Diatomic Molecular Emission Spectroscopy of Laser-induced Titanium Plasma

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Abstract. Previous research regarding laser-induced breakdown spectroscopy (LIBS) of titanium normally focuses on the atomic and ionic Ti spectral transition lines. However, after a characteristic time subsequent to laser ablation, these lines are no longer discernable. During this temporal regime, the diatomic molecular transition lines of titanium monoxide (TiO) are prominent in the laser-induced plasma (LIP) emissions. TiO has long been studied in the contexts of stellar emissions, allowing for some of the molecular transition bands to be accurately computed from theory. In this research, optical emission spectroscopy (OES) of laser-induced plasma (LIP) generated by laser ablation of titanium is performed in order to infer temperature as a function of time subsequent to plasma formation. The emission spectra of the resulting ablation plume is imaged as a function of height above the sample surface. Temperatures are inferred over time delays following plasma formation ranging from 20 μs–200 μs. Computed TiO $A^3\Phi \rightarrow X^3\Delta$, $\Delta v = 0$ transition lines are fit to spectral measurements in order to infer temperature. At $t_{\text{delay}} = 20$ μs–80 μs, the observed plume contains two luminescent regions each with a distinctly different temperature. As the plume evolves in time, the two regions combine and an overall temperature increase is observed.

1. Introduction
Laser-induced breakdown spectroscopy (LIBS), as an experimental technique, has grown in popularity in large part due to the simplicity of the required equipment. The traditional LIBS apparatus consists of a single laser, serving as an excitation source, and a spectrometer equipped with a detector for gathering spectral emissions [1]. The success and growth of future LIBS applications require a deeper understanding of the fundamental processes occurring as a plasma is observed at various time delays, given various experimental conditions [2]. To this extent, much of the ongoing fundamental research utilizing LIBS, seeks to observe and analyze specific atomic and molecular species present in the laser-induced plasma (LIP) [3, 4, 5, 6, 7]. By closely examining the properties of spectra from specific atoms and molecules at various regions of the plasma, as it evolves in time, a description of the characteristic processes going on throughout the plasma can be obtained. Of particular interest is the time domain for which molecular recombination overcomes electron collisions as the dominant mechanism concerning plasma emissions.

As LIP evolves in time, the characteristic emitting species dominating the spectra will evolve as well. An initial LIBS spectrum, typically within the first tens of nanoseconds, is dominated by a spectral continuum contribution. Mechanisms, such as inverse Bremsstrahlung...
and radiative recombination involving free electrons, are responsible for this spectral continuum. As the plasma expands and cools, ionic spectral line transitions appear in the plasma emissions, superposed to the continuum contribution. The more highly ionized species will become prominent first, followed by the lesser ionized species and ultimately the neutral atomic transition lines [8, 9, 10]. Three-body recombination occurring with plasma expansion causes a rapid decrease of the electron density in the plasma [11]. As a consequence of the decreasing electron density in the plasma, each emission line will become progressively more narrow during the plasma expansion [12].

After a characteristic time, depending on electron density, the elements in the plasma and the plasma expansion, emissions from radiative molecular transitions will become discernible as the prominence of atomic spectral lines observed in the plasma decreases [13]. Of particular interest for this research is the diatomic molecular radiative transitions of the plasma. Typically, this phenomenon is attributed to the recombination of atoms to form molecules. However, the detection of diatomic transitions of certain species at far earlier stages of plasma evolution when compared to other diatomic transitions in similar conditions leads to the conclusion that not all diatomic transitions are a product of recombination. In these scenarios, it is hypothesized that the molecule was present prior to plasma formation. However, many diatomic molecules observed in laser-induced plasma are unstable in typical laboratory environments. For such molecules, LIBS offers a suitable method for observation. The spectral transitions of such molecules can be collected typically for tens of microseconds. Often times, these emissions are quite luminous, from the ultra-violet to the infrared.

For the purposes of analyzing the laser ablation plasma above the Ti surface at time delays on the order of tens to hundreds of microseconds, TiO spectral transitions are utilized to infer temperature. This required the computation of new, accurate line-strength tables. Diatomic quantum theory is utilized in computing line-strengths of spectral transitions [4, 14]. The specifics concerning the computation of the line-strengths used in this research are presented elsewhere [16, 17]. Given a few parameters, such as resolution and temperature, the spectral line-strengths can be used generate a synthetic spectrum representative of the radiant transitions of a diatomic molecule. In order to infer micro-plasma parameters, the experimentally collected spectra believed to contain the diatomic spectral signatures are fit with the computed spectra for the molecule [15, 16, 17].

