Chapter 4

Temporal and Spatial Evolution of Laser Induced Plasma from Graphite Target

The emission features of laser ablated graphite plume generated in a helium ambient atmosphere have been investigated with time and space resolved plasma diagnostic technique. Time resolved optical emission spectroscopy is employed to reveal the velocity distribution of different species ejected during ablation. At low laser irradiance levels only a slowly propagating component of C\textsubscript{2} is seen. At high irradiance levels emission from C\textsubscript{2} shows a twin peak distribution in time. The formation of an emission peak with diminished time delay giving a more energetic peak indicating higher velocity component at enhanced laser irradiance levels is attributed to many body recombination. It is also observed that these double peaks get modified into triple peaks for the time of flight distribution at distances greater than 16 mm from the target. The occurrence of multiple peaks in the C\textsubscript{2} emission is mainly due to the delays caused from the different formation mechanism of C\textsubscript{2} species. The velocity distribution of the faster peak exhibits an oscillating character with distance from the target surface.
4.1 Introduction

As indicated in chapter 3, pulsed laser ablation of graphite has become well established as a reliable method for preparation of newly found materials like fullerenes [1-4], carbon clusters and diamond-like carbon (DLC) films [5-12]. However, the underlying physics and chemistry of the processes such as carbon cluster formation or their dissociation are less than well understood. Further, the details of the dynamics of laser interaction with materials are extremely important in the context of optimizing the conditions for depositing good quality thin films. The preparation of DLC film was first reported in 1985 by Nagel and co-workers [13] who determined a critical threshold density of 50 GW cm\(^{-2}\) on the carbon feed stock, above which DLC was condensed from the carbon plasma and below which only soft graphitic layers were deposited. A good understanding of the physics involved in the interaction of laser light with solid targets at these intensities was achieved through theoretical [14] and experimental [15] studies as early as two decades ago. However, only few authors have considered the subsequent expansion of the laser produced plasma over several millimeters on the length scale. A characteristic feature of such adiabatic expanding plasma is the persistence of ions in high charge states in the cold region. Stevefelt and Collins [16] reported a modeling of the free expansion of a carbon plasma produced at moderate intensities, which includes the dominant constituent mechanisms of electron-ion recombination through both three body collisional and radiative processes.

Comparatively, the pulsed laser deposition (PLD) technique is used mainly for producing multicomponent oxides and other dielectric oxides and superconducting materials [17]. It has received less attention in DLC production, partially owing to the high initial cost of high power lasers and related equipment, and mainly owing to the success of other DLC deposition techniques, e.g. ion-beam and magnetron sputtering. However, the decreasing cost of powerful lasers and success in the development of PLD technology for large-area deposition [18], which is currently 100-150 mm in diameter [19], provide the basis for introducing PLD into general engineering fields. One very promising application of PLD is to produce DLC coatings for reducing friction and wear [20] and the capability to produce both hydrogen-free and hydrogenated DLC films allow good control over the mechanical properties important for tribology applications [21]. A comparison of selected properties of DLC films produced by various techniques is presented.
in the review article by Voevodin and Donley [22].

Based on the widely accepted theory of the pulsed laser evaporation [23, 24], the physical model of the laser ablation can be explained as follows. In the initial stage the interaction of the laser beam with the bulk target results in the evaporation of the surface layer. Following this, the interaction of the laser beam with evaporating material leads to the formation of isothermally expanding plasma and this persists until the termination of the laser pulse. In the final stage, adiabatic expansion of the plasma in the forward direction takes place when the target is irradiated under vacuum. Several spectroscopic studies of graphite plasma have been carried out using a variety of laser wavelengths such as 193, 248, 308, 532 and 1064 nm [25]. It has been shown that shorter wavelengths are more effective for penetration into the sample, mainly because of large ablation rates possible at these wavelengths [26]. However, the main advantage in the use of NIR low energy photons is that, they are less likely to invoke photochemistry into the ablation phenomenon.

High quality DLC films are obtained at low laser irradiances where the molecular C_2 emission is most dominant [27]. The relative population of the carbon clusters produced in the laser ablation of graphite has been found to depend on different experimental parameters like laser irradiance, nature of background gas and its pressure, relative position of the plasma volume with respect to target surface etc. The composition and energetic characteristics of the laser-produced carbon plumes depend also on which form of carbon is used as the target material. Plume characteristics in the laser ablation of pressed diamond powder [28], amorphous and glassy carbon [29] or polymer carbon [30] may differ from that of graphite. However, high-purity graphite targets are most commonly used in PLD of DLC films.

In pulsed laser deposition as the amount of ablated material increases, gas dynamic effects are thought to play a leading role in determining the spatial and velocity distribution of the vapourized material. Collisions between the ejectants during the initial expansion are theorized to cause a Knudsen layer (KL) or unstable adiabatic expansion (UAE) zone which results in stopped or backward moving material closed to the target and strongly forward peaked velocity distributions away from the target surface [31-33].

Optical emission spectroscopic technique is concerned with the light emitted by electronically excited species in laser induced plasma produced in front of the target surface. Also optical emission measurements are useful for species identification and in-situ mon-
itoring during deposition. Useful information about the elemental composition of the target material can be obtained from the analysis of the emissions emanating from the plasma plume. Laser ablation has the unique advantage that most of these species are formed in their excited states and hence spectroscopic measurements offer an excellent means to investigate their evolution and dynamics. The carbon clusters like $C_{60}$ and higher fullerenes are well known to be formed as a product of the laser ablation of graphite in an ambient helium atmosphere. Although considerable progress has been achieved in studies involving ablation of large carbon clusters $C_n (n \geq 10)$, including fullerenes from laser irradiated carbon targets, relatively little effort has been expended to study the production and characterization of $C_n$ clusters with $n \leq 10$.

