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Abstract. This paper presents the experimental Stark-broadening and shifting analysis of 40.68 MHz nitrogen RF-CCPs. The non-thermal plasmas were generated in a cylindrical parallel plate plasma reactor under 0.2-0.8 Torr and 50-200 Watt. The physical and chemical spectral analyses of the system were performed by using the OES method. Many N I and N II lines were detected in the UV-Vis-NIR region. The diagnostic measurements of the plasmas were done according to the Saha relation and the Boltzmann plot method, under the LTE assumption. The calculated $T_e$, $T_{\text{gas}}$, $n_e$ and $n_0$ take values in the range of $(10748 \pm 742 - 16144 \pm 653)$ K, $(690 \pm 82 - 833 \pm 22)$ K, $(0.598 \pm 0.024 - 2.87 \pm 0.03) \times 10^{14}$ cm$^{-3}$ and $(2.32 \pm 0.06 - 11.37 \pm 1.44) \times 10^{13}$ cm$^{-3}$, respectively. The normalized Stark-broadening parameters ($\omega_s$ and $d_s$) of the vacuum visible N II multiplets (653.445, 659.749 and 661.545 nm) were determined for 10.000 and 15.000 K.

1. Introduction
Some well-known plasma diagnostic techniques are Langmuir probe, interferometry, mass spectroscopy and optical emission spectroscopy (OES). Among these techniques, OES is the simplest, the cheapest and a non-invasive method for parametrical analysis in low temperature, low pressure (local thermal equilibrium-LTE) laboratory plasmas [1].

The physical structure of plasma is complicated. There are many particles (electrons, radicals, atoms and ions) in the plasma. EM radiation in a specific spectral range is observed as a result of the interactions between these particles, resulting in vibrational, rotational and electronic transitions. Therefore, understanding the origin of these reactions reveals the cause of the spectral lines and shapes. The main origin of these reactions is the kinetic energy of the plasma particles. The kinetic energy of the electrons is defined as the electron temperature ($T_e$) while the kinetic energy of the heavy particles is described as the gas temperature ($T_{\text{gas}}$) [2-4]. These temperatures can be determined by using the Boltzmann plot method related to the plasma emission spectra.

In non-thermal plasmas, under certain experimental conditions, the Lorentzian spectral line profile is correlated with the Stark (Coulomb interactions between the emitting atom and the charged particles), van der Waals (dipolar interaction between the excited atoms and the induced dipole from the neutral perturbers) and natural broadening (transition energy and frequency) [5-8].

This paper reports a detailed experimental parametrical analysis of non-thermal; low-pressure HF (40.68 MHz) nitrogen radio frequency capacitively coupled plasmas (RF-CCPs) by using the OES method. The temperature and the broadening calculations are done in Vis-NIR regions. The plasma ($T_e$, $T_{\text{gas}}$, $n_e$ and $n_0$) and the Stark ($\omega_s$ and $d_s$) parameters are calculated under the assumption of LTE according to the Boltzmann, Saha and the spectral line broadening methods. All the spectral line shapes are fitted by using the Lorentzian fitting routine Origin Pro8, with high $R^2$ for the regression.
2. Theory

2.1. Temperature Calculation
It is assumed the plasma particles have the same localized temperature, which gives information about the internal transitions. Therefore, T\textsubscript{e} and T\textsubscript{gas} are assumed to be equal to the excitation (T\textsubscript{exc}) temperatures of the ionized and neutral atomic lines, respectively.

2.1.1. Electron Temperature. If the profile of the electron velocity distribution function is Maxwellian, the temperature is called as the electron temperature. According to our assumptions, T\textsubscript{e} is calculated from the slope of the Boltzmann plot. This plot is given by the natural logarithm of the relative intensities of atomic lines as in the following equation [8-11].

\[
\ln(I_{\text{II}} \lambda_{\lambda_i} g_e^{-1} A^{-1}_{\text{II}}) = C - E_k k_B^{-1} T_{\text{exc}}^{-1}
\]

where \( I_{\text{II}} \) is the emissivity of the spectral line, \( g_e \) is the statistical weight of the upper level, \( A_{\text{II}} \) is the Einstein transition probability, \( E_k \times k_B^{-1} \) is the normalized energy of the upper level and \( C \) is the partition function depended parameter.

2.1.2. Gas Temperature. This temperature is also known as the average random kinetic energy of the ions and neutrals and is mainly responsible for the molecular atomization processes and the radical generation in the plasma [7]. T\textsubscript{gas} is calculated from the Boltzmann plot of N I atoms.

