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A Study on Air Plasma Characteristics Through LIBS: Spectral Identification and Temperature Estimation

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Abstract

Understanding plasma behaviour is crucial for designing effective thermal protection systems that withstand extreme heat generated during hypersonic flight. This work revolves around various techniques to quantify the temperature of air plasma using Atomic Emission Spectroscopy (AES) and discusses some interesting observations. Laser Induced Breakdown Spectroscopy (LIBS) is a technique to produce plasma by focusing a laser pulse to high irradiance. A 532 nm Q-switched Nd: YAG laser with a pulse duration of 10 ns and frequency of 10Hz is focused on atmospheric air to induce plasma at various laser powers of 250-500 mW. The plasma emission was captured by an optical spectrometer. The species present in the spectrum are identified using the NIST Atomic Spectra Database and the temperature of the air plasma is estimated. The results are discussed. The electronic temperature estimated using N II lines in the Boltzmann plot method under the assumption of local thermodynamic equilibrium (LTE) are in the order of approximately 38,000-39,000 K. The assumption of LTE is validated using stark broadening parameters.

Keywords: LIBS; air plasma temperature; Boltzmann plot; laser power; exposure time

Nomenclature

I – Intensity in counts
λ – Wavelength in nm
g – Statistical weight
A – Einstein coefficient or transition probability
T – Temperature in K
E – Energy level of atom, ion, or molecule
Z – Partition function
N – Population density
N_e – Electron density
k_B – Boltzmann constant
h – Plank's constant
c – speed of light in m/s
w – Electron impact parameter or Stark width
Subscripts
1 – Lower energy state
2 – Upper energy state

1. Introduction

The shock waves that are formed in front of hypersonic flight and spacecraft re-entry, convert most of the vehicles kinetic energy into heat and increase air temperature. This excessive heat around the hypersonic vehicle leads to dissociation and ionization of air molecules which causes the appearance of conductive plasma layer around the vehicle. It is important to acquire detailed knowledge of plasma parameters around the hypersonic vehicle to make an effective design both thermal and aerodynamic considerations.

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Shashurin *et al* [7] conducted a laboratory experiment demonstrates a straightforward method for modelling plasma layers like those near hypersonic vehicles. Using a hypersonic jet from a cathodic arc plasma and a blunt body made from thin refractory foil, the experiment mimics gas flow reflection encountered during real hypersonic flight. Plasma flow around the blunt body was measured, showing densities close to those in actual flight using Langmuir probes at low pressure. This setup validates numerical codes for simulating hypersonic flight and tests radio communication blackout mitigation techniques. Some other well-known plasma diagnostic techniques are interferometry, mass spectroscopy and optical emission spectroscopy (OES). Among these, OES is the simplest and non-invasive method for parametrical analysis in laboratory.

Pulsed Laser-Induced Plasmas (LIP) are easy to produce in laboratory using pulsed lasers. The optical emission spectra of an LIP contain atomic and ionic lines, superimposed on a continuum of radiation. LIBS is a technique to analyze the sample based on the optical emission spectra from an LIP. It is essential that LIP is in LTE and optically thin i.e., there is no self-absorption of radiation happening in the plasma for elemental analysis using LIBS [1-9]. Under LTE conditions the relative population between two energy levels in an atom, ion, or molecule follows Boltzmann distribution and velocity of each species follows Maxwellian velocity distribution.

Shaikh *et al* [2] made spectroscopic investigations of zinc plasma generated in ambient air by a Q-switched pulsed Nd:YAG laser at three harmonics (1064nm, 532nm, and 355nm). The electron temperature is deduced from the intensity ratio of specific transitions of neutral zinc, while the electron number density is derived from the Stark broadening of a specific transition. Analysis reveals a decrease in both parameters with increasing distance from the target surface and an increase with higher laser irradiance.

Unnikrishnan *et al* [1] studied plasma produced by a 355 nm pulsed Nd:YAG laser on a copper sample in air spectroscopically. Temporal variations of plasma parameters, including temperature and electron density, are analyzed within a 300-2000 ns timeframe. The study utilizes time-resolved spectroscopy and echelle spectrograph techniques. Results reveal a window of 700-1000 ns where the plasma reaches optical thinness and local thermodynamic equilibrium, critical for laser-induced breakdown spectroscopy (LIBS) analysis of samples.

Abdellatif *et al* [3] conducted spectroscopic analysis of laser-produced aluminium plasma using a Q-switched Nd:YAG laser at wavelengths of 1064 nm, 532 nm, and 355 nm, with varying energy outputs. Spatial electron temperature and density were determined using Boltzmann plot and Stark broadening methods, respectively, across different laser wavelengths. The study revealed maximum electron temperature at a distance from the target surface dependent on the laser wavelength, while electron density peaked near the target surface. Comparison with existing data confirmed consistency with the theory of local thermodynamic equilibrium (LTE).

