Oxygen line ratio method for the determination of plasma parameters in atmospheric pressure discharges using air as the working gas

N. O’Connor\textsuperscript{1}, H. H. Humphreys\textsuperscript{2}, S. Daniels\textsuperscript{1}

\textsuperscript{1}National Centre for Plasma Science and Technology (NCPST), Dublin City University, Glasnevin, Dublin 9, Ireland
\textsuperscript{2}Dept. of Clinical Microbiology, The Royal College of Surgeons in Ireland and Department of Microbiology, Beaumont Hospital, Dublin 9, Ireland.

In this paper we report a relatively simple and robust spectroscopic methodology for the determination of plasma parameters (EEDF and $T_e$) in non-equilibrium atmospheric pressure discharges using air as the working gas. The methodology utilises the ratio of two oxygen lines (777 nm and 844 nm), which are commonly found in discharges of air, together with the solution of the two term approximation Boltzmann equation. It is shown that the diagnostic method is relatively independent of the discharge gas temperature up to approximately 1500K. As a demonstration we have carried out spectroscopic diagnostics of a non-equilibrium atmospheric pressure plasma jet which uses air as the working gas. The electron temperature is found to be approximately 0.683 ±0.04 eV and is relatively independent of gas flow rate and discharge power conditions.

1. Introduction

In recent years there has been a massive increase in the exploitation of atmospheric pressure plasma technology in fields ranging from materials science to healthcare applications. One of the most attractive forms of this technology is that of the atmospheric plasma jet (APJ) which facilitates the delivery of reactive species far downstream of the plasma producing volume. This method of delivery is extremely important for safety in healthcare applications as the plasma plume expands far away from the high voltage electrodes, reducing the risk of contact between the electrodes and human skin.

The majority of APJ designs to date have used either helium or argon with small admixtures of reactive gases as the working gas. However the use of air as the working gas offers several advantages such as future sustainability and the portability. Relatively few groups have exploited the use of cold atmospheric pressure air plasma jets; most likely due to the difficulties involved in maintain the gas temperature close to room temperature. However some successes have been achieved of late [1, 2, and 3].

In order to forward our understanding and achieve control of outputs of such discharges (and other atmospheric discharges which use air as the working gas e.g. dielectric barrier discharges and corona discharges) it is crucial to employ robust diagnostic methods capable of delivering key information associated with the discharge operation; such as the electron density ($n_e$), electron energy distribution function (EEDF) and electron temperature ($T_e$). Of the available diagnostic methodologies, optical emission spectroscopy (OES) is usually the most attractive owing to it being non-invasive and relatively easy to implement.

In this paper we present a relatively easy to implement OES oxygen line ratio method, using two lines frequently found in such plasmas (777 nm and 844 nm), for obtaining plasma parameters (viz. the EEDF and $T_e$) in nonequilibrium atmospheric pressure air discharges. The method is demonstrated in obtaining these parameters in a cold APJ using air as the working gas.

2. Experimental setup

The plasma jet system and diagnostic set up, shown in Fig. 1, is as detailed in our previous work [1]. Briefly, the plasma jet consists of a cylindrical polyether ether ketone (PEEK) body with a grounded stainless steel conical nozzle. A high voltage (HV) stainless steel pin electrode runs through the axis of the cylinder which is sealed at the end opposite to the nozzle. The high voltage is excited at 8 kHz and the amplitude varies from 1.8 to 3 kV. Compressed air flows through an orifice perpendicular to the jet axis and the flow rate may be varied from 5 to 25 lpm. A HV probe and current monitor are used to provide an electrical characterisation of the system whereas an optical fibre (mounted axially to the jet) coupled to an Ocean Optics HR4000 spectrometer is used to obtain spectra from the discharge bulk.
A typical optical emission spectrum for a gas flow rate of 10 lpm and discharge power of 20 W is shown in Fig. 2. The spectrum is dominated by emissions from the second positive system (SPS) of molecular nitrogen (N$_2$ (C$^3\Pi_u$-$B^3\Pi_g$) at 315-400 nm), atomic nitrogen (742.3, 744.3, 747, 818.3 and 868.3 nm), atomic oxygen (777.4 and 844.6 nm) and atomic nitrogen ions (500.5 and 568.3 nm). There are also weak emissions from the N$_2$ first positive system (FPS) transitions between 600 and 700 nm and the first negative system (FNS) of N$_2^+$ (391.4 and 427.5 nm).

