm 1 \times 10^{19}$ to $0.22 \pm 0.04 \times 10^{19}$ cm^{-3} are inferred from the continuum and the nitrogen spectral line analysis. In addition, the corresponding electron temperatures of 10.1 ± 0.6 eV to 1 ± 0.2 eV are determined from the calculated absolute spectral radiance values in the near infrared region. At the early stages of plasma emission, Balmer series hydrogen lines are embedded in free electron radiation yet the broadening of the N II lines yields reliable electron number density values.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is applied for the characterization of laser-induced plasma. It is quite common to associate the acronym LIBS with the spectral analysis of the radiation emitted from plasma that is generated by the interaction of nanosecond laser pulses with various targets and with a peak irradiance in the range from 0.01 to 1000 GW/cm^2. The LIBS approach offers several advantages over chemical analytical methods. The advantages include fast response, minimal sample preparation and versatility for elemental analysis [1–3].

In general, the continuum emission due to Bremsstrahlung dominates for early time delays. The continuum radiation is attributed to the deceleration of fast electrons by the electromagnetic fields in the plasma and frequently described as being due to free-free transitions [4]. The continuum radiation indicates a plasma state very close to complete thermodynamical equilibrium (CTE) [5]. Therefore, in absence of spectral lines for very early time delays (0–50 ns), the measurement of time-resolved absolute spectral radiance of the continuum towards the near infrared wavelength region yields electron temperatures [4]. Moreover, the measurement of the absolute emission coefficient of the same continuum can be utilized to determine the electron number density of the plasma [4–6].

Traditionally, the electron number density can be measured from the spectral line shape analysis of certain optically thin lines that emerge from plasma, *e.g.*, the Balmer series H_α line [6–8]. This method is based on Stark broadening of the emitted spectral lines due to the local micro-fields produced by the free electrons, and to certain phenomena that are present in the plasma [9]. The Stark effect acts on the upper emitting states and leads to a Lorentzian spectral line shape [10]. The full-width-at half-maximum (FWHM) of the Lorentzian component can be correlated with the electron number density by applying different theories [4,5,9-11]. However, certain conditions need to be satisfied, *e.g.*, the spectral line should be free from self-absorption, the Doppler and other broadening mechanisms such as resonance and van der Waal's broadening should be as small as possible for effective inference of electron number density [10].

The presented work is primarily motivated by the desire to establish a reliable method to determine the plasma electron number density during the early stages of plasma expansion, and possibly avoid tedious absolute calibration procedures. The early continuum component originates from the Bremsstrahlung radiation caused by slowing down fast electrons. In order to measure the electron number density using this continuum, one has to rely on absolute measurements of the emission coefficients in the near IR wavelength

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region. This approach has been communicated recently for ablation plasma diagnostics using the hydrogen alpha Balmer series line [6]. In this context, the use of N II lines are considered for ablation plasma diagnostics during the first few 100 ns in standards LIBS experiments that utilize Q-switched, several nanosecond duration Nd:YAG laser devices for generation of laser-induced plasma. A definite advantage of the use of nitrogen lines is the linear dependence of the nitrogen line width on the electron number density. In the case of the hydrogen lines the dependence is much more complex and must be derived from numerical tables obtained from theoretical calculations.

The nitrogen ionic lines near 500 nm are frequently affected by spectroscopic interference of the lines at 500.51 nm (^{3}D–^{3}F^o transition term) and 500.14 nm (^{3}D–^{3}F^o transition term). The ionic lines near 500 nm have been employed by Qin et al. [12] in modeling the onset of plasma during laser-induced gas breakdown in atmospheric nitrogen. Diwakar and Hahn [13] measured the electron number in double-pulse LIBS for early time delays in conjunction with Thomson scattering. The line at 500.51 nm was explored by Liu et al. [14] to study the effect of laser energy in double pulse LIBS experiment. Jie et al. [15] employed the same line at 500.51 nm to study the temperature and density during lightning in air. Gochitashvili et al. [16] used the combination of two wavelengths (500.14 and 500.51 nm) appearing as a single line in polarization measurements during He II and N II collisions. The amount of Stark broadening of these lines is large enough to cause overlap. From a practical point of view, these lines merge and appear as a single line. Moreover, the optical depth of the plasma for these lines may differ for various conditions [17,18].

In this article, the feasibility of combining the two major nitrogen ionic lines at 500.14 and 500.51 nm are explored for the measurement of the plasma electron number at the early time delays in the range of 50 to 400 ns. Five different types of target materials are examined including wood and plastic that show relatively large hydrogen content. The electron number densities from the two N II lines with the 500.33-nm average wavelength are compared to values obtained from the absolute emission coefficients in the near-infrared wavelength region utilizing an absolutely calibrated LIBS experimental arrangement. At relatively longer time delay delays of 400 ns, the Balmer series H_α line is considered as well in the comparisons.