Bousquet *et al* [6] explored the significance of excitation temperature determined through the Boltzmann plot method and emphasizes the importance of accurately analyzing the obtained temperature. Often overlooked issues in the literature are addressed, including the impact of signal-to-noise ratio (S/N) on Boltzmann plot accuracy, distinctions between average temperature and time/space-integrated temperature (apparent temperature), and the sensitivity of the Boltzmann plot method. Through experiment simulations and real experiments, the paper demonstrates the relevance of these issues. Finally, guidelines for the proper utilization of the Boltzmann plot and interpretation of temperature values are provided.

In present work, the measurements were carried out to find plasma temperature and electron density of air plasma using Boltzmann plot on N II lines and the focus will be mainly on the standardizing the air-plasma temperature measurement procedure for repeatability of the results. Further the measurements are repeated for various power of laser ranging from 250 - 500 mW and the observations are discussed.

2. Experimental Setup

A 1064 nm Quanta-Ray Pro-Series Nd: YAG pulsed laser with 10 ns pulse width and up to 550 mJ/pulse energy is used in the experiment. The 1064 nm laser beam is converted to 532 nm beam with the help of Second Harmonic Generator (SHG). The diffraction error is rectified using a filter which reflects the 532nm beam towards laser iris, the remaining 1064nm light gets transmitted out of the system. The laser iris makes sure that the reflected beam is aligned with the window of the objective lens. The 10x objective lens focuses the laser to a point in its focal plane which will generate LIP in air which normally has a threshold power of 85-90mW. An Ocean Optics USB4000 fiber optic spectrometer is used to capture the emission spectra [Fig. 1]. The laser power is varied from 250-500 mW.

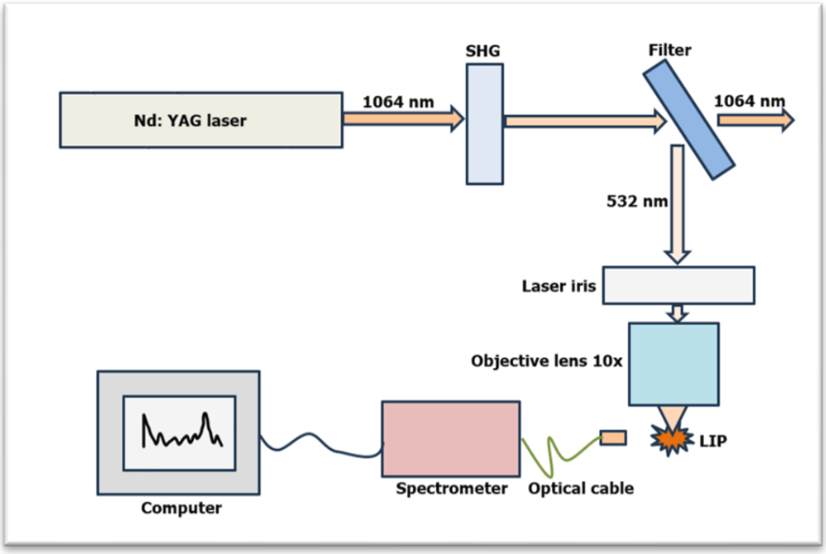

Fig 1. Schematic diagram of experimental setup

3. Theory

3.1. Plasma temperature

The quantitative measure of Laser-Induced Plasma temperature can be obtained through spectral analysis. It is the temperature that controls the electron density, ions and neutrals population densities, and intricacies of processes that occur within the plasma. These processes include photoionization, collisional ionization, radiative and three-body recombination, collisional excitation and de-excitation, radiative decay, photoexcitation, and Bremsstrahlung processes. Fully characterizing the dynamic nature of LIP, marked by its inhomogeneity and transience, poses a considerable challenge. To streamline plasma characterization, thermodynamic conditions are presumed, allowing the plasma to be elucidated by the population density of its constituent species and temperature. Thermodynamic Equilibrium (TE) in a plasma is attained when the rate of a process equals the rate of its reverse counterpart through collisional energy transfer. In a TE state, a plasma can be aptly described by a set of equilibrium laws, all dictated by a single temperature. These laws encompass the Plank, Maxwell, and Boltzmann distributions, as well as the Saha equilibrium [10].