It is worthy to note that there is no evidence of contamination of the discharge by the jet materials in the optical emission spectra (unlike in other groups systems [2, 3]), which may be due to the difference in the melting point of the jet nozzle and pin materials or the relatively weak reduced electric fields in the discharge (see below).

3. Determination of the plasma parameters

Here we present our method for the determination of the electron energy distribution function (EEDF) and electron temperature in the discharge through the analysis of the line ratios of the O$^+$ and O$^+$P atomic oxygen transitions at wavelengths of 777.4 nm and 844.6 nm respectively. The determination assumes the following:

1. The populations of the upper levels are dominated by direct electron impact from the ground state.
2. The depopulation of the upper level is either radiative or through collisional quenching by the surrounding gas.
3. The dissociation fraction is low enough that the quenching reactions are dominated by the major molecular constituents of the gas i.e. N$_2$ and O$_2$.

The intensity of an atomic oxygen spectral line, $I_O$, is then given by the ratio between the production and loss processes i.e [5].

$$I_O = C \frac{h\nu A_j k_e n_e}{\Sigma A_j + \Sigma k_{QM}[M]} [O]$$  \hspace{1cm} (1)

where C is a constant associated with the spectral response of the spectroscopic system at the emission wavelength, $h\nu$ is the energy of the transition, $A_j$ the Einstein coefficient, $k_e$ the rate coefficient for the excitation of the upper state of the transition, $n_e$ the electron density and [O] the ground state atomic oxygen density. $\Sigma A_j$ is the sum of all the radiative transitions from the upper state, $k_{QM}$ the quenching coefficient of the upper state by molecule M and [M] the density of either molecular oxygen or molecular nitrogen in the gas, approximately equal to 21% and 78% of the background gas density, respectively. Note here we do not include the other air constituents as the density of these species is far less than that of O$_2$ and N$_2$.

Taking the ratio of the emission intensities of the 844 nm line to that of the 777 nm line we have,
\[
\frac{I_{844}}{I_{777}} = \frac{C_{844}}{C_{777}} \sum_i \frac{h \nu_i A_{ij} k_i n_v}{\sum_j A_{ij} k_{ij777} n_v + \sum_k k_{qm} [M] + 10^{30}} [O]
\]

This may be reduced to

\[
\frac{I_{844}}{I_{777}} = \frac{C_{844}}{C_{777}} \sum_i \frac{h \nu_i A_{ij} k_i n_v}{\sum_j A_{ij} k_{ij777} n_v + \sum_k k_{qm} [M]} [O]
\]

The molecular nitrogen and molecular oxygen quenching coefficients for the O\(^{3}\)P state are 5.87x10\(^{-10}\) cm\(^3\) s\(^{-1}\) and 7.80x10\(^{-10}\) cm\(^3\) s\(^{-1}\) respectively [6]. For the O\(^{3}\)P state the quenching coefficient for O\(_2\) is 10.8x10\(^{-10}\) cm\(^3\) s\(^{-1}\) [6]. There is no available quenching coefficient for collisions with molecular nitrogen. However, in reference [6] it was assumed that the value for N\(_2\) was the same as that for molecular oxygen and so we will adopt this value here.

