

Measurement and Analysis of Carbon Swan Spectra Following Laser-induced Optical Breakdown in Air

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ABSTRACT: In this work, we report on measurements of time-resolved Carbon Swan spectra following laser ablation of carbon material. Diatomic molecular C_2 line-strengths are utilized to compute the fitting of the measured data. The C_2 molecule shows that its lowest rotational levels are sensitive to temperature variation. However, we record spectra for time delays for which Local Thermodynamic Equilibrium is expected to be established. In this respect, a single temperature fitting will be viable. For laser ablation of graphene with 190 millijoule, 13 nanosecond Nd:YAG pulses at a wavelength of 1064 and 532 nanometers, our results show temperatures in the range of 4000 to 6500 K for delays in the range of 70 to 20 microseconds after optical breakdown.

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I. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) can be applied for accurate determination of unknown materials. When faced with an unknown material, direct handling of the material may not be desired, usually due to concerns of the material being radioactive, unstably explosive, or other such hazards. Most of these substances contain carbon compounds. LIBS offers a mostly non-invasive way in looking at the materials' spectrum to analyze its composition. In order for this procedure to be effective, a reasonable set of precise and accurate "calibration spectra" is preferably available or must be acquired. In other words, precision and accuracy are required. Thus, for applications of LIBS with carbon compounds, experiments that address C_2 molecular spectra are desirable together with an accurate analysis.

Spectral predictions for diatomic molecules require at least a temperature to determine Boltzmann factors and line-strengths that represent the allowed spectral transitions for the molecule¹. Atomic and molecular spectroscopy techniques² allow us to analyze recorded spectra. However, accurate spectral predictions may also include spectral resolution, electron density, reaction rates, collision rates, and pressure. These parameters are adjusted to determine the best fitting model for each spectral measurement. In this investigation, we infer the temperature of C_2 Swan bands for laser ablation events by comparing measured with computed spectra.

II. EXPERIMENTAL ARRANGEMENT

Frequency doubled laser radiation on the order of 75 mJ/pulse is used to generate laser-induced breakdown. The pulse width of the laser radiation amounted to 13 ns, and measurements utilized varying gate widths corresponding to varying time delays ranging from 20 μ s to 70 μ s, with gate width times increased as needed. The time-resolved spectra were recorded with a EG&G PARC linear diode array to record spectra dispersed with a 1800 grooves/mm grating in a HR640 Jobin-Yvon 0.6 m spectrometer. Sensitivity calibration was accomplished by use of a tungsten