In this chapter, a comprehensive study of spatial characteristic emission from $C_2$ using time resolved spectroscopy is presented. In these experiments time resolved spectroscopic observations of the plasma plume from graphite under helium ambient atmosphere were carried out to determine the velocities of the different ablated species inside the plasma. Such temporally and spatially resolved high resolution spectroscopic studies are helpful to optimize parameters of DLC film deposition and to correlate the carbon clusters with plasma dynamics. To the best of our knowledge this is the first report regarding the existence of triple peak in the temporal evolution of $C_2$ emission from laser produced carbon plasma. Our results also indicate that the temporal profile of $C_2$ species produced during laser ablation of graphite exhibits a triple peak structure only beyond a certain spatial separation from the target (16 mm) and thereafter these propagate with three different expansion velocities.

4.2 Experimental Setup

The experimental setup used for the present study is similar to the one described in chapter 2. Briefly, the 1.06 $\mu m$ laser beam from a Q-switched Nd:YAG laser with repetition rate 10 Hz was focused onto a graphite target contained in a vacuum chamber. The graphite target was rotated by a small electric motor so that the laser pulses are made to fall at a new spot every time on the graphite surface. The emission from the carbon plasma was focused at right angles to its expansion direction to produce a 1:1 image on the entrance slit of a monochromator (Jarrell Ash 0.5 m) coupled to a photomultiplier tube. Using a number of apertures and slits emission features from various
vertical segments of the plasma plume can be studied. The characteristic emission lines were selected using the monochromator and the output from the PMT was monitored using a digital storage oscilloscope with a maximum sampling rate of 200 MHz with 50 Ω termination to record the emission pulse shapes. In these experiments spatially resolved studies were carried out for distances up to 25 mm normal to the target surface with an accuracy better than 0.2 mm.

4.3 Results and Discussion

The time resolved studies of emission lines from various species are carried out from the oscilloscope traces which show definite time delays for emission with respect to the incidence of the laser pulse. The time of flight (TOF) measurements provide excellent technique to determine the velocity distribution of the plasma. Our observations show that the emission lines from different emitting species within the plasma possess distinctly different temporal profiles. Each temporal profile represents a complex convolution of different factors that govern the temporal history of the emitting species viz. its production mechanism and rate, its flight past the viewing region and its radiative and collisional decay rates. Time resolved studies of various species are made at irradiance in the range of 10 GW cm\(^{-2}\) to 95 GW cm\(^{-2}\). Typical TOF distributions of C\(_2\) species obtained by monitoring the spectral emission from C\(_2\) in electronic excited state \((d^3\Pi_g) [34,35]\) (at \(\lambda = 516.5\) nm corresponding to the \((0, 0)\) transition \(d^3\Pi_g \rightarrow a^3\Pi_u\) of C\(_2\) Swan system) at distances 5 mm and 10 mm from the target for different laser irradiances are given in figs. 4.1a and 4.1b (helium pressure 0.05 mbar). The initial spike in the figure is due to scattering and/or prompt emission and can be used as a time marker. The interesting feature in TOF pattern of C\(_2\) species is its double peak structure which becomes prominent beyond a threshold laser irradiance. Below this threshold laser irradiance only single peak distribution is observed. It is also noted that these double peak structure gets modified into a triple peak distribution at distances greater than 16 mm and these results are discussed in the preceding section. For simplicity, this section contains spatial studies up to 16 mm from the target. In what follows the first peak is designated as P1 and delayed peak P2. Such double peak structure has already been reported by a few of the earlier workers [36-38] even though no detailed analysis have been attempted.
Figure 4.1: Intensity variation with time for 516.5 nm spectral emission from C₂ observed at different distances from the target surface (A) 5 mm, laser irradiance used (a) 35.4 GW cm⁻² (b) 74.3 GW cm⁻², (c) 77.8 GW cm⁻² and (d) 81.4 GW cm⁻² and (B) 10 mm, laser irradiance used (a) 74.2 GW cm⁻² (b) 76 GW cm⁻² and (c) 77.8 GW cm⁻².
4.3.1 Salient Features of the Double Peaks Observed in the Present Study

1. Appearance of P1 occurs only beyond a threshold laser irradiance about 74.2 GW cm\(^{-2}\) at 5 mm away from the target \((z = 5 \text{ mm})\) and this threshold value increases with increasing distance from the target. (For eg. at \(z = 10 \text{ mm}\) the threshold irradiance is increased to 75.7 GW cm\(^{-2}\)).

2. The time delay for P1 with respect to the separation between the point of observation and the target surface varies in a nonlinear manner; the nonlinearity being more pronounced at lower laser irradiances. As is evident from fig.4.2, the delay of P1 is almost constant up to 10 mm separation which is paradoxical while the delay of P2 varies almost linearly (fig.4.3) with such separation. We do observe a pulsating nature in the time delays for P1 with distance greater than 16 mm.

3. The intensity for P1 is maximum at a point around \(z = 12 \text{ mm}\) (fig.4.4) for all values of irradiances while that of P2 attains maximum around \(z = 5 \text{ mm}\) (fig.4.5).

4. The delay of P1 increases with laser irradiance (fig.4.6) while that of P2 (fig.4.7), decreases sharply after being constant up to a certain value of irradiances.

5. The intensity of P1 increases from zero (at irradiances about 74.2 GW cm\(^{-2}\)) and saturates at higher irradiances (> 84.8 GW cm\(^{-2}\)) (fig.4.8) while that of P2 increases up to an optimum laser irradiance and begins to decrease thereafter (fig.4.9). This behaviour is predominant at points having smaller separation from the target.

6. It is noted that the delay time for the P1 decreases with increasing ambient helium pressure, whereas the delay time corresponding to P2 has been found to increase with respect to helium pressure. Also the first peak gets narrowed while the second peak becomes broadened as the helium pressure is increased.

7. Intensity for the P1 increases steadily with increasing helium pressure and a sudden enhancement is observed at higher helium pressures, while for P2, it is being constant up to a particular helium gas pressure and an enhancement in intensity is observed at high pressures.

