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Asymmetric hydrogen beta electron density diagnostics of laser-induced plasma ☆

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ABSTRACT

The hydrogen beta line has been widely used in determining plasma parameters such as electron density. In conjunction with other Balmer series lines, electron temperature can be inferred. The asymmetric appearance of the hydrogen beta line, due to quadrupole interactions, can be utilized as well for the determination of electron density. Laser-induced optical breakdown is generated in laboratory air, and particularly for electron densities in the range of 0.3 to 1.0×10^{17} cm^{-3} the use of the asymmetry parameter is elaborated for electron density diagnostics. Also included are results of analysis of the hydrogen beta profiles for which the asymmetry indicates an electron density on the order of 2.0×10^{18} cm^{-3}, which is significantly higher than 6.3 to 6.8×10^{17} cm^{-3} maximum that was measured previously from the Stark-broadened hydrogen beta width following laser-induced optical breakdown.

1. Introduction

Analysis of laser-induced micro-plasma typically utilizes laser-spectroscopy techniques, including the use of a spectrometer equipped with a gated detection device. Frequently, Stark-broadening of selected atomic lines is measured to determine electron density [1,2]. However, red shifts and asymmetries [3] can also allow us to develop plasma diagnostics. Plasma spectroscopy with hydrogen Balmer series lines have been reviewed recently [4]. Applications of empirical formulae [4] for laser-induced plasma work well when comparing with predictions from different theory models [5] in the analysis of experimental data that show hydrogen line emissions. Laser-Induced Plasma Spectroscopy (LIPS) and//or Laser-Induced Breakdown Spectroscopy (LIBS) is now a valuable technique for determining elemental composition with the ability to analyze solids, liquids and gasses with little or no sample preparation, suitable for on-site analyses [6–9]. Part of the LIBS versatility as a diagnostic tool is due to its minimally invasive sampling procedure which can be automated and preformed remotely if desired.

The success of LIBS is in part due to the ease of availability of nominal 10-nanosecond Nd:YAG laser radiation from compact devices. Several other laser sources however have been historically applied for generation of micro-plasma with subsequent measurement methods based on the use of atomic emission spectroscopy. Recent interest includes applying dual- and multi- pulse excitations for the purpose of increasing sensitivity of LIBS [10]. Examples of advantages of multi-pulse excitation include an increase of the plasma volume or plasma reheating by the second pulse, in turn, enhancement of detection limits for LIBS 10- to 100-fold and/or a decrease in relative standard deviation when comparing single- with double- pulse bursts. In the work presented here we focus on the application of electron density diagnostics following an optical breakdown event generated by a single laser pulse, the traditional approach to LIBS [11]. Analysis of the recorded spectra following laser-induced optical breakdown in laboratory air addresses H_α and H_β emissions [12–19].

2. Experimental details

For the generation of a micro-plasma we employ a Q-switched Quanta Ray model DCR-2A(10) Nd:YAG laser, operating at the fundamental wavelength of 1064 nm. In the experiments discussed here, we use 13 ns pulses with an energy of 190 mJ per pulse. The laser beam composed of these pulses, generated at a repetition rate of 10 Hz, is aligned parallel to the spectrometer slit by way of three mirrors. A quartz lens focuses the beam into a spot size of about 50 μm in diameter, and laser-induced optical breakdown is accomplished with a peak irradiance of 0.5 to 0.75 TW/cm^2. The resulting plasma is imaged onto the spectrometer slit with a 1:1 magnification by two quartz lenses where the last lens optically couples with the spectrometer's $f^{\#}$ of 5.2. The spectrometer slit height amounts to 20 mm with the optical path oriented perpendicular to the laser beam path. The HR640 0.6-m

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Jobin–Yvon spectrometer equipped with a 1800 grooves/mm grating disperses the imaged plasma and the resulting spectra are collected with an intensified-linear diode array.

In many plasma diagnostic studies concerning laser-induced breakdown, the observed spectral lines are narrow such that the instrumental width may not be negligible. For this investigation with the selected time delays from optical breakdown generation, the observed line widths are quite broad with respect to the width introduced by our instruments or with respect to Doppler broadening as further discussed in Section 4. The instrumental resolution comprised of spectrometer slit width, grating and modulation transfer functions of the intensified array detector amounts to 0.10 nm. To explore the temporal evolution of the plasma, a Stanford model DG535 delay generator was used to control various delay times and gate widths of the intensifier and the optical multichannel analyzer (OMA).

The timing is accomplished as follows: as the beam exits the laser, with fundamental and frequency doubled components, it is passed through a beam splitter, which deflects the 532 nm radiation to a PIN photo-diode detector, while the fundamental component is directed toward the focusing lens. The photo-diode detector is used to monitor the 10 Hz laser pulse triggers in real time on the oscilloscope. The laser radiation is triggered at 10 Hz, while the detection devices are triggered at 50 Hz. Measurements of the initial plasma from optical breakdown defines the zero time delay, and it establishes the data scan to be recorded. The other four scans, commensurate with the 50 Hz operation of the OMA, serve as redundant measurements for the purpose of resetting the linear diode array and intensifier phospor readout.

Sensitivity calibrations were performed by fitting a blackbody curve to tungsten lamp data that was collected. A pyrometer was used to measure the temperature of the calibration lamp to be 2910 K. Wavelength calibrations were performed using standard lamps, including a hydrogen lamp.