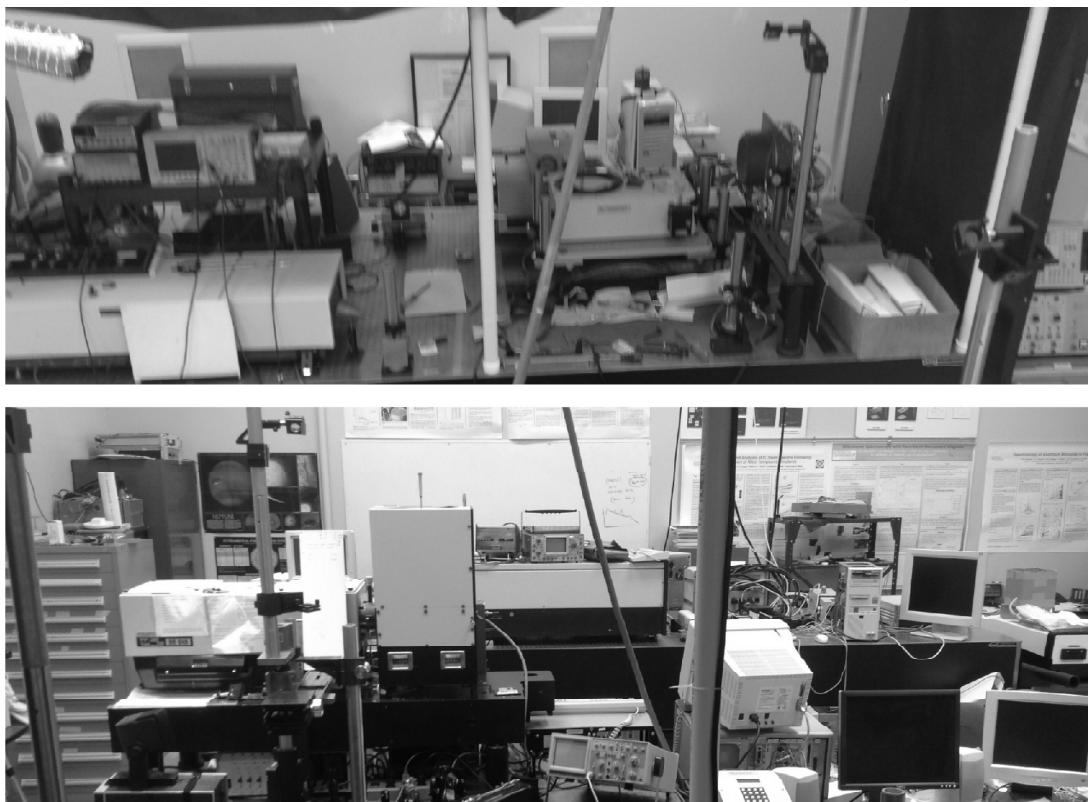


Figure 1: Photographs of experimental arrangement. Top part shows the Nd:YAG laser (bottom left). Bottom part shows the spectrograph (middle left).

standard lamp, measured at an operating temperature of 2910 K. Wavelength calibration was accomplished with a mercury lamp.

Figure 1 shows a photograph of the experimental setup. The carbon sample is either manually held or placed on an angled surface, depending on which allowed the best collection of data. The 532-nm laser radiation is focused onto the sample, ablating it, and the plasma emission is imaged onto the spectrometer entrance slit on the right.

III. RESULTS

The experimental procedures included capture of time-resolved spectra for various time delays, followed by intensity and wavelength calibration. The intensity calibration uses a standard black-body curve calculated for the spectral wavelength band and the recorded intensity profile emitted by a tungsten lamp. The calibration is accomplished using a least-squares algorithm.

Analysis of the experimental records is accomplished by sequentially increasing the accuracy of the comparisons of experimentally recorded and computed molecular spectra. The Calibrated spectra are fit with the predicted C_2 spectra using a Nelder-Mead algorithm, which allows multi-variable fitting. Intensity- and wavelength-calibrated data are run through the so-called Nelder-Mead-Temperature (NMT) program with, first, a fixed FWHM of 0.08 nm. A spectral fit is generated, which is used to linearly wavelength calibrate the data. This generates a new spectrum, allowing a repeat of the process, though with quadratic wavelength fitting this time. Subsequently, the FWHM is set to variable and a new fit is computed. This is followed by generating a cubic wavelength fit. The NMT program is then utilized three times to compute the temperature that generates the best fit between the experimental and theory spectra. This procedure is applied for both the 504-517 nm and the 550-564 nm wavelength bands.