If these values are substituted into the summation of the quenching term and it is assumed the background gas density, \(n_b\), is of the order of 10\(^9\) molecules/cm\(^3\), i.e. approximately the density at standard temperature and pressure, we have

\[
\sum k_{ij777} [M] = n_b (0.78 \times 5.87 \times 10^{-10} + 0.21 \times 7.80 \times 10^{-10}) \tag{4}
\]

\[
= 6 \times 10^9 \text{ s}^{-1}
\]

\[
\sum k_{qm} [M] = n_b (0.78 \times 5.87 \times 10^{-10} + 0.21 \times 10.8 \times 10^{-10}) \tag{5}
\]

\[
= 7 \times 10^9 \text{ s}^{-1}
\]

In both cases the quenching term is around two orders of magnitude greater than the term for the sum of the radiative transitions (~10\(^{-7}\) s\(^{-1}\)) and quenching is by far the dominant depopulation mechanism. In fact, using the ideal gas expression, \(PV=nkT\), where \(P\) is the pressure, \(V\) volume, \(n\) the neutral number density \(k\), Boltzmann’s constant and \(T\) the gas temperature, it can be shown that the quenching term is two orders of magnitude greater than that of the radiative term for gas temperatures up to 1500 K. Although we have no measurement of the gas temperature of the discharge this value is around the maximum value found by other authors for similar devices [2, 4]. Therefore, in the expressions above, omission of the radiative term from the denominator will incur an error of c. 1% at most up to gas temperatures of 1500 K at atmospheric pressure. Neglecting the small error due to omission of the radiative term we now have

\[
\frac{I_{844}}{I_{777}} = \frac{C_{844}}{C_{777}} \frac{h \nu_i A_{ij} k_i n_v}{\sum_j A_{ij} k_{ij777} n_v + \sum_k k_{qm} [M]} \tag{6}
\]

\[
= \frac{n_b (0.78 \times 5.87 \times 10^{-10} + 0.21 \times 7.80 \times 10^{-10})}{n_b (0.78 \times 5.87 \times 10^{-10} + 0.21 \times 10.8 \times 10^{-10})}
\]

\[
= \frac{B_{844} k_{844}}{B_{777} k_{777}}
\]

where \(B_{844}\) and \(B_{777}\) are constants. The constants \(C_{844}\) and \(C_{777}\) are determined by means of calibration of the spectroscopic system with a tungsten ribbon lamp. In order to determine the EEDF and \(T_e\) in the discharge we first solve the Boltzmann equation in the two term approximation using a Boltzmann solver for varying mean electron energy conditions using BOLSIG [7]. Then \(k_{844}\) and \(k_{777}\) are determined using [7]

\[
k_e = \int_0^\infty f(E) \sigma(E) \frac{2E}{m_e} dE
\]

where \(k_e\) is the rate coefficient for excitation to the * upper level, \(E\) is the electron energy, \(\sigma(E)\) is the energy dependent cross section for the excitation (taken from [8]), \(m_e\) is the electron mass and \(f(E)\) is the electron energy distribution function normalised to one. The function resulting from the calculation of the ratios of the excitation coefficients is monotonically increasing. This function is interpolated to the value of the intensity ratio in order to estimate the discharge parameters i.e. \(f(E), T_e\) and the reduced electric field (\(E/n\)) which are provided as outputs in a look up table from the BOLSIG software.

4. Results

The results of the calculation of the electron temperature in our plasma jet system, under varying...
flow rate and discharge power conditions, based on the atomic oxygen emissions are shown in Fig 3. In our calculations we have included the errors involved in neglecting variations in gas temperature up 2000 K.

![Fig 3. Determination of the electron temperature, $T_e$, in the air APJ under varying discharge power and air flow rate conditions.](image)

From the figure it can be observed that the variations in electron temperature and EEDF are relatively weak functions of the discharge power and flow rate with a value of the electron temperature of approximately 0.683 ±0.04 eV across the parameter space. This value corresponds to a mean reduced electric field of approximately 18 Td. It may be noted that the estimation of the EEDF and $T_e$ in the system would be enhanced by an accurate knowledge of the gas temperature using complimentary high resolution spectroscopy of the SPS bands of $N_2$.

5. Future work

Although the method is demonstrated here with time integrated spectra of an APJ, it may easily be invoked in diagnostics of time integrated or time resolved spectra of other air discharge systems to gain an understanding of the bulk and time resolved discharge electron dynamics. This will be the focus of our future work. Furthermore, it would be instructive to compare this method with that of ref [4] in order to establish the validity and applicability of both.

6. References