3.2. Boltzmann Population Distribution Law

The relative population between two energy levels in an atom, ion, or molecules is given by Boltzmann distribution, when the plasma is in TE. The Boltzmann distribution is a way of figuring out the likelihood of finding a particle in a particular state based on the energy of that state and the temperature of the system. In simpler terms, it helps us understand how particles are spread out among different energy levels in a system, depending on how hot or cold it is. If the energy levels and the temperature are known, then the Boltzmann distribution helps predict the probability of finding particles in each of those states. It is given by:

$$N_2 = N_1 \frac{g_2}{g_1} e^{-\left(\frac{\Delta E}{k_B T_{exc}}\right)} \quad (1)$$

Where, N_2 and N_1 are population densities in the upper and lower energy levels, respectively, g_2 and g_1 are statistical weights for the upper and lower energy levels, respectively, ΔE is Energy difference between the upper and lower energy levels. T_{exc} and k_B are excitation temperature and Boltzmann constant respectively.

When incorporating the partition function, denoted as Z(T), into the Boltzmann equation, it offers the probability of finding an atom in a specific energy state. The partition function serves as the sum of the population of all potential energy levels for a given atom, ion, or molecule. Importantly, it is a function dependent on temperature. The partition function provides a comprehensive view of how energy is distributed among different states within a particle, offering insights into the likelihood of finding the particle in a particular energy level at a given temperature.

$$\sum_{m=0}^{m_{max}} N_m = N \quad (2)$$

Where N is total number of particles and m_{max} is the number of excited levels (0,1,2…)

$$Z(T) = \sum_{m=0}^{m_{max}} g_m e^{-\left(\frac{E_m}{k_B T_{exc}}\right)} \quad (3)$$

And

$$\frac{N_2}{N} = \frac{g_2}{Z(T)} e^{-\left(\frac{E_2}{k_B T_{exc}}\right)} \quad (4)$$

3.3. Local Thermodynamic Equilibrium (LTE)

When plasma is in thermodynamic equilibrium, using a single temperature to describe the entire system is common. However, for laser-induced plasma (LIP), which is irregular and quickly changing, assuming Local Thermodynamic Equilibrium (LTE) is a more accurate approach. This is because LIP doesn't behave like an ideal blackbody, and it's not uniform or stable. In this context, deviations from the Plank function occur because some photons escape from the plasma, causing an imbalance between emission and absorption in the blackbody equilibrium. Therefore, describing the entire plasma using the Thermodynamic Equilibrium (TE) state is not practical. Instead, using the LTE assumption in small volumes of the plasma is recognized, acknowledging that the overall plasma does not conform to this equilibrium. If the energy transferred within the plasma through collisions exceeds the energy lost through photons, certain equations like the Boltzmann population distribution, the Maxwellian velocity distribution, and the Saha ionization equation can accurately represent the plasma under the LTE approximation.
The McWhirter criterion is a commonly used condition to determine if a plasma is in LTE. According to this criterion, the rate of collisional processes within the plasma must be at least one order of magnitude higher than the rate of radiative processes. This criterion helps ensure that the energy transfer through collisions prevails, maintaining a certain level of equilibrium within the plasma system.

$$N_e > N_{cr} = 1.6*10^{12}(T)^{0.5}(\Delta E)^3 \quad (5)$$

Where, N_{cr} is critical electron density in cm^{-3}, T is plasma temperature in K, ΔE is largest energy gap between the upper and lower energy levels for an emitter in the plasma in eV.

3.4. Boltzmann Plot Method

The intensity of a spectral line emitted by a species is then expressed as:

$$I_{21} = A_{21} h\nu_{21} N_2 \qquad (6)$$

Where, A_{21} is transition probability, or the Einstein coefficient for the spontaneous emission process in s^{-1}, h is Plank's constant in J*s, ν_{21} is frequency of the emitted light, N_2 is population of electrons in the upper energy level, Subscripts 2 and 1 are assigned to an upper energy state and a lower energy state respectively.

By substituting the population density of particles in the upper energy level (N_2) from the Boltzmann equation (Equation 4) in the equation for the intensity of a spectral line (Equation 6), a relationship is established between the population of excited states and the intensity of that spectral line. This connection allows for an understanding of how the number of particles in higher energy states influences the observed intensity of a specific spectral line.

$$I_{21} = A_{21} h\nu_{21} N \frac{g_2}{Z(T)} e^{-\left(\frac{E_2}{k_B T_{exc}}\right)} \qquad (7)$$

$$h\nu_{21} = \frac{hc}{\lambda_{21}} \qquad (8)$$

$$I_{21} = A_{21} \frac{hc}{\lambda_{21}} N \frac{g_2}{Z(T)} e^{-\left(\frac{E_2}{k_B T_{exc}}\right)} \qquad (9)$$