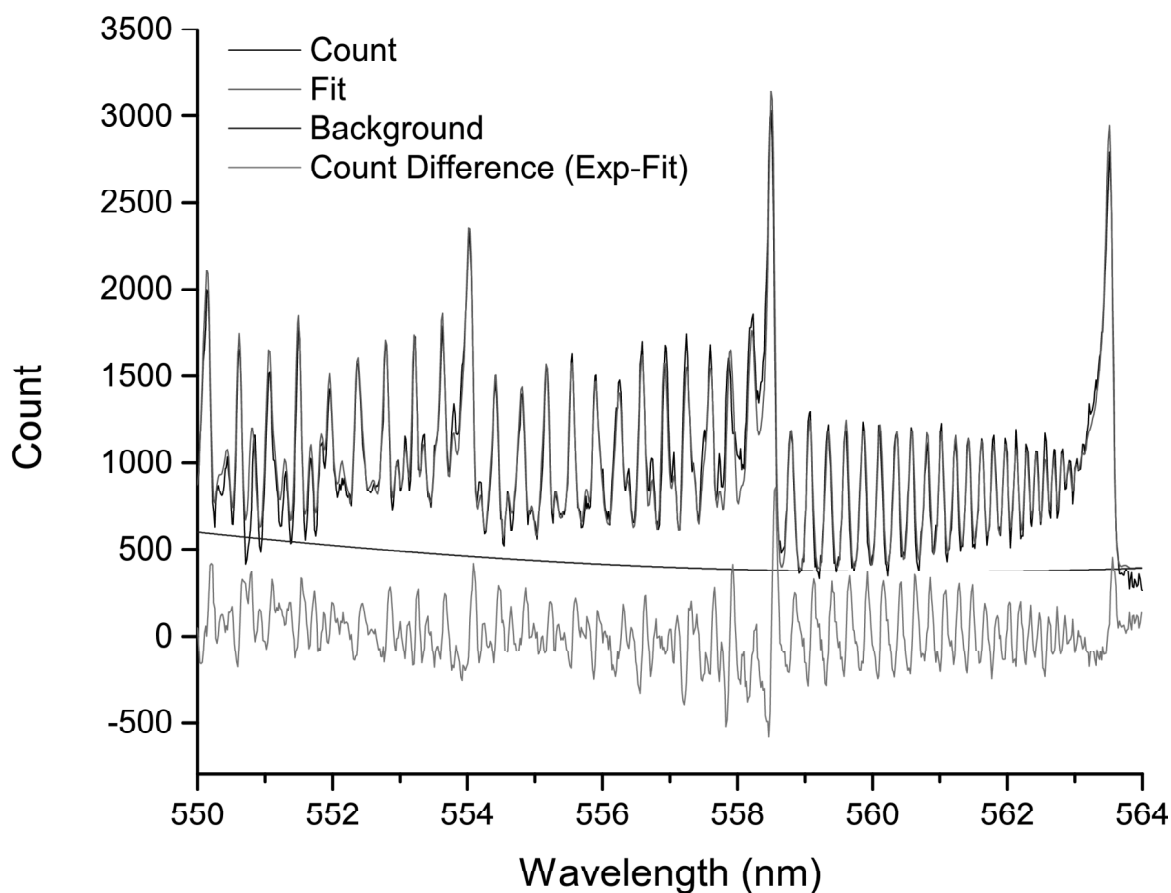


Figure 2: C_2 spectra, with a delay of $30 \mu s$ and a gate-width of $1 \mu s$. Calculated temperature amounts to 4300 K , with a spectral resolution FWHM of 0.086 nm . This graph shows the experimental and the superposed computed spectrum. The curved line indicates the background. The bottom spectrum illustrates the difference between the experimental and fitted data. The difference data shows a standard deviation of 175, the background curve average amounts to 448.

Figure 2 is a representative display of recorded and fitted C_2 spectra for the C_2 550-564 nm wavelength band. As discussed in Refs.^{1,8}, carbon shows four band transitions between 550 and 564 nm: (0-1), (1-2), (2-3), and (3-4) bands. The four expected C_2 peaks, the $C_2 \Delta v = 1$ Swan band sequences, are visible: two prominent (558.5 nm, 563.5 nm), two not so prominent (550.1 nm, 554.0 nm). The experimental data shows nice agreement with the fitted spectra as they nearly overlap. The difference graphs show an average near zero, with standard deviations below the background averages. The spikes coincide around the C_2 peaks.

Figure 3 shows C_2 data for the 504-517 nm bands. The double Swan peaks appear nicely, and the computed spectra line up with the experimental data. The figure also illustrates a near-straight background determined in the fitting procedure. The difference of experiment and computed spectra is shown as well.

Figure 4 displays the temperatures for the 550-564 nm wavelength range. For the early time delay, the temperature amounts to 4400 K and demonstrates a slow downward trend with increasing delay times. Fig. 4 also displays results for the 504-517 nm band. The temperature amounts to 6000 K and shows a moderate decrease, though with a dip near $60 \mu s$ delay.

We further investigated the background and the standard deviation (STD) of the difference between the experimental data and computed spectrum. We find that the 550-564 nm band shows consistently lower STD, while the 504-517 nm band has STD near equal levels to background noise but in one case slightly exceeds it.