3. Measurements

Spectra for the Balmer series hydrogen alpha and beta lines were recorded in laboratory atmosphere with no alterations to the natural environment. Small concentration of naturally occurring water in the laboratory atmosphere causes the appearance of hydrogen Balmer lines in the visible spectrum. For initial experiments, a gate width of 0.05 μs was selected and a time delay ranging from 0.2 to 30 μs was utilized for hydrogen alpha line investigations. A narrow gate width allows us to sufficiently isolate individual measurements for the purpose of capturing the temporal characteristics of the plasma. For a detailed characterization of the hydrogen alpha line's temporal evolution (not reported here) data was recorded for time delays between 0.3 and 1.0 μs in 0.1 μs increments. For these hydrogen alpha measurements a gate width of also 0.05 μs is employed.

In our experimental studies we typically employ varying gate widths to (1) measure the exponential decay of electron density as accurate as possible, and (2) to optimize the signal level for the different delay times from the plasma generation. Early decay times show a reasonably rapid decay of electron density in our line of sight measurements, therefore, narrow gate widths on the order of several nanoseconds are appropriate to accordingly capture data without introducing errors in electron density unnecessarily. As the plasma evolves in time, the signal strength diminishes and the electron number density decays less rapidly, allowing one to use larger gate-widths on the order of several tens to hundreds of nanoseconds. It is also important to note that optical breakdown in air shows sufficiently high electron density such that the hydrogen alpha line becomes measurable with our spectrometer/detector arrangements for time delays in excess of ~0.3 to 0.4 μs after optical breakdown, and the hydrogen beta line becomes recognizable for delays in excess of ~1.4 μs after optical breakdown. Equally, in our measurements discussed here, we employ spectral resolutions of 0.15 nm (1200 g/mm grating) 0.10 nm (1800 g/mm grating) and 0.05 nm (3600 g/mm) for a constant slit width of 100 μm. One can in principle use smaller grating dispersion and possibly demarcate the hydrogen beta line for slightly earlier time delays, but at the expense of diminished spectral resolution. Alternatively, one could scan the spectrometer and use boxcar/photomultiplier methods; however, for a gated array detector and a Czerny–Turner spectrometer, spectral coverage amounts to several tens of nanometer to investigate Stark-broadened Balmer series for electron density diagnostics.

The measurements at earlier time delays will show larger electron density, and only the hydrogen alpha line is available for diagnostics. With increase of time delay, the hydrogen beta line can be utilized. For our spectral resolution, as the time delay increases further, and the hydrogen alpha line decreases in width. For larger time delays from optical breakdown, discrepancies in electron number density may arise as the H_α line-width approaches the instrumental width that we elected to use, yet the H_β width may still be much larger than the employed instrument width to allow one to apply measurement of H_β as an electron density diagnostic. The choice of temporal gate-width is important primarily for capturing the electron density decay.

Measurement results reported here include a systematic study of H_α and H_β lines for time delays from optical breakdown starting at 5 μs in 1 μs steps and a gate width of 1 μs. In addition, hydrogen beta measurements were recorded for time delays between 2 and 5 μs in 0.5 μs increments and a gate width of 0.5 μs, for the purpose of evaluating further the use of the asymmetry as a diagnostics tool.

4. Theory

The hydrogen alpha and beta line shape features are primarily due to Stark broadening. Van der Waal and Doppler components should be considered as well; however, these contributions are especially important in cases of low electron density, or for $N_e << 10^{17}$ cm^{-3}. The Gaussian component, attributed to the Doppler broadening, contributes to the overall line shape as follows: the Doppler half width [20] is given by $\Delta\lambda/\lambda = 7.16 \times 10^{-7}\sqrt{T/A}$, where A denotes the atomic or molecular weight in atomic mass units of the particle, T is the temperature and λ is the wavelength. For hydrogen, the Doppler half width (FWHM) at 656 nm and for T = 10,000 K amounts to 0.05 nm; for T = 100,000 K one has 0.15 nm. These Doppler widths are significantly smaller than the measured hydrogen beta Stark widths for time delays in the range of 3 to 10 μs.

A Lorentzian profile is used solely to determine the full width half maximum; however, the wings of the spectral lines are best fit by a Voigt profile. In the experimental results reported here, the Lorentzian fit provides a value for FWHM of the hydrogen beta line consistent with that of the observed line profile. A single Lorentzian fit is of course insufficient to capture H-beta line shapes including for example the double peak structure that is typically observed in optical breakdown experiments. As one were to fit the measured hydrogen beta line with a Voigt profile, the Stark width is associated with the Lorentzian component [4]. Konjevic et al. noted in Ref. [4] "Such a deconvolution procedure is employed in spite of the fact that the Stark profile has no Lorentz form neither below nor above the FSL [fine structure limit]," and: "Thus, the largest accuracy or zero error, is in the case of $w_L/w_S = 1$." Here w_L is the Lorentzian width and w_S is the Stark width. Again, we utilize Lorentzian profiles to estimate the FWHM and use this value as the Stark width. Note, our hydrogen beta widths are much larger than the instrument and/or Doppler widths. We further note that hydrogen beta is traditionally the more accurate measurement of electron number density with an uncertainty of about 5% in comparison to using the hydrogen alpha line with an uncertainty of 20% [2].

The hydrogen line asymmetry is caused primarily by the ion microfield nonuniformity in the plasma. Detailed computations and availability of a formula relating the electron density, N_e to the line shape asymmetry [21] encourage us to apply this as a diagnostic for