The excitation temperature can be determined by examining the ratio of the intensity of two spectral lines emitted from the same species. If two spectral lines emitted by the same ion are labelled as lines 1 and 2, then the excitation temperature (T_{exc}) can be deduced using the following equations:

$$\frac{I_1}{I_2} = \frac{g_1}{g_2} \frac{A_1}{A_2} \frac{\lambda_2}{\lambda_1} e^{-\left(\frac{E_1 - E_2}{k_B T_{exc}}\right)} \qquad (10)$$

$$T_{exc} = \frac{E_1 - E_2}{\left[ln\left(\frac{I_1 \lambda_1}{g_1 A_1}\right) - ln\left(\frac{I_2 \lambda_2}{g_2 A_2}\right)\right] k_B} \qquad (11)$$

This method for determining plasma temperature involves examining the relative intensity of two spectral lines emitted by the same element or ion. This method is advantageous due to its simplicity and speed. It only requires the analysis of two emission lines with a noticeable difference in their upper-level energy. This straightforward approach makes it a quick and efficient way to estimate plasma temperature. Graphically, the two-line method involves plotting the $ln\left(\frac{I_1 \lambda_1}{g_1 A_1}\right)$ and $ln\left(\frac{I_2 \lambda_2}{g_2 A_2}\right)$ of two spectral lines against their corresponding upper energy levels. The temperature can then be extracted by determining the slope of the resulting line. While the minimum requirement for a temperature measurement is the analysis of two emission lines, the Boltzmann plot offers a more accurate temperature measurement. This is because it considers multiple emission lines, providing a more comprehensive and reliable assessment of the plasma temperature.

$$\frac{I_{21} \lambda_{21}}{g_{21} A_{21}} = \frac{hcN}{Z(T)} e^{-\left(\frac{E_2}{k_B T_{exc}}\right)} \qquad (12)$$

s

$$ln\left(\frac{I_{21} \lambda_{21}}{g_{21} A_{21}}\right) = -\frac{1}{k_B T} E_2 + ln\left(\frac{hcN}{Z(T)}\right) \qquad (13)$$

3.5. Line Broadening Mechanism

Three mechanisms that are expected to significantly influence the observed line width in the generated plasma include Doppler broadening, resonance pressure broadening, and Stark broadening. Often the other broadening mechanisms are neglected because their order of magnitude is comparatively less than the Stark broadening [10]. A highly effective spectroscopic method for reasonably accurate determination of electron density involves measuring the Stark broadening profile of an isolated atom or singly charged ion. This phenomenon arises when emitters collide with charged particles like ions or electrons. The presence of an electric field from an ion or electron leads to the splitting of energy levels within an atom into sublevels, all of which contribute to emission. Consequently, a wavelength shift occurs due to electron transitions between the sublevels of the two primary electronic levels.

4. Results and Discussion

The calibration of the spectrometer is done by using a standard mercury lamp by comparing the wavelength of peaks at 404.66, 435.83, 546.07 nm [Fig 2.]. The average shift in wavelength is found to be 0.03333 nm, which is very small compared to the significant digit for assigning peaks to the lines and are corrected.

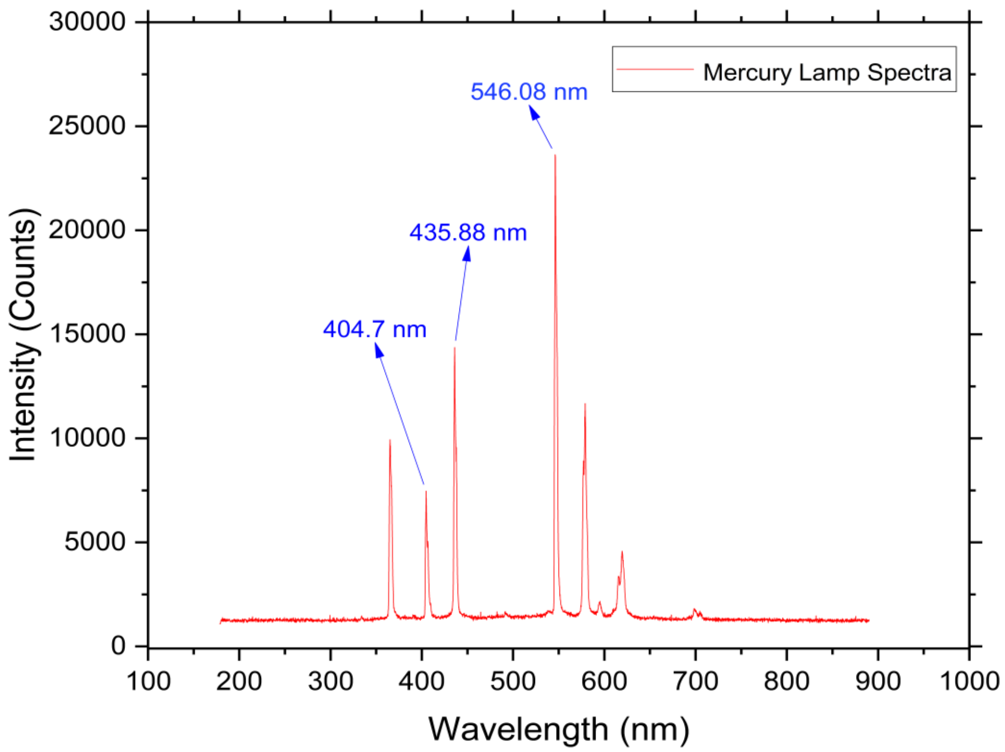

Fig 2. Spectra of Mercury lamp used for calibration of spectrometer.

