Appendix A

Estimation of surface temperature on the surfaces

In this appendix it is shown that the radiative energy flux encountered in the initial stage of a surface discharge is adequate to heat the surface layers of at least a few micron thickness to temperatures $\sim 500^\circ C$ in about 100 ns. The temperature of this order is well beyond the rated working temperature of most polymers at which vaporization or direct sublimation is possible, in addition to rapid desorption of adsorbed molecules.

Consider a one dimensional heat conduction problem, on a semi-infinite solid of density $\rho$, thermal conductivity $K$, specific heat capacity $C$, on which a constant heat flux $F_0$ is incident, starting at time $t = 0$. If the initial temperature (room temperature) is taken as $T_i$, then the solution of the diffusion equation i.e. the temperature at a depth $'x'$ as a function of time '$t'$ is given by [37]

$$T(x,t) - T_i = \frac{2F_0}{K} \sqrt{\frac{\kappa t}{\pi}} \exp\left(-\frac{x^2}{4\kappa t}\right) - \frac{F_0 x}{K} \left(1 - erf\left(\frac{x}{2\sqrt{\kappa t}}\right)\right)$$

Here $\kappa = \frac{K}{\rho C}$ is the diffusivity of the material.

The simulated profile for the temperature evolution for the observed flux of $2 \times 10^6$ W/cm$^2$, which is the energy flux estimated by integrating all the photons in the range 3300-6000 $\AA^\circ$ from the spectral data, is shown in figure A.1. Here the assumption made is that the surface absorbs all the energy within a depth of a few wavelengths and none is reflected back. Typical values of various physical quantities are $K=0.167$ W/m.K, $\rho=1.2$ gm/cc, $C=1.37$ J/gm.K and initial temperature $T_i$ is taken to be 298 K. The rise in temperature near the surface exceeds 500 degrees
Appendix A: Estimation of Surface Temperature...

(over the room temperature) within a few hundreds of nanoseconds.

Figure A.1: Simulated temperature for a flux of $2 \times 10^5 \text{ W/cm}^2$. Curves show the temperature profiles for the time periods in nanoseconds (a) 100, (b) 300, (c) 500 (d) 700 and (e) 900

It should also be noted from the curves shown that if the same rate of energy flux on the surface continues beyond 250 ns, the surface temperature predicted would be unrealistically high. It is proposed that the vapor from the surface intercepts the photon flux from the plasma channel and thereby considerably reducing the value of $F_o$ at later times.
Appendix B

Calibration of the OMA System

B.1 Instrumental Line-Width

The instrumental line-width is usually measured using a known narrow line radiation source like a HeNe laser. In a CCD based OMA system the instrumental line-width will depend mostly on the pixel size. In the ICCD system used in this work the size of a single pixel is 27 μm. But because of the spill over of electrons in the Intensifier, the effective resolution is limited to four or five pixels for the light. The spectrometer is 0.5 m and 1200 grooves/mm and has a dispersion of 16Å/mm. The instrumental line-width for this setup is expected to be ~1.6Å.

To determine the experimental line-width, a HeNe laser is projected directly onto the entrance slit (set to a value of ~10μ) of the spectrometer, after attenuating the intensity of the beam with neutral density filters, to ensure that the ICCD does not get saturated. Spectra are recorded by setting the spectrometer at three different wavelengths (6328, 6378, 6278 Å) and the linear dispersion (pixels per Å) is calculated as Δp/Δλ, where Δp is the number of pixels by which the HeNe line shifts for a Δλ shift in the set wavelength. This quantity is measured to be ~2.3 pixels per Angstrom in this range. The number of the pixels at FWHM (i.e. Full Width at the Half Maximum of the intensity from which the background has been subtracted) is found to be 5 and hence the instrumental line-width is taken as 5/2.3 ~ 2.17 Å at worst. A similar check was made at the other wavelength regions using Cadmium and Aluminum lines from the respective hollow cathode lamps and the FWHM was consistently found to be 4-5 pixels.
B.2 Wavelength calibration

