Abstract.
This article addresses hydrogen Balmer series measurements following laser-induced optical breakdown. Electron density on the order of $1 \times 10^{25} \text{ m}^{-3}$ can be inferred using H$\alpha$ Stark width and shift for plasma generated in 1 to $1.3 \times 10^5 \text{ Pa}$, gaseous hydrogen. The H$\beta$ line can be utilized for electron density up to $7 \times 10^{23} \text{ m}^{-3}$. Laser ablation of aluminium reveals limits of application of the Balmer series. Electron excitation temperature is inferred utilizing Boltzmann plot techniques that include H$\alpha$, H$\beta$ and H$\gamma$ atomic lines. H$\beta$ and H$\gamma$ lines show presence of molecular carbon in a 2.7 and $6.5 \times 10^5 \text{ Pa}$, expanding methane flow. Occurrence of superposition spectra in the plasma decay due to recombination or due to onset of chemical reactions necessitates consideration of both atomic and molecular emissions following laser-induced optical breakdown.

1. Introduction
In this paper we explore hydrogen plasma spectra generated by high intensity laser radiation. Investigated are the H$\alpha$, H$\beta$, and also H$\gamma$ lines and their characteristics as well as broadening and shifts. This article elaborates on previously communicated emission spectroscopy data of the hydrogen Balmer series [1, 2, 3, 4, 5]. Laser-induced breakdown spectroscopy (LIBS) historically embraces elemental analysis, or atomic spectroscopy, and to a lesser extent molecular spectroscopy. Time-resolved diagnostics allow us to record atomic emission profiles separate from molecular recombination and/or excitation; however, atomic and molecular species can occur simultaneously within a selected spectral window, for our expanding methane experiments typically on the order of 1 to 2 micro-seconds after optical breakdown.

Following the invention of laser devices, Laser-Induced Breakdown Spectroscopy (LIBS) evolved into one of the favorite topics not only in atomic and chemical physics but also in chemistry, biology, environmental science, material engineering, and recently space exploration. Modeling of the hydrogen line shapes for the diagnostic for International Thermonuclear Experimental Reactor (ITER) is an important ongoing investigation, and it is based on the Balmer lines of the hydrogen isotopes. The use of hydrogen Balmer lines has been employed to measure the temperature and electron density in plasmas, including several theoretical approximations [6, 7, 8, 9]. In typical LIBS experiments, the main broadening mechanism
of spectral lines is the Stark effect. Line broadening has been studied comprehensively by H. Griem [10]. A large, linear Stark effect in hydrogen makes its lines attractive for recent research [11]. According to theory, the shapes and shifts of plasma-broadened isolated lines are mainly determined by electron impact with the radiating atom or ion, and a smaller contribution arises from the electric micro-fields generated by essentially static plasma ions. In addition, at a given electron number density of the plasma, the hydrogen lines are broader with respect to the lines of other elements. Doppler broadening has information about velocity distribution, and Stark broadening gives information on electron density [12]. These features make their use particularly interesting in LIBS experiments performed with typically 0.1-nm spectral resolution spectrometers where the instrumental broadening introduced by the spectrometer might be comparable, or even larger, than the broadening of the emission lines of elements different from hydrogen. Moreover, the Stark broadening of the emission lines is independent from the fulfillment of local thermodynamic equilibrium (LTE) conditions [13], and this aspect makes this approach for the electron density measurement an interesting and powerful tool. Measurements of line shapes are important in plasma diagnostics allowing us to investigate fundamental atomic structure as well as inferring plasma temperature and electron density. In particular, the H\textbeta line is one of the most studied lines, and its use has become a standard technique in plasma spectroscopy [14].

