Time-resolved dual-comb measurement of number density and temperature in a laser-induced plasma

YU ZHANG1,2, CAROLINE LECAPLAINE2, REAGAN R. D. WEEKS2, JEREMY YEAK3, SIVANANDAN S. HRILAL4, MARK C. PHILLIPS2,3,4, AND R. JASON JONES2,*

1Department of Physics, University of Arizona, 1118 E. Fourth Street, Tucson, Arizona 85721, USA
2College of Optical Sciences, University of Arizona, 1630 E. University Boulevard, Tucson, Arizona 85721, USA
3Opticslah, 2350 Alamo Avenue SE, Suite 280, Albuquerque, New Mexico 87106, USA
4Pacific Northwest National Laboratory, Richland, Washington 99352, USA
*Corresponding author: rjones@optics.arizona.edu

We utilize time-resolved dual-comb spectroscopy to measure the temporal evolution of the population number densities and absorption excitation temperature of Fe in a laser induced plasma. The spectrum of three excited-state transitions of Fe around 533 nm are simultaneously measured at different time delays following laser ablation of a stainless steel sample. This work probes late-time behavior of laser-induced ablation plumes during plasma cooling. The high spectral resolution and broad spectral coverage of the dual-comb technique, combined with the time-resolved measurement capability shown here, will aid in the characterization of laser induced plasmas, including species identification and molecule and particle formation that can occur at later times in the plasma evolution.

Laser-induced plasmas (LIPs) provide a powerful tool for analysis of solid materials [1]. Examples include isotopic analysis of nuclear materials [2], geochemistry [3], and identification of chemical and drug compounds in the pharmaceutical industry [4]. The commonly used emission spectroscopy technique laser-induced breakdown spectroscopy (LIBS) is a powerful tool for elemental analysis of solid materials. LIBS is capable of measuring the optical emission from multiple elements and transitions over a broad spectral range and can be used for plasma diagnostics such as determining excitation temperature. Emission spectroscopy relies on the population density in the excited level. At early times, the emission signal is strong but dominated by Stark broadening. At late times, the Stark broadening decreases, but the emission also decreases as the plasma cools, limiting its capability to track late-time plasma evolution. Moreover, emission spectroscopy suffers from self-absorption, which has the effect of distorting and broadening the spectral lines for optically thick plasmas, especially for transitions to states with low energy levels, including ground states. As a result of these issues, emission spectroscopy is not well-suited to probing late-time plasma properties. Indeed, characterization of LIPs at later times is nearly non-existent in the literature except for ex-situ measurement of particles generated after ablation. Thus, in-situ measurements of plasma properties such as excitation temperature and atomic number densities are needed over longer time scales to better understand when and where molecules and particles are formed in a LIP system.

Absorption spectroscopy techniques such as laser absorption spectroscopy (LAS) [5, 6] and laser-induced fluorescence using tunable continuous-wave (CW) lasers [7] do not suffer from these limitations. LAS can probe ground-state resonance lines to more accurately quantify number densities and can be used for characterizing LIP at later times throughout the plasma evolution. LAS based on CW lasers provides high spectral resolution. However, most tunable CW lasers offer a limited scan range or speed, making it challenging to observe a broad spectrum containing multiple transitions needed for characterization. Absorption spectroscopy utilizing broadband sources coupled to spectrometers for characterizing transient processes (e.g. explosions, electric discharge plasmas) have previously demonstrated the advantages of multi-level and multi-species detection [8, 9]. While providing important diagnostic capability, the reliance on a dispersive spectrograph results in fundamental trade-offs between spectral resolution and bandwidth.