2.2. Number Density Calculation
In a plasma reactor, many chemical reactions take place during the gas-plasma phase transition. The first two ionization chemical reactions for the nitrogen atom are written as;

\[
\begin{align*}
N & \leftrightarrow N^+ + e + E_I (N_I) \\
N^+ & \leftrightarrow N^{2+} + e + E_{II} (N_{II})
\end{align*}
\]

where E is the ground electronic state ionization energy of the atoms and the ions.

If the ionization and the recombination chemical reactions at T\textsubscript{exc} are in LTE, then \( n_e \) is calculated from the ionization degree of the operating gas, as described by the following Saha-Boltzmann equation [8, 10, 11].

\[
n_{\text{e}} n_{\text{II}}^{-1} = g_e g_{\text{II}} \exp\left(\frac{2\pi m_e k_B T_{\text{II}} h^2}{E_I k_B T_{\text{II}}} - 1\right)
\]

where \( n \) (e: electron, I: N-atom and II: N\textsuperscript{+}-ion), \( g \) (e: 2, I: 4 and II: 1), \( T_{\text{II}} \) is the T\textsubscript{exc} of N\textsuperscript{+}, \( E_I \) is the ground electronic state ionisation energy of N (14.5341 eV or 168 661 K).

The gas pressure of the plasma system is given by [10];

\[
P = (n_e + n_i + n_{\text{II}}) k_B T
\]

If Equations (4) and (5) are solved together with the assumption of quasi-neutrality (\( n_e = n_{II} \)) in the plasma, the numerical value of the \( n_e \) is obtained.

2.3. Stark Broadening Parameters
The Stark broadening parameters are mostly defined as the electron impact width (\( \omega_e \)) and the electron impact shift (\( \delta_e \)) [13, 14]. As T\textsubscript{gas} is much less than T\textsubscript{e} in the plasmas the ion quasi-static term can be neglected [7]. The spectral line is broadened due to a strong and chaotic electric field. The central position of the line is shifted depending on the strength and direction of the static electric field [11]. These parameters are correlated with \( n_e \) and T\textsubscript{e} [15] as shown in Equation (6) [6, 12, 16].

\[
\omega (n_e, T_{\text{e}}) = 2 \omega_e = 2 (n_e n_{e0}^{-1}) \omega_{S0} (T_{\text{e}})
\]

where \( \omega \) is the FWHM of the emitted ionic line (nm), \( \omega_e \) (nm), \( n_e \) (cm\textsuperscript{3}), \( \omega_{S0} \) (nm) is the normalized Stark parameter for the given line and \( n_{e0} (10^{17} \text{cm}^3) \) is the normalized electron density.
3. Results and Discussion

3.1. Temperature Calculation

For HF RF-CCPs in LTE, \( T_{\text{exc}} \) is calculated from the relative intensities of N I and N II emission lines in the 200-1100 nm spectral region, using the Equation (1). Even though many peaks are eliminated to get more accurate (high R²) measurement results. The extracted atomic lines and their parameters are listed in Table 1.