The above observations indicate that the plasma apparently develops fast and slow components above a threshold laser irradiance. There are only a few reports available in the literature which describe twin peak TOF distribution in laser generated plasma from graphite target. Abhilasha et al [39] reported a peculiar double peak structure in the temporal profile of C II species at 426.8 nm in a laser produced carbon plasma at various
Figure 4.2: Variation of time delays with distance of P1 for different laser irradiances (◦) 81.34 GW cm⁻², (Δ) 88.42 GW cm⁻² and (+) 95.5 GW cm⁻².

Figure 4.3: Variation of time delays with distance of P2 for different laser irradiances (◦) 81.34 GW cm⁻², (Δ) 88.42 GW cm⁻² and (+) 95.5 GW cm⁻².
Figure 4.4: Change in intensity with distance for different laser irradiances for the peak P1 (o) 81.34 GW cm\(^{-2}\), (Δ) 88.42 GW cm\(^{-2}\) and (+) 95.5 GW cm\(^{-2}\).

Figure 4.5: Change in intensity with distance for different laser irradiances for the peak P2 (o) 81.34 GW cm\(^{-2}\), (Δ) 88.42 GW cm\(^{-2}\) and (+) 95.5 GW cm\(^{-2}\).
Figure 4.6: Plot of time delays on laser irradiance of P1 for different distances (×) 5 mm, (□) 10 mm and (★) 15 mm

Figure 4.7: Plot of time delays on laser irradiance of P2 for different distances (×) 5 mm, (□) 10 mm and (★) 15 mm
Figure 4.8: Variation of intensity of P1 with laser irradiance for (x) 5 mm, (□) 10 mm and (★) 15 mm.

Figure 4.9: Variation of intensity of P2 with laser irradiance for (x) 5 mm, (□) 10 mm and (★) 15 mm.
Figure 4.10: Schematic representation of laser ablation of graphite target (a) at low irradiance levels (b) at high irradiance levels

air pressures and they proposed that, this may be due to stratification of the plasma into fast and slow ion components at the interface where the occurrence of Rayleigh-Taylor instability causes deceleration of the plasma front by ambient gas (In fact we also observed the same double peak structure in the time profile of C II species at 426.8 nm). Dixon and Seely [37,38] also observed a double peak structure in C II species and they explain it as due to collisional interaction like resonance charge transfer which has been shown to be a velocity dependent one. In fact the existence of twin peak structure for the C$_2$ species from the laser induced plasma observed previously has been explained as due to emission from the 'shell' (fast) and the 'core' (slow) components [36]. Attributing peaks P1 and P2 solely to fast and slow components will not explain the unusual spatial dependence of time delays as depicted in figures 4.2 and 4.3 respectively. We have also observed a twin peak structure for Y I and YO emission in the laser produced plasma from YBa$_2$Cu$_3$O$_y$ and the twin peaks were assigned as due to species corresponding to those generated directly/in the vicinity of the target surface and to those generated from collisional and recombination processes [40].

4.3.2 Formation Mechanisms

The schematic diagram of the laser ablation of graphite target at low and high irradiance levels is shown in fig. 4.10. This figure also exhibits the effect of laser irradiance on the size of the ablated particles. Two mechanisms could exist for the particle formation, viz., dissociative and recombinational. Harano et al [41] have suggested the strip-off mechanism for the formation of carbon clusters by considering the balance between the total mass of the carbon particles and the laser irradiance used for the ablation. Most
of the models of fullerene formation are based on the recombination mechanism, i.e.,
the formation by nucleation from carbon vapour consisting of carbon atoms and very
small carbon molecules [42]. It is well known that graphite exhibits a large difference
between the inter-layer and the intra-layer bond strengths. It is expected that at low
laser irradiance levels, graphite will be ablated layer by layer producing large particles
which in turn get dissociated to form $C_2$ species [43]. The dissociative mechanism can
further be supported by the observation of long duration of Swan band emission at low
irradiances. At low laser irradiance levels only a slowly propagating component with low
kinetic energy is observed. The larger masses of $C_n$ will result in longer delays which
are observed in the $C_2$ emission (P2) occurring at the lower laser irradiances. Above
a distance $\approx 6$ mm from the target, the plasma is colder compared with the same in
core region and collisional effects become insufficient to cause dissociation of $C_n$. The
dominant mechanism for the production of $C_2$ Swan band emission at low irradiances is
the electron collision with $C_n$ cations and neutrals ($n > 2$) followed by dissociation where
one of the fragments is an ejected $C_2$ molecule [43]. As the laser irradiance is increased,
clusters with lower values of $n$ will be ejected directly from the target. Above a threshold
laser irradiance, temperature of the plasma becomes so large so as to dissociate $C_n$ to
neutral and ionized carbon atoms just outside the target. At higher irradiance levels
Swan band formation is mainly due to electron-ion and ion-ion recombination. It is
observed here that at high laser irradiances, after a threshold, an emission peak showing
a faster component with higher kinetic energy for $C_2$ molecules begins to appear.

Spectral analyses show that at low irradiance levels, the emission spectrum is domi­
nated by $C_2$ molecules whereas at higher irradiance levels the plasma emission is mainly
due to ionic species of carbon up to $C$ IV along with $C_2$ species. It is also observed
that the ions have higher velocity as compared to neutrals and molecules because of
the Coulomb fields which are generated by negatively charged electrons escaping from
the plume. It is in fact observed that the emission intensity of the ionized species does
increase drastically above this threshold laser irradiance. Once ions and electrons are
produced, one can have neutral carbon atoms by three body collision processes like

$$C^+ + e + e \rightarrow C + e \quad (4.1)$$

Collisional ionization is also possible through processes like
In the vicinity of the target, (4.2) may be predominant over (4.1) so that we get excited state \( C_2 \) formation slightly away from the target, giving emission peak P1. The threshold like phenomenon in the case of P1 also shows the initiation of production of ionized species so as to open the channels (4.1) and (4.2) at higher laser irradiances. As the laser intensity is increased beyond 74.2 GW cm\(^{-2}\), the probability of cluster formation of the type \( C_n \) (\( n > 2 \)) in the plasma diminishes, thereby causing a drastic decrease in the intensity of P2. Moreover, as the laser irradiance is increased, the trailing edge of the laser pulse will enhance the dissociation of \( C_n \) by multiphoton absorption through laser plasma interaction. This could cause the formation of \( C_2 \) nearer the target surface. Koren and Yeh [37] also have observed such double peaks in the case of \( C_2 \) from polymide target and their interpretation in terms of the fast and slow components does not completely explain our observations. We are therefore compelled to attribute the double peak formation due to the delays inherent in the distinctly different formation mechanisms of \( C_2 \) in the plasma.