In previous studies by Parigger et al. [15], analysis of Stark broadening and shifts in measured H\textalpha and H\textbeta spectra, combined with Boltzmann plots from H\textalpha, H\textbeta and H\textgamma lines to infer the temperature, have been discussed for the electron densities in the range of $10^{22} - 10^{25}$ m$^{-3}$, and for the temperatures in the range of 6,000 to 100,000 K. Lines H\textalpha, H\textbeta and H\textgamma were recorded at different delay times from optical breakdown. The electron density was evaluated using different theoretical approaches that are commonly employed for plasma diagnostics [3]. We previously reported measurements [1, 2, 3, 4, 5] and comprehensive studies of the diagnostic application of Balmer lines.

2. Experimental Details

For generation of a micro-plasma, a laboratory Nd:YAG laser operated at the fundamental wavelength of 1064-nm was used. For the hydrogen plasma investigations, a Continuum YG680S-10 Nd:YAG with 150-mJ energy per pulse and 7.5-ns pulse duration, was focused to typically 1,400 GW/cm$^2$ in a pressure cell that was filled with gaseous hydrogen to a pressure of 810 ± 25 Torr ($1.07 \times 10^5$ Pa) and 1010 ± 25 Torr ($1.33 \times 10^5$ Pa), subsequent to evacuation of the cell with a diffusion pump. Spectrometer and detector arrangements are discussed in the Parigger and Ok's review article[1].

Recording of shadow graphs (not illustrated here) was accomplished with Coherent Infinity 40-100 Nd:YAG laser with 50-mJ and 300-mJ pulse energy and 3.5-ns pulse width was focused in laboratory air to an irradiance of typically 10,000 GW/cm$^2$. Perpendicular to the laser beam generating LIB, we typically employed pulsed laser radiation from a 308-nm XeCl excimer laser.

In the expanding methane experiments [4], we used a 1/2 m model 500 SpectraPro Acton Research Corporation spectrometer together with an intensified linear diode array (model 1460 Princeton Applied Research detector/controller optical multichannel analyzer). Averaged over 100 individual LIB events, the captured time-resolved data (measurement window of 0.1 \(\mu\)s) from the methane breakdown events were detector-noise/background corrected and wavelength and detector sensitivity calibrated using standard calibration lamps.

3. Experimental Results

Measurements of individual profiles of the Balmer series lines H\textalpha, H\textbeta and H\textgamma allows us to infer electron excitation temperature. However, the inferred temperature will show error-bar contributions due to the broadened atomic emissions. Presence of the molecular emissions will
add to the background for the hydrogen Balmer series diagnostic. We treat the Hβ and Hγ lines as background contribution to extract molecular temperature information for analysis of molecular excitations [5].

Time resolved spectroscopy measurements of hydrogen- alpha, -beta, and -gamma emissions were performed in an expanding flow of methane gas. Hydrogen Stark widths were used to characterize the plasma decay during the first 2 microseconds after laser-induced optical breakdown [4]. Analysis of the recorded hydrogen spectra include measurements of full-width-half-maximum (FWHM) and full-width-half-area (FWHA) to infer electron density Ne [2]. Temperature was determined from incomplete hydrogen Balmer Series lines [3]. Yet for time delays on the order of 1 µs, molecular emissions can be recognized from the C2 Swan system, superposed to the Hβ and Hγ Balmer series lines. C2 emissions are clearly recognizable for time delays on the order of 2 µs. Figures 1 and 2 show these results.

**Figure 1.** Hβ recorded and fitted spectra. Delay time Δτ = 1.1 µs. Ne = 1.0 × 10^{23} m^{-3}.

Figs. 1 and 2 indicate the presence of C2 molecular emissions for a delay time of Δτ = 2.1 µs. Temperature inferred from the fitting of the C2 “fingerprints” revealed molecular temperatures in the range of 4000 - 6000 Kelvin [5]. The Hβ profile at a delay time of Δτ = 2.1 µs shows an electron density of 0.5 × 10^{23} m^{-3}. The electron excitation temperature for delay times on the order of 1.1 to 2.1 µs amounts to 1.3 to 1.1 × 10^4 K [3], while the molecular temperature of the residual carbon, see Fig. 2, is determined to be 0.52 × 10^4 K.