**Table 1.** List of NI and NII atomic transition lines and their NIST spectral database

| Vac.λ(nm) | Transition Array | Rel. Int.(a.u.) | \( g_eA_e \) (s⁻¹) | \( E_e \) (cm⁻¹) |
|-----------|------------------|----------------|---------------------|----------------|
| 610.506   | \( 2s^2p^2(^3P)s^0P_{1/2} - 2s^2p^2(^1D)3s^0D_{3/2} \) | 45.93774137 | 8.40E-04 | 99663.912 |
| 644.2718  | \( 2s^2p^2(^3P)p^3D_{5/2} - 2s^2p^2(^1P)p^4D_{7/2} \) | 105.9742895 | 1.06E+07 | 11040.322 |
| 650.8822  | \( 2s^2p^2(^3P)p^3D_{3/2} - 2s^2p^2(^1P)p^4F_{3/2} \) | 184.0754597 | 3.88E+05 | 11019.465 |
| 660.8     | \( 2s^2p^2(^3P)p^3D_{5/2} - 2s^2p^2(^1P)p^4D_{5/2} \) | 315.803019 | 5.32E+05 | 109926.66 |
| 734.9594  | \( 2s^2p^2(^3P)p^3D_{5/2} - 2s^2p^2(^1P)p^4D_{3/2} \) | 202.6686562 | 3.33E+06 | 110470.24 |
| 738.0546  | \( 2s^2p^2(^3P)p^3S_{3/2} - 2s^2p^2(^1P)p^4S_{3/2} \) | 185.0878238 | 7.80E+06 | 110299.97 |
| 866.9316  | \( 2s^2p^2(^1D)3s^0D_{3/2} - 2s^2p^2(^1P)p^2P_{0/2} \) | 22.83340573 | 1.21E+07 | 111198.85 |
| 599.233   | \( 2s^2p^3d(^3F)_{5/2} - 2s^2p^3d(^1P)_{1/2} \) | 41.43542388 | 7.80E+04 | 203258.98 |
| 638.608   | \( 2s^2p^3d(^3F)_{5/2} - 2s^2p^3d(^1P)_{1/2} \) | 57.2563414 | 2.36E+06 | 202170.63 |
| 643.521   | \( 2s^2p^3d(^3P)_{3/2} - 2s^2p^3d(^1P)_{1/2} \) | 26.49384973 | 6.10E+04 | 170666.23 |
| 655.628   | \( 2s^2p^3d(^1D)_{5/2} - 2s^2p^3d(^1P)_{1/2} \) | 104 | 4.29E+06 | 202714.12 |
| 659.749   | \( 2s^2p^3d(^1D)_{5/2} - 2s^2p^3d(^1P)_{1/2} \) | 229.8159747 | 2.11E+07 | 211749.35 |
| 697.756   | \( 2s^2p^3d(^1D)_{5/2} - 2s^2p^3d(^1P)_{1/2} \) | 8.041914435 | 1.03E+07 | 203189.03 |
| 885.773   | \( 2s^2p^3d(^3P)_{3/2} - 2s^2p^3d(^1P)_{1/2} \) | 21.78130777 | 7.53E+06 | 223069.02 |

\( T_{\text{gas}} \) of the N I and \( T_e \) of the NII species in the RF plasma at 0.2 Torr-100 Watt are calculated as \( T_{\text{gas}} = 735 ± 57 \) K and \( T_e = 16144 ± 653 \) K from the linear Boltzmann plot. From these results, it is possible to claim that the dominant temperature in the plasma is \( T_e \) as it is much higher than \( T_{\text{gas}} \).

**Table 2.** List of the calculated \( T_e \) and \( T_{\text{gas}} \) with their operating conditions according to the Boltzmann plot method

| PC (Torr -Watt) | \( T_e \) (K) | \( T_{\text{gas}} \) (K) |
|----------------|-------------|------------------|
| 0.2 - 50       | 16144 ± 653 | 833 ± 22         |
| 0.2 - 100      | 14292 ± 574 | 735 ± 57         |
| 0.2 - 200      | 11746 ± 928 | 735 ± 52         |
| 0.3 - 50       | 14990 ± 770 | 735 ± 87         |
| 0.3 - 100      | 13490 ± 754 | 704 ± 60         |
| 0.3 - 200      | 13889 ± 705 | 725 ± 82         |
| 0.4 - 50       | 11827 ± 550 | 794 ± 60         |
| 0.4 - 100      | 15216 ± 761 | 735 ± 79         |
| 0.4 - 200      | 10748 ± 742 | 714 ± 90         |
| 0.5 - 50       | 14673 ± 1267| 725 ± 93         |
| 0.5 - 100      | 12741 ± 285 | 752 ± 91         |
| 0.5 - 200      | 12372 ± 350 | 741 ± 100        |
| 0.8 - 50       | 12901 ± 1045| 758 ± 93         |
| 0.8 - 100      | 13628 ± 598 | 690 ± 82         |
| 0.8 - 200      | 12718 ± 512 | 719 ± 97         |
Table 3. List of the calculated $n_e$ and $n_0$ with their operating conditions according to the Saha relation and the Boltzmann plot method, respectively