Figs. 4.6 and 4.7 give respectively the variation in time delay for P1 and P2 with laser irradiance for different distances from the target. From fig. 4.6, we see that the time delay for P1 increases with respect to increase in laser irradiance which is against the normal observation where velocity usually increases with the intensity of the incident laser pulse. By considering the velocity distribution, this anomaly can be explained only if one can have some type of a "negative diffusion" or anomalous diffusion of \( C_2 \) towards the target. Similar observations by one of the previous workers have been explained as due to selective depletion of high velocity \( C_2 \) species [44]. However, one can have slightly different scenario as explained below. As the laser irradiance increases, the electron, atom and ion number densities of the plasma and plasma temperature are also increased. This may cause larger probability for events (4.1) and (4.2) indicated in the previous paragraph. It is also believed that ions are accelerated by Coulomb fields generated by fast moving electrons escaping from the plume. One should also consider the multiphoton dissociation of \( C_n \) by the trailing edge of the laser pulse so as to produce \( C_2 \) nearer to the target surface. Due to these processes \( C_2 \) may thus be formed at points nearer to the target surface by recombination processes, but with more than usual delay in the appearance of P1. In other words, decrease in delay with laser irradiance compete
with the increase in delay due to shift of "formation site" of C\textsubscript{2} nearer to the target surface. Therefore, as far as P1 is concerned, delay due to the location of formation site is more predominant in the range of laser irradiances considered here thereby causing the observed enhancement in the delay on increasing the laser irradiance. This is further born out by the fact that there is a perceptible increase in the half width of peak P1 as the intensity of the laser pulse is increased.

Similar arguments can be made in the case of the measured time delays corresponding to P2. Contrary to the case of P1, delay of P2 remains almost constant up to a threshold laser irradiance and thereafter it decreases. As noted earlier P2 is found to be formed due to dissociation of carbon clusters C\textsubscript{n} (n > 2). As the laser irradiance is increased the formation of C\textsubscript{2} through dissociation of C\textsubscript{n} will occur nearer to the target surface, thereby causing an increase in the delay as opposed to its decrease due to enhancement of kinetic energy of the species with laser irradiance. Up to a threshold laser irradiance, these two time delays are more or less balanced to give an effectively constant time delay as observed in fig. 4.7. Above this threshold irradiance, enhancement in kinetic energy becomes so large that there will be a notable decrease in time delay for P2.

The nature of variation of delay with distance also exhibit certain peculiarities in terms of the behaviour of peaks P1 and P2 (figs. 4.2 and 4.3). Beyond a distance of 8 mm there is a sudden enhancement in delay for P1 especially at comparatively lower levels of irradiances but well above the threshold. The unusual spatial dependence of time delay is observed only for P1 and the variation differs widely as the laser irradiance is changed. However for P2 the nearly linear spatial dependence of the delay is observed. The intensity variation for the peaks P1 and P2 with respect to distance is shown in figs. 4.4 and 4.5. The spatial maximum (the distance at which the intensity of the peak is maximum) of P1 is at about 12 mm while that for P2 is at 6 mm. It is also clear from fig. 4.9 that the intensity of P2 decreases after the threshold laser irradiance whereas intensity of P1 increases from zero (at 74.2 GW cm\textsuperscript{-2} for z = 5 mm) and saturates at higher irradiance levels (fig. 4.8). It indicates a decrease in the population of C\textsubscript{n} (n > 2) when irradiance is increased (fig. 4.9). The saturation effect of plasma emission can be explained as due to the absorption of the trailing part of the laser radiation by the plasma. This absorption will be more pronounced at higher plasma densities so that effective laser power reaching the target will be reduced. Such "shielding effect" of target from the laser radiation will result in the observed saturation effect.
4.3.3 Effect of Helium gas

In order to understand the mechanism more clearly, experiments were carried out by varying the helium gas pressure in the plasma chamber. Variation of time delay for the peaks P1 and P2 with respect to helium ambient gas pressure is shown in figs. 4.11 & 4.12 receptively. It is interesting to note that the delay for the first peak decreases and for the second peak it is increased with increasing helium pressure. The presence of helium gas helps cooling of plasma so as to reduce the plasma temperature. It is also supported by the fact that the increase of helium pressure decreases vibrational temperature of C$_2$ species [45]. The enhancement of delay time with the increase in gas pressure for P2 in the temporal profile is, therefore, due to the reduction in the velocity of C$_2$ species. However, the time delay dependence on helium pressure corresponding to P1 cannot be explained easily as in the case of P2. Decrease in time delay of P1 with increase in pressure can be understood, at least qualitatively, as follows. Presence of helium gas reduces the plasma temperature [46] so that the formation of bulk of C$_2$ through recombination process shifts towards the target surface. This reduction in time
delay due to shift in formation site will exceed the enhancement in time delay due to reduction in velocity of C₂ species. This is in conformity with the observation of increase in delay with laser irradiance.