The Hβ profiles typically show a double-peak structure consistent with computed line profiles that appear asymmetric early in the plasma decay. The major broadening mechanism here is due to the Stark effect, which should cause a Lorentzian profile, and the dip at the line center is due to absence of computed Hβ shifts [16, 17] and in part due to electrostatic interactions with ions [18]. The theory for widths of the hydrogenic lines is mostly accurate and best agrees for Hβ, where the overall error is about 5%. For hydrogenic systems a relatively large portion of the broadening is due to quasi-static effects.

Electron density in plasma can be found by measuring Stark broadening, and this is the most precise technique for determining the electron density Ne in plasma. This broadening will become significant for Ne > 10^{21} m^{-3}. Stark broadening is due to collision between radiating species with charged species, like electrons and ions. Not only the Hβ Stark width but also the
separation of the $H_\beta$ double-peak structure is a measure for the free electron density [15]. Oks’ theory of Stark widths incorporates several major theoretical advances and new phenomena in the Stark broadening of hydrogen lines in plasmas [19]. The Stark linewidth $\Delta \lambda_{FWHM}$ at full-width-half maximum (FWHM) can be extracted from the measured line width $\Delta \lambda_{observed}$ by subtracting instrumental $\Delta \lambda_{instrumental}$ and Doppler line broadening $\Delta \lambda_{Doppler}$ [20]. A large electron density ($N_e > 10^{23}$ m$^{-3}$) causes Stark broadening that is typically much larger than employed instrumental resolution and Doppler broadening. Experimental studies of aluminum laser ablation [21] within an evacuated cell reveals the limitation of Balmer series diagnostic for electron density and temperature. Early in the plasma decay, the $H_\alpha$ line becomes discernable at delays on the order of 0.025 to 0.050 $\mu$s after LIB, showing an electron density of $10^{24}$ m$^{-3}$. The $H_\beta$ line appears recognizable at delays on the order of 0.075 to 0.100 $\mu$s, showing an electron density of $4 \times 10^{23}$ m$^{-3}$.

4. Discussion

A plasma’s temperature and density are important for its stability. For high-temperature nuclear fusion plasma, non-invasive plasma diagnostics (like optical emission spectroscopy) are necessary [22]. A typical method to infer plasma temperature is to construct a so-called Boltzmann plot [23] including consideration of non-uniformity of laser-induced plasma [24]. Relative ion populations in local thermodynamic equilibrium (LTE) can be computed using the Saha (or Saha-Eggert) equation. However, when applying the Saha equations to obtain temperature, called the temperature of the ionization equilibrium, relative intensities of lines from different ion stages of the same atom (occasionally different atoms) need to be measured [25].

The recorded emission spectra of the hydrogen Balmer series allow us to infer electron number density, using previously tabulated values. The displayed hydrogen emission profiles are also convolved with the Doppler width that amounts to 0.05 nm at 10,000 K and 0.15 nm at 100,000 K. There is a substantial red shift of the $H_\alpha$ line profile from its unperturbed position for $N_e$

![Figure 2. H$\beta$ recorded and fitted spectra. Delay time $\Delta \tau = 2.1 \mu$s. $N_e = 0.5 \times 10^{23}$ m$^{-3}$.](image-url)
on the order of $10^{24}$ m$^{-3}$. Larger red shifts in the forward region of the breakdown plasma correspond to higher temperature and also electron density, therefore, we infer that there is an electron (or excitation) temperature gradient across the length of the plasma. Temperatures on the order of 100,000 K can be found early in the plasma decay [15]. Use of Oks’ theory allowed us to enhance significantly the agreement of theory and our experimental results.

Superposition spectra occur due to recombination or due to onset of chemical reactions. Analysis of both atomic and molecular emission spectra following laser-induced optical breakdown require utilizing molecular diagnostics [26] based on so-called line-strength files. The illustrated spectroscopic data display both the Balmer series hydrogen beta line and molecular $C_2$ Swan band presence. The molecular excitation temperature is determined using modified Boltzmann plots and fitting of spectra from selected molecular transitions [27].

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