The lines in the spectra of air-plasma at laser power of 200 mW are identified by performing elemental analysis through NIST Atomic database [11] with the help of spectrum analyzer [12]. Here the closest emission wavelength in the database is assigned to the detected peak in the spectrum. There are also several other ways to assign species to the peaks [10].

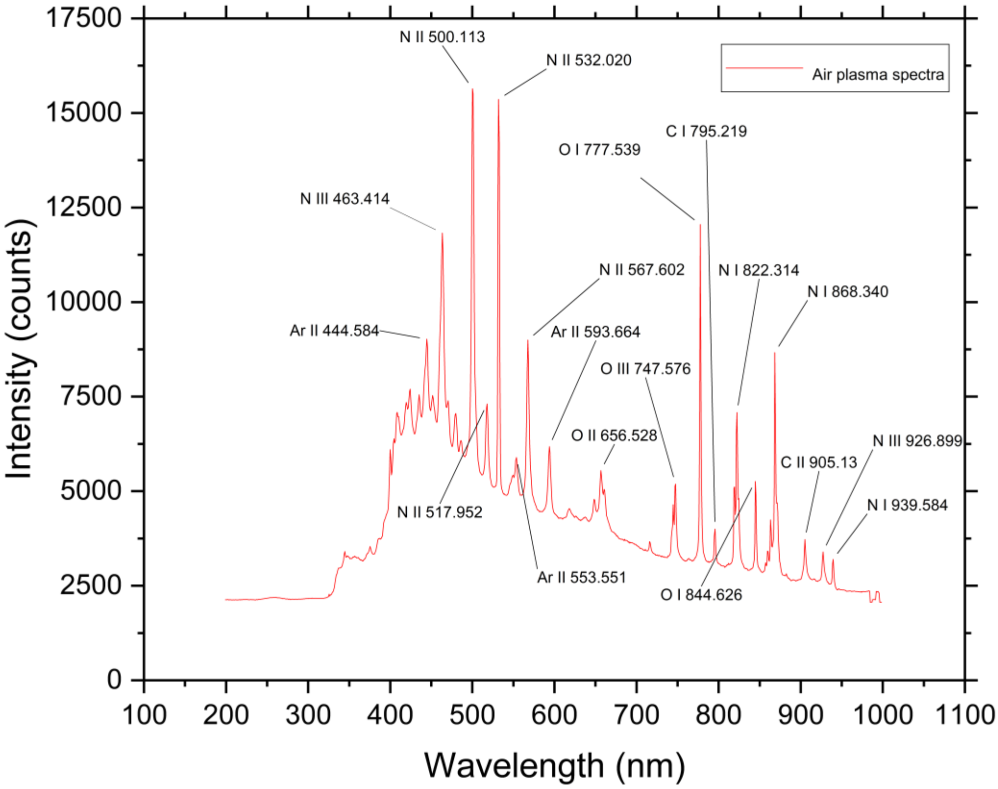

Fig 3. Species identification on air-plasma spectra

The electron temperature is found using Boltzmann plot method by solving the equation (13) by fitting a line with minimum absolute error. The Boltzmann plot method is valid for a single species under the LTE. It is assumed that under LTE, the Boltzmann population distribution and Maxwellian velocity distribution are valid [1,2]. Temperature can be found by plotting $ln\left(\frac{I_{21}\lambda_{21}}{g_2 A_{21}}\right)$ vs E_2, then fitting a slope which will be equal to $-\frac{1}{k_B T}$.

Among the lines that are identified in the spectra, only the lines that have known transition probability in NIST Atomic database are chosen to evaluate temperature. The minimum number of points required for Boltzmann plot is two, but the plot must be chosen such that a greater number of points are available, and they all fit a line with minimum least squared error which can be measured using R-squared value. An R-squared (R2) value is a statistical measure that represents the proportion of the variance for a dependent variable that's explained by an independent variable in a regression model, its value ranges between 0 to 1. R-squared value of 1 indicates a perfect fit of line and it is desired. Here, Boltzmann plot is plotted taking various combinations of lines of same species and the corresponding temperatures are obtained. The temperature value that are negative which are obtained through the positive slope of line in Boltzmann plot are neglected. In the [Fig. 4], it can be observed that by using different lines of the same species in Boltzmann plot, different temperatures can be obtained but the correct estimate of temperature by using the Boltzmann plot where there is more points and the R-squared value closer to 1, in case of air-plasma the Boltzmann plot that is obtained using N II lines of wavelength 500.113, 517.952, 567.602 [Table 1] provides a good estimate of temperature of 39698.5 K and an R-squared value of 0.98. Similar observation and temperature were reported by Francisco *et al* [4].