Previous studies observed the TiO $B^3\Pi \rightarrow X^3\Delta$ and $A^3\Phi \rightarrow X^3\Delta$, $\Delta v = 0$ transition bands in the ablation plasma [17, 18]. The collected spectra were then fit with computed spectra in order to infer temperature as a function of delay time. Temperature inferences, resulting from the use of an intensified linear diode array arrangement to gather time-resolved spectra, typically contained a local minimum occurring between a 40 $\mu$s and 60 $\mu$s delay time. At 60 $\mu$s, when the expanding plasma is thought to be cooling, this unexpected result indicated an increase in temperature. In order to further investigate the situation, the current research observes the TiO $A^3\Phi \rightarrow X^3\Delta$, $\Delta v = 0$ transition band at time delays ranging from 20 $\mu$s–200 $\mu$s. Utilizing a gated two-dimensional ICCD detector, the gathered emissions are time-resolved and imaged as a function of height above an ablation surface. The gathered spectra are then fit with computed spectra representing the TiO $A^3\Phi \rightarrow X^3\Delta$ band to infer temperature.

2. Experiment

A Ti 6-4 sample is ablated by radiation from a Nd:YAG laser with 160 mJ per pulse and a nominal pulse width of 13 ns. The laser radiation is supplied at 10 Hz and focused to approximately a 1 mm spot size. The beam propagates vertically downward onto the flat Ti surface such that the beam path is parallel to the slit aperture of a Jobin-Yvon spectrometer. The resulting ablation plume emissions are imaged onto the slit in a 1:1 manner. The spectrometer is equipped with an Andor iStar ICCD camera, providing both temporal and spatial resolution. In order to enhance
the signal to noise ratio, the $1024 \times 1024$ pixels provided by the detector are consolidated into 32 spectra ($1024$ pixels across) gathered along the height of the plume for each image. Additionally, $200$ accumulations are used to produce each image. At $t_{\text{delay}} = 20–200$ $\mu$s, spectra in the range of $705$ nm–$715$ nm are collected every $20$ $\mu$s utilizing a $2$ $\mu$s gate width. In this spectral region, at these time delays, TiO transition lines are collected. The gathered spectra are then fit with computed spectra from the TiO $A^3\Phi - X^3\Delta$, $\Delta v = 0$ transition band in order to infer temperature.

3. Results
Figure 1 provides an example of an experimentally obtained spectrum fit with a computed spectrum for the TiO $\gamma$ transition. The collected spectrum of Fig. 1 represents a single horizontal slice of a larger image. Fig. 2 is an example of such an image. The plot just below the image in Fig. 2 represents the vertical sum of the pixels in the image. Such a summation is likened to using a linear diode array detector. While spectra computed from theory are used to infer the TiO transition temperature along the height of the image, the spectrum obtained by integrating the height of the detector can be similarly analyzed. The result is typically a temperature corresponding to the inferred temperature at the hottest region of the image.

![Figure 1.](image)

Figure 1. The above plot represents a horizontal slice of one the gathered images fit with computed spectra corresponding to $T = 3400$ K. The measured spectrum was collected at $t_{\text{delay}} = 160$ $\mu$s.

By studying Figures 2–6, some very interesting phenomena becomes apparent. The temperature inferred from the TiO molecular transitions increases with height along the ablation plume. This phenomena is consistent throughout $t_{\text{delay}} = 20–200$ $\mu$s. More interestingly, it is clear that between $t_{\text{delay}} = 20–60$ $\mu$s there are two distinct regions of the plasma. One region rests several millimeters above the sample surface, while the other appears to rise from the surface before the two ultimately combine. After the two regions combine ($\sim 100$ $\mu$s), there is a noticeable bulge in uppermost part of the intensity profile.

When the temperature inferences made from emissions of the two regions are compared, it is apparent that the inferred temperature of the TiO emissions from the region closer to the
Figure 2. The above image represents spectra of laser ablation plasma above a titanium surface recorded at $t_{\text{delay}} = 40 \mu s$ with a 2 $\mu s$ gate width.

Figure 3. The above image represents spectra of laser ablation plasma above a titanium surface recorded at $t_{\text{delay}} = 60 \mu s$ with a 2 $\mu s$ gate width.