Dual-comb spectroscopy (DCS) [10] can offer both broad bandwidth and high spectral resolution needed for absorption spectroscopy of LIPs [11]. DCS utilizes the broad spectrum from a fs frequency comb to probe a sample. The absorption spectrum of the probe laser can be easily detected with a single photodiode from the RF beatnotes between the probe comb and a second nearly identical reference comb operating at a slightly different repetition rate. In a time domain description, the pair of lasers act as a Fourier transform spectrometer, where the interferogram is formed from interference of successive pulse pairs from each laser. Thus, the system can be adjusted to optimize as needed the inherent trade-offs between spectral resolution and acquisition time. Recently, we reported DCS of a LIP for the first time [11]. In that work, we demonstrated the broadband and
Fig. 1. Schematic of the dual-comb laser system for time-resolved spectroscopy of laser-induced plasmas. Dashed lines represent electrical connections while solid lines indicate optical beam paths. PD: photodiode; L: lens; M: mirror; BS: beam-splitter; WP: waveplate, PBS: polarized beamsplitter.

The high-resolution capability of DCS by resolving the ground-state hyperfine splitting and isotopic shift of $^{85}$Rb and $^{87}$Rb following a single laser ablation shot of NIST SRM 610 glass while detecting the $D_1$ and $D_2$ lines of K located over 5 THz away. Here, we perform the first time-resolved spectroscopic measurements of the plasma evolution using DCS. We measure absorption spectra of three Fe transitions near 533 nm with unapodized spectral resolution of $\sim 8$ GHz (0.0076 nm) and temporal resolution of $20$ µs. Analysis of the absorption spectra yields the excitation temperature and path-integrated number density of Fe in the plasma for time delays of 11 - 140 µs after ablation.

The experimental layout is shown in the schematic of Fig. 1. A Q-switched Nd:YAG laser (Continuum Surelite III) running at $\sim 10$ Hz delivers 365 mJ pulses at 1064 nm with a pulse duration of $\sim 5$ ns. The pulse is focused with a 12.5 cm lens located 10 cm above the target onto a stainless steel sample to avoid ionizing the buffer gas. The sample is located inside a vacuum chamber filled with 100 Torr of argon. The focus spot is $\sim 1$ mm diameter in size, with a power density of 7.8 GW/cm$^2$. The dual-comb laser system is composed of two homemade Yb fiber lasers. Both fs lasers are stabilized to a common narrow-line CW laser at 1064 nm (NPRO) using optical phase-locked loops and by controlling the cavity length using a piezo-electric transducer attached to a cavity mirror. Both fs lasers are frequency doubled using BBO crystals (500 µm thickness). The beam from fs comb-2 is focused into the vacuum chamber to a diameter of $\sim 70$ µm at 0.83 mm above the surface of the stainless steel sample to probe the laser ablation plume. The fs combs are spatially overlapped after the vacuum chamber using a polarized beam splitter (PBS). A half-wave plate and second PBS are used to project the beams onto a common polarization. Although the spectral bandwidth available from the fs lasers exceeds 10 nm (10 THz), a grating and slit are used to select a $\sim 1$ nm (1 THz) region of the spectrum near the Fe transitions of interest. After the slit, the dual-comb interferogram is detected on a silicon photodiode with a total power of $\sim 20$ µW.

The two combs operate at a repetition rate $f_{\text{rep}}$ of $\sim 78$ MHz with a repetition rate difference $\Delta f_{\text{rep}}$ of $\sim 510$ Hz. $f_{\text{rep}}$ is detected individually for each comb and sent to a mixer to generate a signal at $\Delta f_{\text{rep}}$. A field-programmable gate array (FPGA Nexys 4 Artix-7) down-converts this signal to trigger the Nd:YAG laser at 10 Hz. The FPGA controls the timing delay between the ablation pulse and the following signal interferogram. The FPGA also controls an RF switch that selects this signal interferogram and a reference interferogram that precedes each ablation pulse. The reference interferogram provides a plasma-free background for normalization. The signal and reference interferograms are recorded on two Alazar 9440 14-bit acquisition boards at a sampling rate of 125 MHz. A 20 µs window recorded from each interferogram sets the temporal resolution.

In Fig. 2 we present the time-resolved measurements of three transitions of Fe near 533 nm recorded from the stainless steel sample while probing the plasma plume at various time delays. The related energy levels for these excited state transitions are shown in Fig. 3(a). For each delay, signal and reference interferograms were recorded for 800 laser ablation shots without moving the sample. A new sample location was used for each delay. After Fourier transformation, the amplitude of the normalized spectra were averaged.