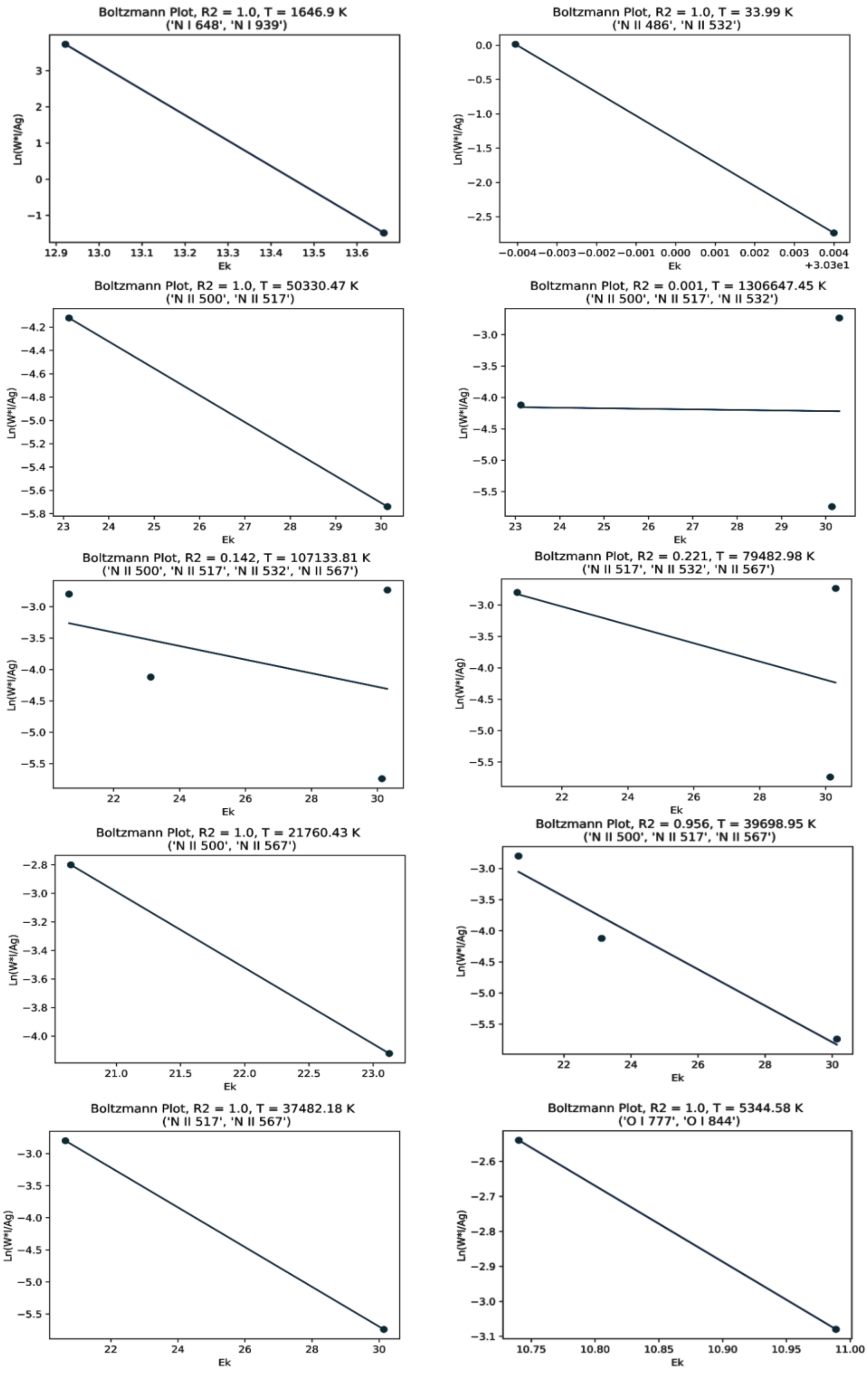

Fig 4. Boltzmann plot for various combinations of species in air-spectra

Table 1. NIST Atomic Spectra Database Lines Data of N II

Species	Wavelength (nm)	E_k (eV)	g_kA_{ki} (S^{-1})
N II	500.1134	188857.4	3.71E+08
N II	517.9521	243086.9	1.18E+09
N II	567.602	166678.6	8.40E+07

The electron density can be evaluated using stark broadening of spectral lines. For a single ionized ion N II, the full width half-maximum (FWHM) of stark broadening is given by,

$$\lambda_{\frac{1}{2}} = 2w\left(\frac{N_e}{10^{17}}\right) \tag{14}$$

Where, w is electron impact parameter or Stark width, N_e is electron number density in cm^{-3} [8]. The FWHM is determined by fitting Voigt function on the N II 532 nm line in the spectra [Fig 5]. The stark width of 0.064 nm is obtained from NIST experimental Stark widths and shifts for spectral lines [5].