The sample surface is distinctly lower than that of the region further above the surface. This is most clearly evident in Figures 2 and 3. Particularly when examining the inferred temperatures of Fig. 2, it is important to keep in mind that we are struggling to make temperature inferences resulting from fitting computed TiO spectra to the collected spectra on account of signal to noise issues. Notice at the earlier time delays, the characteristic structure of the TiO $A^3\Phi - X^3\Delta$ band is hardly discernable. Much of the spectral signatures observed in this time domain are atomic line shapes. When inspecting the inferred temperature more confidence is given to those values inferred from the brighter regions of the plume. These regions are made brighter by the luminescent TiO transitions. This conveniently allows for succinct comparison between the two brightest regions of Fig. 2, as the TiO spectral signatures in the dimmer regions are less discernable from the other spectral contributions.
Figure 4. The above image represents spectra of laser ablation plasma above a titanium surface recorded at $t_{\text{delay}} = 80$ $\mu$s with a 2 $\mu$s gate width.

Figure 5. The above image represents spectra of laser ablation plasma above a titanium surface recorded at $t_{\text{delay}} = 100$ $\mu$s with a 2 $\mu$s gate width.

Examining the plots to the left of the images in Figures 2 - 6 provides insight into the luminosity along the height of the plasma. The motion of the lower peak towards the upper peak can be used as a measure of the kinetics of the luminous lower region of the plasma. These plots for Fig. 2 - 4 also illustrate an increase in luminosity of the lower region as it approaches the upper. At later time delays, $t_{\text{delay}} = 100$–200 $\mu$s, a hump is observed at the top luminous region of the ablation plume. The height of the plasma corresponding to the slight dip below the hump is determined to be hotter than the regions above or below the dip. While hump appears to be a consequence of a snowplow effect at the top of the plasma, two-dimensional spatial imaging of the plume would possibly provide an explanation. The current apparatus observes primarily along the axial distance perpendicular to the surface; however, imaging in the radial direction would likely provide a crown-shaped profile, as in Fig. 8 of Aguilera et al.
Figure 6. The above image represents spectra of laser ablation plasma above a titanium surface recorded at $t_{\text{delay}} = 200 \, \mu s$ with a 2 $\mu s$ gate width.

Figure 7. The plot above illustrates the temperature as function of time delay inferred from the analysis of the spectra resulting from integrating along the height of the detector.

4. Discussion
By comparing the inferred temperature from the upper region of Figure 2, we find remarkable agreement with the results obtained previously at this same time delay ($t_{\text{delay}} = 40 \, \mu s$) using this same window (2 $\mu s$) [18]. If we make the same comparison with the upper region of Fig. 3 and Woods et al. [18] at $t_{\text{delay}} = 60 \, \mu s$, there is some agreement for the inferred temperatures here as well. When the spectra obtained by integrating over the height of the images are analyzed, the inferred temperatures typically correspond to a temperature slightly elevated from that of the upper luminescent region (see Figure 7).

Examining Figure 7, a temperature increase of $\approx 100 \, \text{K}$ occurs at $t_{\text{delay}} = 100 \, \mu s$. Previous investigations concerning both the TiO $B^3\Pi \rightarrow X^3\Delta$ and $A^3\Phi - X^3\Delta$ systems have also found
an unexpected temperature increase at later time delays [17, 18]. Inspection of the inferred temperatures along the height of the image over $t_{\text{delay}} = 40–100$ μs indicate that the lower region undergoes drastic heating, as the cooler TiO molecules of the lower luminescent region interact with the warmer TiO molecules of the upper region. This interaction results in an overall increase in TiO temperature in the plasma.

While more investigations are required to fully characterize this bright region rising from the surface, some hypotheses can be formed. By the ability to fit computed TiO spectra to this emitting region, it is determined that the TiO molecule is the dominant emitter. In the upper region, the TiO transitions are likely the result of recombination. This is consistent with the delay time in which the transitions become discernible given the excitation source and the evolution of the temperature and electron density, as determined by the measurements made within the first hundreds of nanoseconds. The drastic temperature difference at $t_{\text{delay}} = 40$ μs between the upper and lower luminescent regions remains largely unexplained. As the cooler plasma temperatures are typically found to be in the lower regions, perhaps a sudden flurry of recombination occurs near the sample surface, overtaking electron impacts as the driving mechanism for emissions. This trend then rises along the plasma until it reaches the upper region. However, because the temperatures inferred from the TiO transitions in the lower region are starkly less than those of the upper region and gradually increase as the regions interact, an alternate theory would maintain that the mechanism causing the radiative transitions of the diatomic molecule is different between the two regions. During laser ablation at this intensity, the sample surface will become molten for a characteristic duration [20]. Considering the lower region is much cooler and appears to heat as it leaves the surface, possibly the TiO emissions in this region are emanating from bulk titanium being ejected from the sample surface.

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