Figs. 4.13 and 4.14 give the intensity variation for the P1 and P2 respectively with helium gas pressure. From fig. 4.13, it is clear that the intensity of the P1 increases steadily with increase in helium pressure. But in the case of P2, the intensities are almost constant up to a pressure of 1.3 mbar, then it enhances. The helium serves to cool the hot electrons by collisions leading to a more efficient electron impact excitation and plasma recombination, leading also to the plasma confinement near to the target which enhances the emission from these species. Fig. 4.15 gives the temporal profile of C₂ species for different helium ambient pressures, from which it is clear that with increasing pressure P1 becomes more and more narrow with decreasing time delay, while P2 broadens with increasing time delay. The increase in helium pressure improves the spatial confinement of the plasma which in turn increases the collisions. The kinetic energy distributions are more sensitive to collisions because elastic scattering cross-sections are usually considerably larger than the cross-sections for rotational or vibrational energy transfer [47].
Figure 4.13: Change in intensity of P1 with ambient helium gas pressure (\(\times\)) 5 mm and
(\(\Box\)) 8 mm (laser irradiance 81.34 GW cm\(^{-2}\))

Figure 4.14: Change in intensity of P2 with ambient helium gas pressure (\(\times\)) 5 mm an
(\(\Box\)) 8 mm (laser irradiance 81.34 GW cm\(^{-2}\))
Collisions make kinetic energy distributions more narrow, but with large peak velocity. In addition collisions can cool the rotational and vibrational energies of the molecules in the expansion. With sufficient number of collisions the energy initially stored in the rotational and vibrational degrees of freedom can be converted into direct translational energy of the species [48]. The broadening of P2 especially at high pressures is because of high cooling by the helium gas which improves the clustering of molecular species.

4.3.4 Plume Dynamics

The presence of helium gas during the ablation process has dramatic consequences on the expansion dynamics. The present results show that laser irradiance and pressure of the ambient helium gas have opposite effects on the plasma expansion processes. As irradiance increases, time delay for P1 increases while time delay for P2 is more or less constant up to a threshold irradiance and then decreases. Similarly increase in helium gas pressure decreases the time delay for P1 and in the case of P2, time delay is being constant up to a particular pressure and then increases. This can be explained by assuming a simple adiabatic model.
The plume length \( L \) can be estimated if it is assumed that at the end of the laser pulse the ablation products occupy a volume \( V \), at high pressure and subsequently expand adiabatically. Assuming adiabatic expansion model [49-51], the ablated material pushes the gas species until the plasma and gas pressures equilibriate. Then the length of the plasma is given by [49]

\[
L = A[(\gamma - 1)E]^{1/3\gamma}P_0^{-1/3\gamma}V_1^{(\gamma - 1)/3\gamma} \tag{4.3}
\]

where \( A \) is the geometric factor related to the shape of the laser spot at the target surface, \( \gamma \) is the specific heat ratio \( (C_p/C_v) \), \( E \) is the laser energy density, \( P_0 \) is ambient gas pressure, \( V_1 \) is the initial volume of the plasma \( (V_1 = v_0\tau_{\text{laser}}w, v_0 \) being the initial species velocity, \( \tau_{\text{laser}} \) is the laser pulse duration and \( w \), the laser spot size at the target surface). The factor \( A \) depends on the expansion geometry and for a conical plume with a spherical tip (inset of fig. 4.16) and expansion angle \( \theta \) (for circular laser spot)

\[
A = (1 + 1/\tan \theta) \left( \frac{3\tan \theta}{\pi + 2\pi \tan \theta} \right)^{1/3} \tag{4.4}
\]

From eqn.(4.3), it is clear that \( E/P_0 \) is the parameter controlling the length of the plasma if the experimental geometry remains constant; therefore, \( E \) and \( P_0 \) have opposite effects as experimentally observed in the present work. According to this model, the length of the plasma \( L \) is expected to increase as the laser energy density is increased or ambient gas pressure is decreased. Considering the experimental parameters used in this work, evaluating eqn. 4.3 with \( \theta = 35^\circ \) (then \( A = 1.6 \), \( \gamma = 2.56 \) [47], \( E = 270 \text{ mJ}, v_0 = 4.8 \times 10^6 \text{ cm s}^{-1}, \tau_{\text{laser}} \approx 9 \text{ ns} \), gives a straight line as shown in fig. 4.16 corresponding to the present experimental pressure range. In our experiments, the estimated length of the plasma at a helium pressure of 0.05 mbar is 25 mm. Both the predicted pressure dependence and absolute value of \( L \) are seen to be reasonably in good agreement with experiment. The small error occurring in these calculations is mainly due to uncertainties in the value of \( \gamma \) and \( \theta \). It must be noted that the deposition rate and kinetic energy of ablated species will fall into a very low value for substrates located beyond \( L \) because of the subsequent cooling which tends to pull the material back to the target [52]. The dimension of the plasma, which is closely related to density, the excitation temperature and the coupling of laser radiation, are influenced by the atmosphere through eqn. (4.3). The pressure of the ambient atmosphere is one of the controlling parameters of the
Figure 4.16: Estimated length of the ablation plume $L$ as a function of helium pressure, laser irradiance 81.34 GW cm$^{-2}$

plasma characteristics, as well as factors related to the laser energy absorption [53].

### 4.3.5 Spatial Analysis at Greater Distances - Triple Peak Structure in TOF Distribution

In this section, a comprehensive study of spatial characteristic emission from C$_2$ using time resolved spectroscopy is given. In these experiments time resolved spectroscopic observations of the plasma plume from graphite under helium ambient atmosphere were carried out to determine the velocities of the ablated C$_2$ species. Such temporally and spatially resolved high resolution spectroscopic studies are helpful to optimize parameters of DLC film deposition and to correlate the carbon clusters with plasma dynamics. Our results show the existence of triple peak in the temporal history of C$_2$ emission from laser produced carbon plasma. It also indicates that the temporal profile of C$_2$ species produced during laser ablation of graphite exhibits a triple peak structure only beyond a certain spatial separation from the target (16 mm) and thereafter they propagate with three different expansion velocities.