The OMA system is found to be able to accommodate a range of 260 Angstroms in the width of the CCD chip. So to cover the range from 3000-6000 Angstroms, many frames of spectra have to be taken. In each of the frames, dispersion may vary according to the set wavelength in the OMA. So the OMA was calibrated in the whole range by using discharge spectral lamps. A Ne-Al hollow cathode and a cadmium vapor lamps are used to do this. In each frame, it is made sure that a minimum of two lines are present, unambiguously identified. With these two lines (or more, if present), and assuming a linear variation of dispersion, the wavelength corresponding to each pixel is calculated. In this way, the whole range of wavelengths is covered in steps of 150 Angstroms, by allowing some overlapping. It is found that for this setup the wavelength set in the spectrometer always falls on the 433±1 pixel. Figure B.2 shows the variation of dispersion over the wavelength range used in this experiment. As is evident, the dispersion varies from 2.22 at 3000 to 2.30 at 6000 A°.

A short MATLAB FUNCTIONAL program is used to calculate the wavelength \( \lambda_p \) for a given pixel \( p \) by

\[
\lambda_p = \lambda_{set} - \frac{(433 - p)}{disp_\lambda}
\]

where \( \lambda_{set} \) is the set wavelength and \( disp_\lambda \) is the corresponding dispersion as determined from the above figure B.2. This program has been used for plotting and viewing all the spectra recorded using the OMA.

B.3 Absolute Intensity Calibration

The OMA system is also intensity calibrated for converting the signal counts at the CCD pixels to absolute photon fluxes. This is done using a standard Tungsten ribbon lamp. This replaces the discharge source in the experimental setup keeping all the other optics unchanged. In both the arrangements the full "etendue" of the system could be filled, simplifying the calibration procedure. The expression for the signal counts from the calibration \( (C_c) \) and experimental \( (C_x) \) arrangements can be written as

\[
C_c = \xi_c A_\Omega \tau_c d\lambda
\]
Figure B.1: Wavelength calibration of the OMA System

\[ C_x = \xi_x A \Omega \tau_x d\lambda \]

Then the expression for the emissivity (\( \xi_x \)) of the experimental source can be written as

\[ \xi_x = \frac{C_x}{\tau_x} \times C.F. \]

where C.F. is the calibration factor. Here A is the area subtended by the angle \( \Omega \) through which the light is collected, and \( \tau_e \) and \( \tau_x \) are the time periods for which the photons are integrated. Figure B.3 shows this calibration factor plotted against the wavelength.

The counts at any pixel for a frame set for a particular wavelength were found to vary linearly with the exposure time (gate width), which confirmed the linearity of the response of the pixels in the wavelength range employed.

This calibration factor was used to correct for the wavelength response in the calculations involving intensities.
Appendix B: Calibration of the ICCD

Figure B.2: Absolute Intensity calibration of the OMA system
Appendix C

Electron Temperature by Boltzmann plot

C.1 LTE model and its validity

Typical laboratory plasmas usually have a small optical depth and hence any radiation emitted are more likely to escape, before the repetitive absorption and re-emission by the plasma itself. Hence the distribution of photons among different wavelengths will not be Planckian. But if it is assumed that the collision processes dominate over the radiative processes, the resultant stationary state can be described by the same set of laws for various energy levels which actually govern Complete Thermodynamic Equilibrium. These plasmas are said to be in Local Thermodynamic Equilibrium (LTE). According to Greim [38] the above assumption is valid for a homogeneous, optically thin and transient plasma, if the following relations hold:

(i) the electron density

\[ n_e \geq 9 \times 10^{17} \left( \frac{\Delta E}{E_H} \right) \left( \frac{kT}{E_H} \right)^{\frac{1}{2}} \text{ cm}^{-3} \]

(ii) the time for the electrons of mass \( m_e \) and atoms or ions of mass \( M \) to attain kinetic equilibrium is given by

\[ \tau_{\text{kin}} \approx \left[ 7.5 \times 10^{-7} \frac{E_H}{kT} \right]^{-1} N M / n_i m_e \text{ sec} \]
(iii) and the same quantity (as (ii)) for electrons and singly charged ions is given by

\[ \tau_{\text{kin}}^1 \approx \left( 7.5 \times 10^{-7} \frac{E_H}{kT} \right) \frac{1}{M/n_e \text{sec}} \]

where \( \Delta E \) is the maximum difference of energy in eV in the energy levels used and \( E_H \) is the ionization potential of the hydrogen atom (13.6 eV), \( n_i \) is the ion density and \( N \) is the total number density of particles of same kind.

