Laser-Induced Spectroscopy of Graphene Ablation in Air

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Abstract. Carbon Swan spectra are observed following laser ablation of graphene in laboratory air. Previous experiments showed temperatures that ranged from 4500 to 7500 K for the \( \Delta \nu = 0 \) transition and 4200 to 4500 K for the \( \Delta \nu = -1 \) transition for time delays on the order of 1.6 \( \mu \)s to 70 \( \mu \)s. This experiment explored in greater detail time delays > 10 \( \mu \)s for both molecular bands. Temperatures were found to be similar, ranging from 4500 to 6700 K for the \( \Delta \nu = 1 \) transition and 3200 to 5500 K for the \( \Delta \nu = -1 \) transition. Investigation is also made into spatially resolving the plasma emissions along the slit height. In addition, efforts are made to investigate the applicability of the local thermodynamic equilibrium (LTE) assumption. Comparisons are discussed in view of previous work that utilized Stark broadening of the H\( \beta \) line, confirming LTE for delays < 10 \( \mu \)s, yet further research needed for later delays.

1. Introduction
Laser-induced breakdown spectroscopy (LIBS) is a technique utilized for analyzing a substance’s composition [1]. It is a non-invasive and non-contact technique that only requires a small amount of the substance to be useful while still allowing for accurate determination of unknown material [2]. This becomes especially useful when the substance itself or its environment is hazardous in nature. However, in order to be of use as a diagnostic tool, known models are required. Previous investigations had been made [4, 3, 5] into C\( _2 \), though limited. To that end, investigations are made into carbon Swan spectra emissions from laser-induced plasma.

2. Experimental approach
The experiment utilizes a Nd:YAG pulsed laser operating at 1064-nm with 13 nanosecond, 190 mJ/pulse to generate laser-induced breakdown. The emitted spectra were dispersed with an 1800 grooves/mm grating in a HR640 Jobin-Yvon 0.6 m spectrometer and then recorded with an Andor iStar ICCD. Measurements were time-resolved with varying time delays (10 \( \mu \)s to 100 \( \mu \)s) and corresponding gate widths (1 \( \mu \)s to 20 \( \mu \)s). Spectra were sensitivity and wavelength calibrated with a standard tungsten and mercury lamp, respectively.

3. Computational approach
For diatomic molecules, spectral predictions require a temperature along with line-strengths [6], for the allowed spectral transitions. In order to fit the spectra, the Nelder-Mead algorithm is utilized [7] through the so-called Nelder-Mead-Temperature (NMT) program.
The NMT program generates a single temperature spectral fit for the recorded data. This fit, within the accuracy and precision bounds, is also used to refine the calibration the data. This is repeated several times, with each run increasing from a linear, quadratic, to finally a cubic calibration. After that, the program is run three times in succession to ensure accuracy of the computed temperature.

4. Results
Figures 1 and 2 are representative of the results from the NMT program for carbon Swan spectra of the $\Delta v = 0$ and $\Delta v = -1$ bands. Seen in both are the clear vibrational peaks and underlying rotational structure. No atomic lines are present. Note, there is good matching between the experimental and theory spectra as the count difference between both is generally within the computed background line.

Figure 1. 40 $\mu$s delay, 5 $\mu$s gate width. Temperatures are 5500 K and 4400 K, left and right.

Figure 2. 70 $\mu$s delay, 10 $\mu$s gate width. Temperatures are 5800 K and 3200 K, left and right.

Figure 3 shows a 2-D image of the $C_2$ spectra for the $\Delta v = 0$ band. Calculated temperatures range from 6600 K to 7700 K, increasing towards 7 mm, with a dip just under it at 6 mm. Also of note is the slight vertical symmetry.
Figure 3. Raw image of two dimensional C\textsubscript{2} spectra at 15 \(\mu\)s delay and 5 \(\mu\)s gate width. The FWHM averaged to 0.13 nm for each of the individual spectral lines.

5. Conclusions

For our theory models, we have used a single temperature for fitting with assumption of LTE. For early time delays on the order of 1 \(\mu\)s with large laser energy per pulse, time-delayed spectra indicate LTE due to the presence of H\textsubscript{\(\beta\)} [3].

Past that, there is some indication for LTE at later delays: The experimental spectra having good agreement with computed theory spectra within background variations. However, there is no definite indication of LTE at later delays. As the electron density diminishes, H\textsubscript{\(\beta\)} emissions disappear in the measured spectra past 10 \(\mu\)s. There is some indication that LTE is absent since there appears to be different temperature ranges for the different wavelength bands, as seen in comparing the \(\Delta v = 0\) and \(\Delta v = -1\) bands.

From the recorded 2-D data, we conclude that the plasma shows a higher temperature towards the top of the recorded emission spectra near 7 mm but is cooler away from it. Just below that region, there appear to be significant variations in inferred temperature. These temperature differences could indicate non-LTE conditions. Consequently, exploration and utilization of Abel and Radon techniques [8] in better analyzing the plasma is called for.

Acknowledgments

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References

[1] Parigger C G 2012 Spectrochim. Acta Part B 78-79 4
[2] De Lucia Jr F C, Harmon R S, McNesby K L, Winkel Jr R J and Miziolek A W 2003 Appl. Opt. 42 6148
[3] Witte M J and Parigger C G 2013 Int. Rev. At. Mol. Phys. 4 63
[4] Witte M J, Parigger C G, Bullock N A, Merten J A and Allen S D 2014 Appl. Spectrosc. 68 367
[5] Parigger C G, Woods A A, Witte M J, Swafford L D and Surnick D M 2014 J. Vis. Exp. 84 E51250
[6] Hornkohl J O, Nemes L and Parigger C G 2011 Spectroscopy of Carbon Containing Diatomic Molecules in Spectroscopy, Dynamics and Molecular Theory of Carbon Plasmas and Vapors eds L Nemes, S Irle (Singapore: World Scientific Publishing) chapter 4 pp 113–165
[7] Woods A C, Parigger C G and Hornkohl J O 2012 Opt. Lett. 37 5139
[8] Gornushkin I B, Merk S, Demidov A, Panne U, Shabanov S V, Smith B W, Omenetto N 2012 Spectrochim. Acta Part B 76 203