The typical temporal profiles for emission from C$_2$ species (choosing $\lambda = 516.5$ nm
corresponding to (0,0) band of Swan system) at a laser irradiance of 81 GW cm$^{-2}$ for different axial distances from the target are shown in the figs. 4.17(a-f). The time resolved observation presented here characterizes the axial expansion of the plasma i.e., strictly along a direction perpendicular to the target surface. Figs. 4.17 (a) and (b) represent the oscilloscope traces of TOF distribution of C$_2$ molecules at distances 5 mm and 10 mm from the target. At these distances, there exists a double peak structure. The emergence of the new peak occurs only at distances greater than 16 mm from the target. Fig. 4.17 (c) shows the formation of the new peak in between the aforesaid twin peaks. Figs. 4.17 (d-f) show the triple fold TOF distribution of the C$_2$ species at distances 18 mm, 20 mm and 22 mm away from the target surface. The time evolution of the spectral emission obtained in the present work clearly reveals that the C$_2$ species ejected from graphite target has a twin peak distribution up to a certain distance from the target (16 mm) and at farther distances the TOF pattern shows a triple peak structure. It has also been found that there is a well defined threshold irradiance to observe this triple peak structure in the TOF distribution.

There are only a few reports which describe the triple fold TOF distribution in laser generated plasma from graphite target. Lowndes et al [6] recently observed three ‘modes’ of incident species in the TOF profile using ion probe method and they attributed it to scattered ions, ions that are slowed by gas phase collisions and slow moving clusters formed through collisions respectively. Tasaka et al [54,55] observed triple fold plume structure during Nd:YAG laser ablation of graphite in helium ambient atmosphere. During optical emission studies using streak camera they found that, the fastest component is composed of carbon ions, second fastest component is due to compressed neutral molecules and the slowest component is the radial vapour from the graphite target. Bulgakov and Bulgakova [56] made a theoretical model for the plume expansion into ambient gas and have shown that the pulsating character in the velocity distribution can be explained using back and forth shock wave propagation and they also indicated that ionization and recombination processes have no significant effect on these pulsations. But they could not succeed in explaining the triple structure for BaO molecule during mass spectroscopic studies [51] using cloud ionization model.

TOF distributions give the time of arrival at a certain point in space with a known flight length and these can easily be transformed into velocity distribution. Variation of time delay with distance for P1 and P2 are given in figs. 4.18 and 4.19. It is seen from
Figure 4.17: Intensity variation of spectral emission with time for C$_2$ species (516.5 nm) at different distances from the target. Distances are (a) 5 mm, (b) 10 mm, (c) 17 mm, (d) 18 mm, (e) 20 mm and (f) 22 mm. These TOF spectra are recorded at a laser irradiance 81.34 GW cm$^{-2}$. 
Figure 4.18: Variation of time delay in the peak intensities with distance for the P1 of C$_2$ at different laser irradiances. (o) 81.34 GW cm$^{-2}$ and (Δ) 88.4 GW cm$^{-2}$.

Figure 4.19: Variation of time delay in the peak intensities with distance for P2 of C$_2$ at different laser irradiances (o) 81.34 GW cm$^{-2}$ and (Δ) 88.4 GW cm$^{-2}$.
Figure 4.20: Expansion velocities as a function of distance for P1 of C₂ for laser irradiance (○) - 81.34 GW cm⁻² and (Δ) - 88.4 GW cm⁻².

Figure 4.21: Expansion velocities as a function of distance for P2 of C₂ for laser irradiance (○) - 81.34 GW cm⁻² and (Δ) 88.4 GW cm⁻².
fig. 4.18 that the time delay for the faster peak is constant up to 10 mm from the target and then increases. It is also noted that after 17 mm the delays for P1 decreases sharply. From the plots of delay time vs distance, one can obtain instantaneous velocities for C₂ molecules and these are given in figs. 4.20 and 4.21 respectively. It may be noted that the velocities are not constant and they vary with distance from the target. From the mean velocity distribution of these species it is clear that the velocity of P1 increases with spatial separation from the target up to \( z = 10 \) mm. The sudden decrease in the velocity of these species after 10 mm shows the deceleration of the C₂ species. However at distances greater than \( z = 15 \) mm, the velocity of the particles again gets enhanced. In the case of P2 (figure 4.21) the velocity increases with spatial separation from the target until it reaches 6 mm and then the expansion velocity is found to be somewhat constant (8 Km s⁻¹) up to \( z = 20 \) mm and then decreases. The intensity variation of these peaks with spatial separation shows different spatial maxima for faster (\( z = 12 \) mm) and delayed peak (5 mm). The variation of time delay for newly generated peak beyond \( z = 17 \) mm is given in fig. 4.22 from which it is clear that the time delay is increasing with increasing distance in this case.
In order to identify whether the multiply ionized carbon species have any role in this peculiar appearance of three peaks in the C\textsubscript{2} emission spectrum, optical emission analysis from carbon ions were also carried out. Emission originating from ionic species appears when the laser irradiance is sufficient to create a predominantly ionized plasma medium. Temporal profiles are recorded for the ionized carbon species, at 426.7 nm of C\textsubscript{II} (3d\textsuperscript{2}D\textsubscript{2} - 4f\textsuperscript{2}F\textsuperscript{0}), 569.5 nm of C\textsubscript{III} (3p\textsuperscript{1}P\textsuperscript{0} - 3d\textsuperscript{1}D\textsuperscript{0}) and 580.1 nm of C\textsubscript{IV} (3s\textsuperscript{2}S\textsuperscript{0} - 3p\textsuperscript{2}P\textsuperscript{0}) for different distances from the target. The ionic species are characterized by faster and narrower TOF distributions in comparison with atomic or molecular species. We observed a peculiar double peak structure for C\textsuperscript{+} emission at 426.8 nm similar to the one observed by Abhilasha et al. [39]. They attributed it to stratification of plasma into fast and slow ion components occurring at the interface where fast component penetrates the ambient gas and slow one decelerate and consequently gives rise to a distinct double peak structure [57].