The spectrum in Fig. 2(a) strongly depends on the time de-
lay at which the plasma is probed given that state populations rapidly evolve as the ablation plume expands and cools. Although ground state resonance lines in the plasma can persist for very long times (~ ms), the lines’ characterization in the present experiment is limited to ~ 150 µs due to the selection of excited transitions that remain populated only at higher temperatures. Beginning at a time delay of 11 µs, we observe three strong absorption lines originating from excited states of Fe I. By 140 µs only the lowest lying absorption line is observed.

Figure 2(b) shows the path-integrated number densities \( n_i \cdot L \) for the lower level of each transition versus time. The values were calculated by first assuming a uniform (average) spatial distribution of atoms along a path length \( L \) in order to relate the absorption coefficient \( a(v) \) to the measured transmittance spectra \( T \) via \( a(v) \cdot L = -\ln(T) \). The absorption coefficient can be expressed as [12]:

\[
a_{ij}(v) = \tilde{\sigma}_0 \cdot g_i \cdot f_{ij} \cdot [n_i / g_i - n_j / g_j] \cdot \chi(v) \tag{1}
\]

where \( i \) or \( j \) denotes the lower or upper level of each transition, \( \tilde{\sigma}_0 = \frac{2 \cdot \sigma_0 \cdot T}{<\rho> \cdot \nu} \) is the integrated absorption cross section constant, equal to \( 2.654 \times 10^{-6} \) m\(^2\)/s, \( g \) is the level degeneracy, \( f_{ij} \) is the transition oscillator strength, \( n_i \) is the number density in the \( i \)-th level (cm\(^{-3}\)), and \( \chi(v) \) is the normalized lineshape function. Given \( n_i \ll n_i \) at these wavelengths and temperatures, integration of Eq.(1) over frequency gives:

\[
n_i L = \left( \tilde{\sigma}_0 f_{ij} \right)^{-1} \int a_{ij}(v) \cdot L \cdot dv \tag{2}
\]

To obtain the path-integrated number densities, a Voigt lineshape function was fit to each transition in Fig.2(a) prior to the integration of Eq.(2). The population densities shown in Fig.2(b) exhibit the expected dependence versus time, with the two highest level transitions having the smallest populations and decreasing rapidly with time as the plasma cools. The population of the strongest 532.80 nm (in air) transition is seen to momentarily increase as upper levels decay into it, and then gradually decrease as the plasma cools further.

The absorption spectrum of the selected Fe I transitions versus temperature were numerically simulated to qualitatively compare with the measured spectra. The level populations were assumed to follow a Boltzmann distribution given by [12]

\[
n_i = g_i \cdot n_{tot} \cdot \exp(-E_i/(k_B T)) / \sum_j g_j \cdot \exp(-E_j/(k_B T)) = n_i(T) / n_{tot}
\]

where \( n_{tot} \) is the total atomic number density, \( E_i \) is the energy of level \( i \), \( k_B \) is the Boltzmann constant, and \( T \) is the electronic excitation temperature. The partition function \( Z(T) = \sum_j g_j \cdot \exp(-E_j/(k_B T)) \) was calculated using energy level data from NIST and is plotted in Fig.3(b) along with the population ratios \( n_i(T) / n_{tot} \). Due to the large difference in lower state energy levels, the level populations have a strong dependence on temperature. To model the absorption spectrum, parameters for the Fe I transitions were obtained from the Kurucz online database [13]. A Voigt lineshape function was used, with Gaussian width calculated from Doppler broadening and Lorentzian width of 2 GHz (full width at half maximum) representing an estimated pressure broadening in 100 Torr Ar [12]. Figure 3(c) shows modeled absorption spectra for the three Fe I transitions at temperatures spanning the range 2,000-10,000 K and with \( n_{tot} = 10^{19} \) cm\(^{-3}\). The simulated spectra are in reasonable agreement with the observed data and calculated temperatures as described below.