For this work the maximum \( T_e \) being 2.5 eV and \( \Delta E \) of the order of 2.5 eV, the necessary \( n_e \) for LTE to be valid is \( 4 \times 10^{15} \text{ cm}^{-3} \), which is much lower than the minimum \( n_e \) encountered in the experiment. Both \( \tau_{\text{kin}} \) and \( \tau_{\text{kin}}^1 \) are estimated to be around 10 ns which is less than the actual time resolution aimed for this work which is \( \sim 100 \text{ ns} \).

**C.2 Boltzmann plot**

Boltzmann plot is an old method for the estimation of electron temperature in plasmas which can be assumed to be in LTE. If the atomic state distribution function is assumed to be Boltzmann, then in these plasmas, the densities in the various energy states are proportional to the quantity \( g \exp \frac{-E_k}{k_B T} \) where \( 'g' \) is the statistical weight of that state and \( 'E_k' \) is the excitation energy, \( 'k_B' \) the Boltzmann Constant and \( T \) is the temperature. Then, if the quantity \( -\ln \frac{I_{\lambda}}{g_k f_{ik}} \) is plotted against the excitation energy \( E_k \) of the upper level \( 'k' \) corresponding to the wavelength \( '\lambda' \), they would form a straight line, whose slope will give the electron temperature. Here

\( \lambda \) is the wavelength of the line in \( \text{A}^0 \)

\( I_\lambda \) is the intensity of the line \( \lambda \)

\( g_k \) is the statistical weight for the energy level \( 'k' \)

\( f_{ik} \) is the absorption oscillator strength.

**C.3 Species and lines selection**

In a Boltzmann plot, all the data points plotted are for a unique species. Hence for a particular plasma, the species selected should have enough well defined and well
separated lines in the wavelength range for which the detector system has a linear response. The difference between the upper level of the excited energy state of any two lines must be comparable to the expected temperature. Only then, the intensity ratio of the lines would be sensitive to a small change in the temperature. For all the lines selected, validated spectroscopic data should be available in literature. With these points in mind, in this experiment singly ionized nitrogen ($N^+$) was selected. The lines selected were 3437, 3995, 4630, 4447, 4803, 5676, 5478, all in Angstroms. The spectroscopic data for all these lines were downloaded from NIST web page http://physics.nist.gov.

C.4 Line Widths assuming Lorentzian

In the estimation for the intensity for using in the Boltzmann plot, broadening of the spectral lines have to be taken into account. In this work, lines were seen broadened more than the instrumental width itself. Here Stark broadening is the dominant phenomenon for the broadened line, which results in a Lorentzian shape. So for each and every line a Lorentzian curve was fitted by least square method and then the area under the Lorentzian curve was used for intensity estimations. After correcting for the wavelength dependent sensitivities. For some lines multiple Lorentzians were fitted to minimize the contributions from the other nearby lines. Figure C.1 shows an example of multiple Lorentzians fitted to a bunch of $N^+$ lines in the vicinity of 4630 Å.

It may be noted that selected Lorentzian fitted lines were also used for the estimation of electron densities.

C.5 Estimating electron temperature

On the data points thus obtained, a straight line was fitted using MATLAB FUNCTIONAL programs. Then the slope of the line gives the electron temperature $T_e$. The error in this $T_e$ estimation is a combination of the uncertainties in the intensity (about 20%) and the atomic parameters ($f_{ik}$, the absorption oscillator strength, which is about 25%) and the error in the straight-line fitting. The standard deviation of the straight line fitting was found to vary in the range 20-40%. Taking this
Figure C.1: Multiple Lorentzians fitted. 'a' → actual data, 'b' → resultant curve, 'c' → Line at 4630 Å, 'd' → residue.

as the error in the slope of the fitted line itself, we can say that the error in the $T_e$ estimation is also in the range 20-40 %. The contributions of the intensity and the atomic parameters are very small due to the fact that they come only through the natural logarithmic values of these quantities which are small. However the fact that the temperatures have been derived by combining data (out of necessity) acquired in a large number of discharges is probably the chief source of uncertainty.