The time delays observed for different ionized species with respect to the axial distance from the target is given in the figure 4.23 at an irradiance of 70.7 GW cm\textsuperscript{-2}. The inverse slope of the curve drawn through the points gives their instantaneous velocities of these ionized species at a given time and distance. The expansion velocities of the ionized species are found to be increasing with degree of ionization. It is noted that the maximum expansion velocities of C\textsubscript{II} (taking the case of faster peak), C\textsubscript{III} and C\textsubscript{IV} are found to be at 40 Km/s, 58 Km/s and 80 Km/s respectively. The maximum spatial range for the ions were limited by the exponential drop in recorded intensity with distance (fig. 4.24) and the time. When ablation takes place in a gaseous environment at relatively high pressure (\(\geq 0.05\) mbar), the ablated material acts to sweep-up and drive the background gas at supersonic velocities as it expands outwards [58]. A shock wave is produced in the undisturbed gas, with the shock front being separated from the contact surface (boundary of the ablation products) by a layer of shock heated, compressed gas. In the early stages of expansion, the motion is unaffected by the gaseous background due to the high pressure of the ablation products [59]. However, as the plume expands and encompasses more gas, its velocity falls and, over a restricted range, the motion can be described by an ideal blast wave for which the shock boundary varies as [60,61]
Figure 4.23: Variation of time delay in peak intensity with distance for different ionic species of carbon at a laser irradiance of 70.7 GW cm\(^{-2}\). $\star$ - C II transition ($3d^2D - 4f^2F^0$) at 426.7 nm, $\circ$ - C III transition ($3p^1P^0 - 3d^1D$) at 580.1 nm and $\nabla$ - C IV transition ($3s^2S - 3p^2P^0$) at 569.5 nm.

Figure 4.24: Change in intensity with distance for different ionic species of carbon. $\star$ - C II transition ($3d^2D - 4f^2F^0$) at 426.7 nm, $\circ$ - C III transition ($3p^1P^0 - 3d^1D$) at 580.1 nm and $\Delta$ - C IV transition ($3s^2S - 3p^2P^0$) at 569.5 nm.
Figure 4.25: Distance (R) - time (t) plots for different ionic species. The solid line have the form $R \propto t^{0.4}$. + - C II transition $(3d^2 D - 4f^2 F^0)$ at 426.7 nm, ○ - C III transition $(3p^1 P^0 - 3d^1 D)$ at 580.1 nm and ▽ - C IV transition $(3s^2 S - 3p^2 P^0)$ at 569.5 nm.

$$z = \epsilon_0 (E/P_0)^{1/5} t^{2/5} \quad (4.5)$$

where $\epsilon_0$ is a constant of order unity, $E$ is laser energy density absorbed and $P_0$ is the ambient gas pressure. This equation is valid only if, the pressure of the ablation products greatly exceeds the ambient pressure $P_0$. Distance (z) - time (t) plots for different ionic species in the laser produced carbon plasma is given in fig. 4.25, these measurements are carried out at an irradiance of 70.7 GW cm$^{-2}$. Good agreement with $t^{0.4}$ dependence for $R$ has been seen at the later times at a modest ambient gas pressure of 0.1 mbar. Therefore these results agree fairly well with the blast wave over most of the range observed. At distances close to the target, fits of the form $R = at^n$ suggest that exponent $n \geq 1$; not agreeing with this model. Blast wave interactions occurring in the presence of background gas may play an important role in multiple peak. But we do not observe such a $t^{0.4}$ dependence for the multiple peaks of the $C_2$ species. If it is assumed that the terminal stage of the plume can be modeled as a free expansion into the vacuum, the expansion velocity $V$ can be written as [31,47]

$$V = \sqrt{\frac{2\kappa T}{M}} \quad (4.6)$$
where \( M \) is the mass of the species, \( \eta \) is the number of internal degrees of freedom which varies from 2.53 to 3.28 associated with ionization and excitation, \( T \) is the temperature of the plasma and \( k \) is the Boltzmann constant. The above equation shows that the time delay of the plasma species depends upon the temperature and dimensions of the plasma along with mass of the concerned species. According to eqn. (4.6), due to identical masses, different ionic species of carbon should have identical time delays. However, in actual practice, it is observed that the species with higher degree of ionization have higher velocities because of the Coulomb fields which are generated by negatively charged electrons escaping from the plume. These results are in consistent with our earlier observations suggesting the occurrence of faster peak in the temporal profile of \( \text{C}_2 \) above a certain threshold laser irradiance is caused by recombination of these ions. It is also supported by the fact that the molecules giving rise to these recombination peaks have almost identical kinetic energy distribution in comparison with highly energetic ions.

Another important observation is that the intensity of the ionized species increases with laser irradiances but get saturated at higher irradiance levels as is given in fig. 4.26. There is a laser intensity threshold for the appearance of multiply charged ions and this
threshold increases with degree of ionization. It is also noted that the expansion velocities 
of these ionic species increase with increasing laser irradiance. The exponential increase 
in the intensity of emission of positive ions with irradiance is in accordance with the 
Richardson-Saha laws [62]. The saturation in intensity at high laser intensities is due to 
a change in the efficiency of laser coupling to the target by increased absorption and/or 
reflection from the laser induced plasma, a process known as plasma shielding [63,64]. 
The increase in ionization and intensity saturation with varying laser irradiance also 
seem to suggest strong interaction of the laser pulse with the dense plasma formed near 
the target within the pulse duration.

4.3.7 Expansion Dynamics

From fig. 4.17, it is seen that at higher spatial distance from the target (> 16 mm), the 
recombinational peak splits further into two forming a three fold TOF profile for the 
C₂ species. The reason for the occurrence of twin peak structure in the recombination 
emission intensity profile can be attributed to delays caused by different recombinational 
formation mechanism of C₂ species in the plasma. It is also seen from fig. 4.22 that the 
time delays for these newly generated C₂ species are increasing steadily with increasing 
distance from the target.