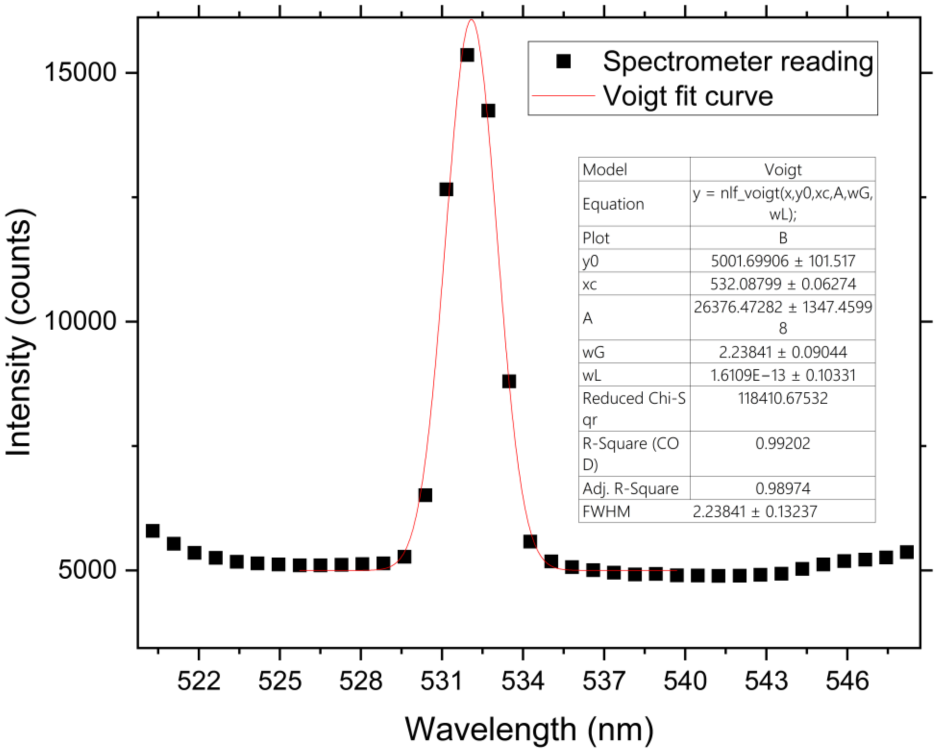

Fig 5. Voigt fit on N II 532 line spectra.

The electron density obtained from stark broadening is 1.748*10^18 cm^{-3} which is greater than the critical electron density of 4.75061*10^16 cm^{-3} which conforms with the McWhirter criterion for validation of assumption of LTE. To check the correctness of electron density obtained, the same calculation is done on O I 777 nm spectra line, which yielded electron density of 1.656*10^18 cm^{-3} which is close to the electron density obtained from N II 532 nm spectra. Note that the actual FWHM (Stark Broadening) = FWHM (Experimental) – Instrumental Broadening, in this work the instrumental broadening is not taken into consideration because the order of instrument broadening which is around 0.01-0.09 nm can't me measured using the low-resolution Ocean Optics USB 4000 spectrometer which has wavelength resolution of 0.22 nm. However, checking the validity of LTE is given priority here so it is safe to neglect the instrument broadening because in McWhirter criterion is satisfied for the obtained critical electron density if the instrument broadening is less than 2.177 nm.

The above procedure is repeated on the spectrum obtained at various powers of Nd: YAG laser [Fig 6]. Further the temperature of air plasma was calculated by using N II lines in which the decrease in temperature was observed while increasing the laser power [Fig 7]. The reason for this is speculated to be as the intensity increases the number of dissociation of atoms or ions which absorbs energy increases, so the plasma temperature is decreasing as the laser power increases. And the actual reason for this phenomenon is yet to be studied.