2. Experimental arrangement

The experimental arrangement is illustrated in Fig. 1. It is comprised of a Nd:YAG laser device that delivers 700 mJ during the pulse duration of 5 ns at the fundamental wavelength of 1064 nm. The laser light is focused onto different plane targets in ambient laboratory air using a plano-convex lens (f = 100 mm).

The targets are positioned at a distance of 5 mm in front of the focus in order to avoid air optical breakdown. The laser spot at the targets is measured with thermal paper supplied by Quantel®. The burn pattern is circular of diameter 0.5 ± 0.1 mm resulting in a peak irradiance of 70 GW/cm^2. The light emitted from the plasma plume is directed to the entrance aperture of an echelle spectrograph (SE 200 Echelle) with a spectral resolution of 50 pixels per nm. A 25 μm quartz optical fiber is positioned at distance of 10 mm perpendicular to the optical axis. The spectrograph is equipped with time-gated, intensified charge coupled device (ICCD) with a pixel size of 13 × 13 μm^2 (Andor iStar model DH734-18F).

Data processing is accomplished with the software KesterlSpec3.9®. A gate-open time of 10 ns is used for all experiments, and the radiation from the plasma is collected over a 25 consecutive events for time delays ranging from 25 ns to 400 ns. The irradiance level is kept constant at 70 GW/cm^2 during the experiments within the typical 6% peak-peak variation in energy per pulse of the Nd:YAG laser radiation. The target is mounted onto a xyφ-stage and is rotated in order to expose pristine surface areas in the LIBS studies.

In order to reconstruct the plasma emitted spectral intensity in absolute units of Watt/(m^3 sr) in the wavelength region from 200 to 900 nm, the experimental setup was absolutely calibrated prior to the experimental studies. The calibration included optical fiber, spectrograph and ICCD. For the calibration, a UV-VIS-NIR standard deuterium-halogen light source (Ocean Optics DH-2000-CAL) was utilized with an adaptor to connect to the optical fiber [6]. The adaptor is of cylindrical form with radius of 2 mm and length of 5 mm, leading to a lamp emitting area of 1.3×10^{-5} m^2. The data sheet of the calibration lamp was supplied with spectral intensity units of μWatt/(cm^2 nm) or 10^7 Watt/m^3 assigned at each wavelength in the range from 200 to 900 nm. This supplied data sheet was further adapted due to the convolution by the spectrograph resulting in a bandwidth of 0.12 nm, measured with low pressure mercury lamp (Ocean Optics Type 1 mercury lamp).

In the absolute calibration procedures, the emission spectrum from the calibration lamp (Ocean Optics DH-2000-CAL) was measured for different gate-open durations of 0.5, 1 and 2 s. The average spectra were recorded in detector counts for the selected gate-open durations, and subsequently, were corrected for the selected gate widths in the laser-plasma experiment. The direct comparison between the measured spectra and the provided, corrected data sheet for spectral intensity leads to the absolute sensitivity values of the setup over the entire wavelength region. The inset in Fig. 1 shows the calibration in Watt/count. Accurate knowledge of the camera gate-open duration is important, however, the gate width is kept constant at 10 ns. Knowledge of the distance from optical fiber tip to laser-plasma axis (fixed at 10 ± 0.2 mm in the experiments) and of the plasma emitting volume is required to evaluate the optical fiber receiving solid angle of 2.83×10^{-3} sr. The detailed procedures are presented in the supplement on the intensity calibration.

The measurement of the plasma emitting volume likely introduces error margins in the absolute calibration in the LIBS experiments. First, the plasma is inhomogeneous due to its inherently hot core and a cool periphery [8]. Second, the different sensitivity of camera pixels to different wavelengths emitted from plasma can lead to chromatic aberration and hence cause blurred images. And third, the plasma is not stationary but rapidly expands at supersonic speed thereby increasing the plasma volume. To address the expansion,the plasma is directly imaged with a 100 mm focal length achromatic lens. This lens is positioned at a distance of 200 mm from the optical axis for 1:1 imaging of the plasma plume onto the entrance aperture of the ICCD. Neutral density filters are used to attenuate the plasma radiation. The plasma direct imaging reveals that the plasma shape is almost spherical with radii ranging from 0.25 mm at the early time delay of 25 ns, and it expands up to 0.37 mm at the time delay of 450 ns. Fig. 1 illustrates the 25 ns time delay image. It is worth noting that the plasma initially expands rapidly but slows down due to the plasma confinement by the ambient air. Typical early expansion speeds attain 10 km/s and subsequently reduce to 1 km/s or 1 mm/μs for time delays of the order of 1 μs [19].

3. Plasma parameters

For early time delays, a strong continuum due to Bremsstrahlung dominates plasma emission as free-free transitions occur between electrons in continuum states [4]. In this case, the plasma state is nearly in complete thermodynamical equilibrium (CTE) and hence, the plasma emits like a gray body [4]. For near infrared wavelengths, the electron temperature, T_e, can be deduced directly from