Using \( n_i \cdot L \) combined with Eq. (3), the electronic excitation temperature and total path-integrated number density \( n_{tot} \) were determined using a so-called "Boltzmann plot". The analysis is similar to that used routinely for plasma temperature characterization in emission spectroscopy and is based on the assumption of local thermal equilibrium (LTE) [14]. LTE requires that collisional processes dominate over radiative processes such that Eq. (3) remains locally valid within regions of the inhomogeneous plasma, which is typically satisfied in LIPs. Rearranging Eq. (3) as \( \ln(n_i \cdot L / g_i) = \ln[n_{tot} \cdot L / Z(T)] - E_i / k_B T \) shows that a linear fit of \( \ln(n_i \cdot L / g_i) \) versus \( E_i \) provides the excitation temperature from the slope and \( n_{tot} \cdot L / Z(T) \) from the y-intercept. Figure 4(a) shows the Boltzmann plots for each delay time, and Fig.4(b) shows the temperature determined from the linear fits. The measured temperatures are reasonable compared to emission based results given the ablation pulse energy and background pressure used [14]. Comparisons with most prior work can only be made at early time delays (11 µs) given that emission techniques are limited to probing early time behaviour of the plasma. \( n_{tot} L \) shown in Fig.4(c) was calculated from the y-intercepts of the Boltzmann plots, and scaling using the partition function at the temperature determined from the slopes. The ability to measure total number densities is a powerful diagnostic tool to help quantify the amount of a material that is detected in the ablation plume. The relatively constant value \( n_{tot} L \) here is consistent with the expectation that molecules and solid clusters do not form under these conditions.

The measurement of the plasma temperature out to time delays of 140 µs as shown in Fig.4(b) demonstrates the ability of this technique to characterize late-time plume evolution long after the plasma emission has ceased. Determination of plasma excitation temperature using absorption requires probing multiple transitions with lower state energies populated at the desired temperature range \( T \sim E_i / k_B \). For the Fe measurements re-
reported here, the lowest temperature is determined by the energy state at 7377 cm$^{-1}$, which enables temperatures of $T \sim 4000$ K at a delay of 140 µs to be measured. Lower temperatures could be measured by changing the wavelength range probed by the DCS to include transitions with lower energies, including ground state resonance lines. In emission spectroscopy, however, it is well-known that the Boltzmann plot method cannot be used for transitions with low-lying energy levels $E_i \ll k_B T$ due to effects of self-absorption and self-reversal which result in incorrect determination of emission peak areas [14, 15]. As a result, emission spectroscopy is best suited to determination of relatively high excitation temperatures existing at early times after ablation. In contrast, absorption spectroscopy can probe low-lying energy states which remain populated at lower temperatures. Ultimately, a combination of both emission and absorption spectroscopy will provide the most complete characterization of plasma properties throughout its evolution.

An absorption measurement of a single transition can determine the atomic number density in a particular state, but is insufficient to determine total number density unless the excitation temperature is known. By simultaneously measuring multiple transitions across a broad spectral range to determine temperature, the DCS technique also provides quantitative measurements of path-integrated state and total atomic number densities within uncertainties in path length and distribution of atoms along the line of sight. It should be noted that effects from spatial gradients of excitation temperature and atomic number density are greatly reduced at later times in plasma evolution. In addition, while the present work does not address the important spatial evolution of the ablation plume, when combined with plasma imaging and/or plasma hydrodynamic modeling, a more complete picture of the temperature and atomic number densities determined from absorption measurements can be obtained. Previous work using emission [16] and absorption techniques [15, 17] have reported such spatially resolved measurements. Future work will utilize broader spectra to observe additional transitions and multiple species to better characterize statistical uncertainties and test the validity of the LTE assumption.

In summary, we report the first time-resolved DCS measurements capable of tracking the evolution of constituents within a LIP. We utilize three excited-state Fe transitions following laser ablation of a stainless steel sample and perform multi-level absorption based atomic analysis to calculate number densities and excitation temperature. The use of DCS offers the potential for extremely broadband absorption spectroscopy without the spectral bandwidth limitations of single frequency lasers or the trade off in bandwidth and spectral resolution of spectrometer based approaches. The technique can also be extended to track longer timescales approaching 1 ms by including resonance lines for plasma characterization.

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