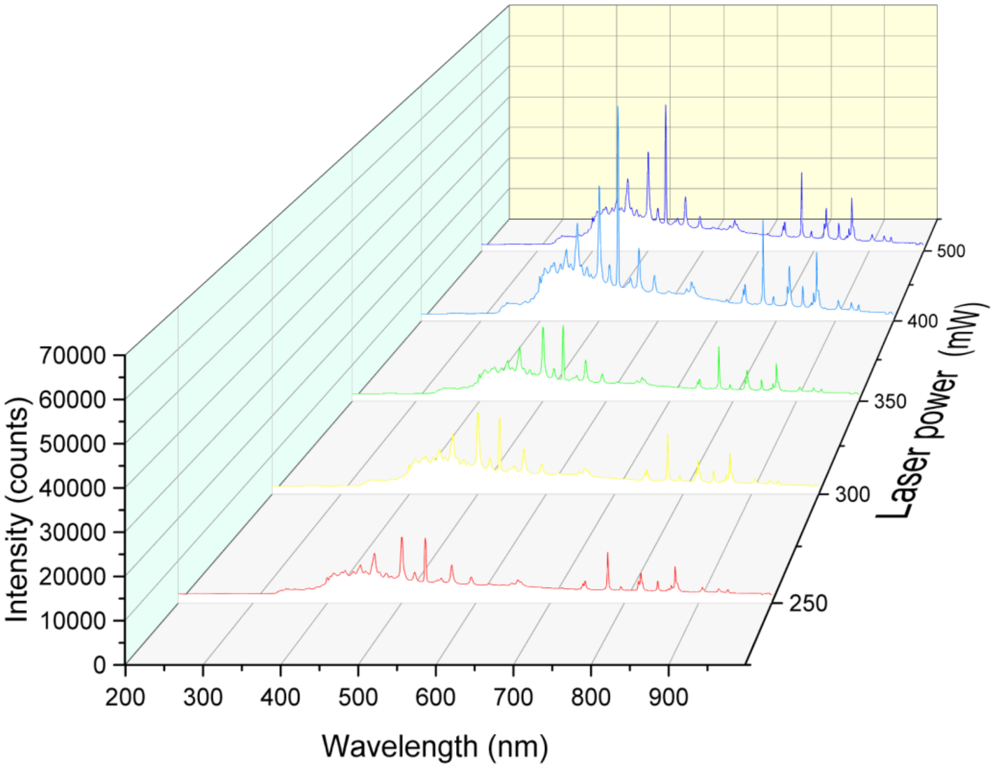

Fig 6. Air-plasma spectra at various laser powers

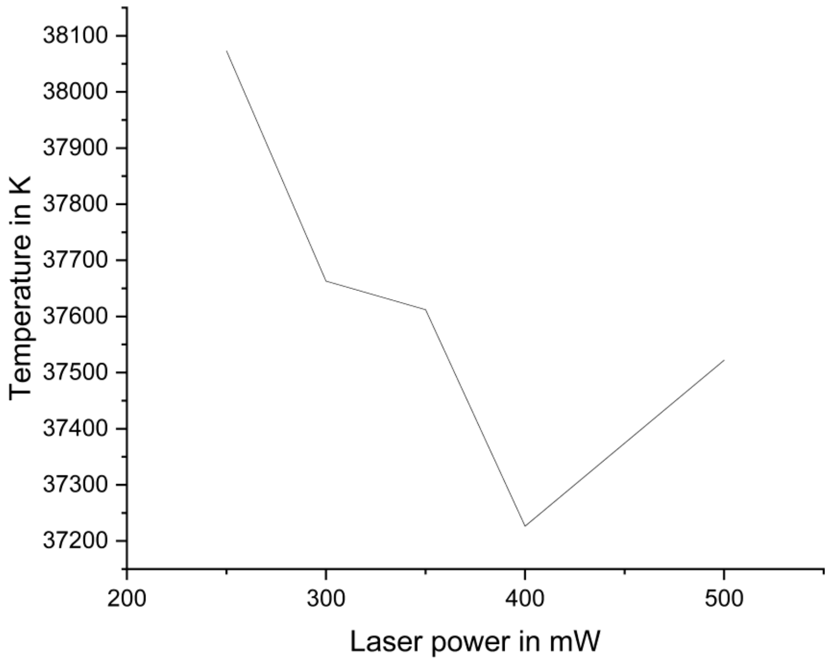

Fig 7. Variation of temperature of air-plasma with laser power

5. Conclusion

Spectrum of Air-plasma was collected, and the species present in it were found with the help of NIST Atomic database. The temperature and electron densities are estimated using LIBS and AES under the assumption of LTE. A standard way of estimating the temperature of air-plasma is proposed using N II lines in the spectra which will help in understanding plasma behavior at hypersonic speed and designing better TPS for re-entry vehicles. The validity of LTE is proven with the help of McWhirter criteria. The temperature of air-plasma at various laser power in LIBS was studied and speculated reason behind it was discussed.

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