| PC (Torr-Watt) | $n_e$ ($\times 10^{14}$ cm$^{-3}$) | $n_0$ ($\times 10^{15}$ cm$^{-3}$) |
|---------------|-----------------------------------|-----------------------------------|
| 0.2 - 50      | 0.598 ± 0.024                     | 2.32 ± 0.06                       |
| 0.2 - 100     | 0.674 ± 0.026                     | 2.64 ± 0.20                       |
| 0.2 - 200     | 0.769 ± 0.018                     | 2.64 ± 0.18                       |
| 0.3 - 50      | 0.965 ± 0.048                     | 3.99 ± 0.47                       |
| 0.3 - 100     | 1.06 ± 0.05                       | 4.14 ± 0.35                       |
| 0.3 - 200     | 1.04 ± 0.05                       | 4.04 ± 0.45                       |
| 0.4 - 50      | 1.50 ± 0.02                       | 4.89 ± 0.37                       |
| 0.4 - 100     | 1.27 ± 0.06                       | 5.31 ± 0.57                       |
| 0.4 - 200     | 1.26 ± 0.24                       | 5.49 ± 0.69                       |
| 0.5 - 50      | 1.64 ± 0.13                       | 6.76 ± 0.87                       |
| 0.5 - 100     | 1.86 ± 0.01                       | 6.51 ± 0.78                       |
| 0.5 - 200     | 1.85 ± 0.02                       | 6.63 ± 0.90                       |
| 0.8 - 50      | 2.81 ± 0.07                       | 10.34 ± 1.27                      |
| 0.8 - 100     | 2.78 ± 0.09                       | 11.37 ± 1.44                      |
| 0.8 - 200     | 2.87 ± 0.03                       | 10.92 ± 1.48                      |

3.2. Number Density Calculation

The plasma state of matter contains atoms, molecules, radicals, ions and electrons. Therefore, it is important to understand the physical mechanism ($n$ & $T$) of these species to characterize the plasma medium. In lab plasmas, $n$ is determined by $T_{ex}$ as soon as the plasma medium is in LTE. Under the LTE and quasi-neutrality principle, the $n_e$ and $n_0$ are calculated by the Saha-Boltzmann relation written in the Equation (4). The numerical calculated results of the HF RF-CCP system under certain experimental conditions are listed in Table 3.

3.3. Stark Broadening Parameters

I determined the Stark widths and shifts of some strong vacuum visible NII Multiplets (653.445, 659.749 and 661.545 nm). The Lorentzian fitting analysis of these emitted ionic spectral lines of the vacuum nitrogen plasmas under 0.2 Torr-50 Watt are clearly represented in Figure 1.

Figure 1. Lorentz fitting procedures of the N II Multiplets a) 653.445 b) 659.752 and c) 661.762 nm under 0.2 Torr-50 Watt.
These fitted $\omega_e$ values, for the selected peaks, were substituted into the Equation (6) to calculate $\omega_e$ and $d_e$, associated with the $\alpha_e$ calculated from the Saha relation. After normalizing $\alpha_e$ to $10^{17}$ cm$^{-3}$, $\omega_e$ was computed for each $T_e$. Temperature power fitting relations of $\omega_e$ for the N II/653.445, 659.749 and 661.545 nm lines are given in Table 4. According to these relations, $\omega_e$ and $d_e$ of the N II multiplets are normalized to 10,000 and 15,000 K, as seen in Table 5.

Table 4. Temperature dependence of $\omega_e$ for the N II multiplets

| Multiplet (nm) | $T$ (K) | 10,000 | 15,000 |
|---------------|---------|--------|--------|
| 653.445       | 7.89$^2$| 1.28$^3$|        |
| 659.749       | 2.38$^4$| 2.81$^4$|        |
| 661.545       | 2.45$^4$| 2.22$^4$|        |

Table 5. Calculated Stark-broadening parameters of the N II multiplets

| Multiplet (nm) | $\omega_e$ | $d_e$ | $\omega_e$ | $d_e$ |
|---------------|------------|-------|------------|-------|
| 653.445       | 7.89$^2$   | -2.45$^4$| 1.28$^3$   | -2.22$^4$|
| 659.749       | 2.38$^4$   | -9.34$^4$| 2.81$^4$   | 6.50$^4$|
| 661.545       | 4.54$^2$   | 1.02$^3$ | 2.22$^4$   | 6.50$^4$|

The values of the Stark broadening parameters listed in Table 5 are higher as compared to the results in the literature. There are two important reasons of this variation: the peak profile shape and the experimental conditions. In the literature, the experiments are mostly performed under atmospheric conditions and the spectral lines are fitted with a Voigt profile. This type of fitting is the convolution of Gaussian and Lorentzian profiles [7, 8, 14, 16, 17]. On the other hand, the HF RF plasmas for this study are generated under laboratory vacuum conditions and the emitted spectral lines were found to be best represent by a Lorentzian profile.

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