From fig. 4.20, one sees an anomalous variation of expansion velocity of the C₂ 
species with axial separation from the target. Gas dynamic effects are thought to play 
a major role in determining the spatial and velocity distribution of the vaporized mate­
rial. The velocity at any point inside the plasma depends upon the spatial separation 
from the target surface. The atoms, molecules and ions undergo collisions in the high 
density region near the target forming the so called Knudsen layer, to create a highly 
directional expansion perpendicular to the target [65,66]. The density of the plasma will 
be maximum near the target due to collisions and hence the mean drift velocity normal 
to surface will be a minimum at very close to the target. The plasma expansion in a 
direction perpendicular to the target surface can be written as [24]

\[
Z(t) \left[ \frac{1}{2t} \frac{dZ}{dt} + \frac{d^2Z}{dt^2} \right] = \frac{6kT_0}{M}
\]

(4.7)

where \(dZ/dt\) is the expansion velocity of the plasma in the Z direction, \(k\), the Boltzmann 
constant, \(T_0\) the isothermal temperature of the plasma and \(M\) is the molecular weight 
of the particle. The above equation evidently shows that the expansion velocities are
low and acceleration is very high during the initial stages of expansion. But when the expansion velocities increase, acceleration starts to decrease. The laser pulse being short, the plasma cloud within the pulse duration has a minimum size in the direction normal to the target surface. A dense plasma can absorb strongly the trailing part of the laser pulse. Thus the absorption of the laser radiation by the plasma increases the velocity of the species inside the plasma and the hydrodynamic expansion is directed right angles to the surface of the target. This is found to be true as seen in figs. 4.20 and 4.21 respectively at distances near the target where expansion velocities increase very rapidly with respect to the spatial separation from the target. During the initial stages of the plasma expansion, the velocity in the direction perpendicular to the target surface is very high as a result of the small dimension of the plasma in that direction. It is reported that [67,68] during shorter time intervals the expansion of the plume is one dimensional while for longer time scales the expansion is essentially three dimensional. This has also been supported by ultrafast photography of laser ablation plumes [69]. The dimensionality of the laser generated plasma, may deviate from these values depending several factors including laser irradiance, plasma temperature, irradiated spot shape, mass of the species etc.

After the termination of the laser pulse, adiabatic expansion of the plasma begins. During this process, the thermal energy is converted to kinetic energy with the plasma attaining high expansion velocities. The adiabatic expansion of the plasma in the $Z$ direction can be written as [24]

$$Z(t) \left[ \frac{d^2 Z}{dt^2} \right] = \frac{6kT_0}{M} \left[ \frac{Z_0}{Z(t)} \right]^{\alpha - 1}$$  \hspace{1cm} (4.8)

where $Z_0$ is the edge of the plasma at which the laser pulse is terminated and $\alpha$, the maximum attainable particle velocity. In the adiabatic expansion region, the acceleration depends on the initial temperature and the mass of the species.

From fig. 4.21 it is seen that, the velocity of P2 is constant (8 km/s) after the initial expansion of the plasma. The velocities of these are found to be decreased at the boundary of the plasma which is in accordance with drag model [70] which predicts that the plume eventually comes to rest due to resistance from collision with background gas. For low pressures, when the driven mass of the background gas is small compared with the driver mass of the expanding vapour, the drag force model can be applied. In this case the viscous force is proportional to the velocity of ejected material and the plasma propagation can thus be written as
\[ Z(t) = Z_0 \left[ 1 - \exp \frac{u_0 t}{Z_0} \right] \]  \hspace{1cm} (4.9)

where \( u_0 \) is the initial expansion velocity and \( Z_0 = \frac{u_0}{\beta} \) the so-called stopping distance.

Fig. 4.20 shows that between distances 10 mm to 15 mm from the target surface, the expansion velocity decreases for PI while it increases again at farther distances. This peculiar velocity pulsations can be explained as follows. During the adiabatic expansions, the thermal energy is rapidly converted into kinetic energy, thereby attaining high expansion velocities. It has been reported that for spherical plasmas, temperature drops off as the square of its radius [71]. A rapid drop in temperature occurs when the spherical plasmas expand. This may be the reason for the decrease in kinetic energy for PI in the region between 10 mm to 15 mm. However the temperature drop will not continue with respect to square of the radius of the spherical plasmas indefinitely, because cooling due to expansion will be balanced by the energy gained from the recombination processes of the ions.

4.4 Conclusions

A graphite target was ablated by 1.06 \( \mu m \) radiation from a Q-switched Nd:YAG laser in ambient helium atmosphere. Time resolved spectroscopic analysis of emission from \( C_2 \) species was carried out. The present work has differentiated the various mechanisms of the formation of \( C_2 \) species in the laser produced plasma from graphite in a helium gas atmosphere. Measurements of spatial dependence of the TOF emission intensities are made up to 25 mm away from the target. An oscillatory behavior is observed in the TOF distribution of \( C_2 \) species and this is observed only above a certain threshold value for irradiance. At distances greater than 16 mm from the target surface, a three fold TOF distribution is observed and the reason for the formation for these peaks is discussed. The peak due to low kinetic energy component which is observed at all levels of irradiance is formed as a result of dissociation of higher clusters. The departure of single peak velocity distribution at higher laser irradiances is due to processes like recombination of the high energetic particles. The energy released on recombination is converted into kinetic energy of the molecules, atoms and ions, which may give rise to a group of relatively faster \( C_2 \) species. It is found that at farther distances from the target the recombinational peak gets modified in to two due to inherent delays caused...
by different recombination and excitation mechanisms. It is also found that these results are consistent with kinetic energy distribution of ionic species. The different expansion dynamics of C₂ species in the ambient gas are also discussed. The velocity pulsations in the faster peak during expansion into ambient gas are attributed to nonequilibrium kinetic energy transfer because of many-body recombination.

A blast wave model appears to be in good agreement in considering the expansion dynamics of ionic species. But in the case of C₂ species, this model does not succeed. A simple adiabatic expansion model appears to provide a good description of the plume range and this may prove useful for scaling deposition experiments in terms of pressure, laser irradiance and deposition range.

Finally, the present work clearly points to the existence of the various mechanisms of the formation of C₂ species in the laser induced plasma. Analysis of these data provides a fairly clear picture of the evolution and dynamics of C₂ species in the laser induced plasma from graphite as well as the role of carbon clusters in the same.
4.5 References


[45] See Chapter 3 of this thesis.

[46] See Chapter 5 of this thesis.


[53] See Chapter 5.


[64] See Chapter 5.