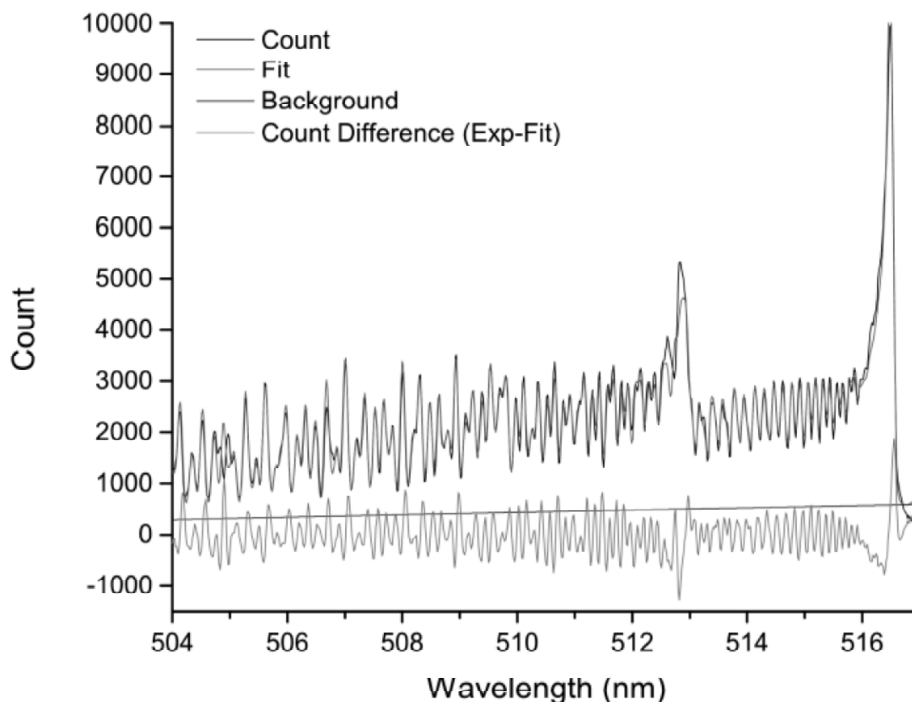


Figure 3: C₂ spectra, with a delay of 20 μ s and a gate of 1 μ s. Calculated temperature amounts to 6000 K, with a FWHM of 0.096 nm. This graph shows the experimental and the superposed computed spectrum. Below is the background curve and then the difference between the experimental and fitted data. The difference data has a standard deviation of 364, and the background curve average amounts to 442.

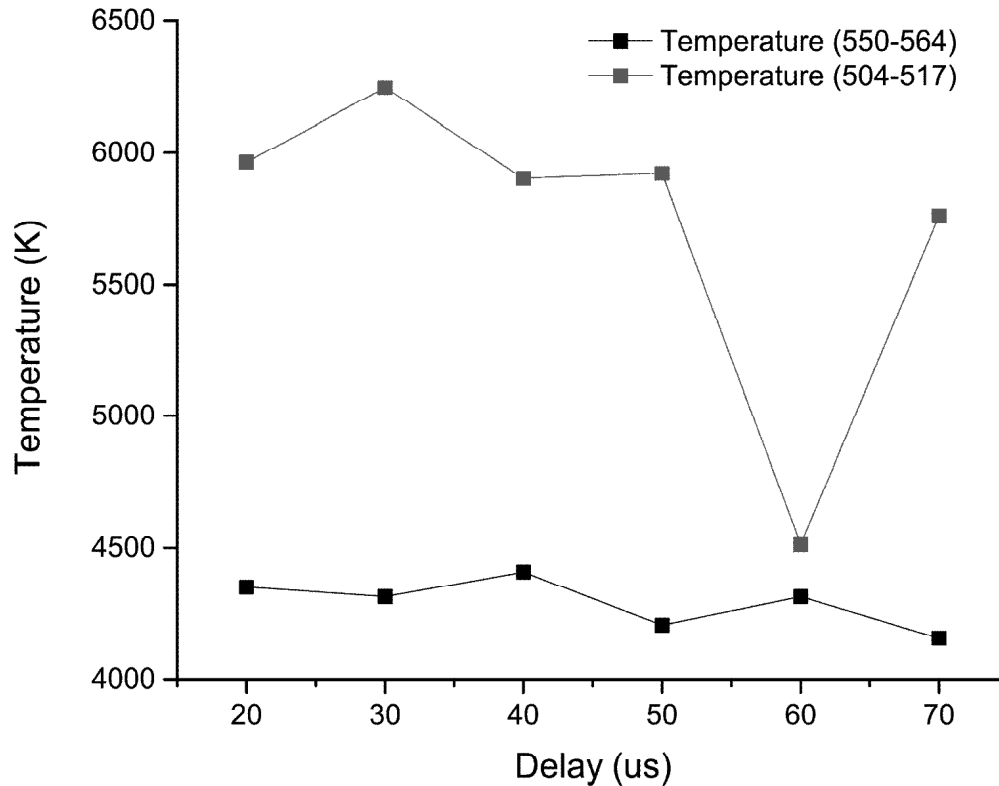


Figure 4: Shows temperatures at various delays for each bandwidth. Notable is the difference in temperatures and that solitary dip.

IV. CONCLUSIONS

Throughout most of the measurements, results have been within expected parameter ranges for temperature, background, and spectral resolution. However, there have been some discrepancies. As seen in figure 4, two major ones are the differences in temperatures between the two bands, and the dip at 60 μs for the 504-517 band. There can be several reasons for the differences. For example, differences can be due to volume-averaging over time, as the laser-induced plasma is recorded over a range of 20 to 70 microseconds time delays after micro-plasma generation during laser ablation with gate widths on the order of 1-10 μs . In addition, the plasma is volume-averaged over space as the linear diode array only allows for a one-dimensional spectrum. This is partially mitigated by the difference graph which can help reinforce the agreement between experiment and theory, and indicate a lower bounds for significant results.

Future experimental studies show two main interests. One, increase in spectral resolution by employing a higher grooves/mm grating to possibly address some of the differences in inferred temperature. Two, recording of spatially resolved data will be of interest possibly followed by application of Abel and Radon inverse transformations in order to better study the discrepancies that are indicated.

Acknowledgements

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