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Spatial analysis of C_2 band emission from laser produced plasma

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Abstract. Time and space resolved spectroscopic studies of the molecular band emission from C_2 are performed in the plasma produced by irradiating a graphite target with 1.06 μm radiation from a Q-switched Nd:YAG laser. High-resolution spectra are recorded from points located at distances up to 15 mm from the target in the presence of ambient helium gas pressure. Depending on the laser irradiance, time of observation and position of the sampled volume of the plasma the features of the emission spectrum are found to change drastically. The vibrational temperature and population distribution in the different vibrational levels of C_2 molecules have been evaluated as a function of distance for different time delays and laser irradiance. It is also found that the vibrational temperature of C_2 molecules decreases with increasing helium pressure.

1. Introduction

Recently, there has been growing interest in the production of carbon clusters and their properties following the first report of the existence of stable carbon clusters like C_{60} and other fullerenes [1–4]. Since then, a large number of publications related to carbon cluster formation have appeared in the literature. Laser ablation is a convenient method for the production of C_{60} and higher fullerenes [4, 5]. When a graphite surface is vaporized by intense laser pulses in a helium atmosphere of moderate pressure remarkably stable carbon clusters are produced. Depending upon the time of observation, position of the sampled volume of the plasma, energy of irradiation and nature and pressure of the ambient gas, the relative abundance of the different carbon clusters changes. Also pulsed laser ablation of high-purity graphite is considered to be an effective method for deposition of diamond-like carbon (DLC) thin films [6–9]. The C_2 radical has been considered to be important in astrophysics and flame spectroscopy [10, 11]. Recent measurements performed over a wide range of expansion durations of C_2 species have demonstrated a complicated gas dynamic picture of plume ambient gas interaction which is characterized by different phases and is accompanied by plume oscillations at rather high background pressure [12–14]. Chen *et al* [15] reported C_2 and CN emission of laser induced plasma from graphite in an ambient gas mixture of hydrogen and argon. They have calculated the molecular vibrational temperatures from the emission intensities and found that these quantities are much higher than the graphite melting point and explained it as due to possible direct heating of the plasma plume.

The infrared pulses from a high-power laser usually generate intense plasma emission from the target surface. The physical properties of the plasma plume such as the vibrational temperature of the molecular species, plasma density, plasma temperature etc directly affect the characteristics of the thin film prepared using laser ablation. Different aspects of studies of laser induced plasma such as charge and velocity distribution of ablated species, specular reflection of laser light, second-harmonic generation, ablation pressure, x-ray emission etc using high-power laser pulses have been investigated in detail by many workers [16–19]. The nature and characteristics of a laser induced plasma from a solid target depend on various parameters like the chemical composition of the target, wavelength of irradiation, energy deposited on the target, pressure of the residual gas in the plasma chamber etc [20–22]. The abundance of various types of molecular, atomic as well as ionic species in the plasma will also depend on the point of observation from the target.

In this paper we report spatially and time resolved studies of the C_2 Swan band ($d^3\Pi_g \rightarrow a^3\Pi_u$) for the wavelength range 400–670 nm in the graphite plasma. The vibrational temperature and population distribution in the different vibrational levels of C_2 molecules have been studied as a function of distance from the target in ambient helium gas and this throws some light on the plasma evolution process as well as few aspects of its dynamics.

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2. Experimental details

The schematic diagram for the experimental set-up is given in figure 1. Plasma was generated by the irradiation of a high-purity graphite target with 1.06 μm laser radiation from a Q-switched Nd:YAG laser (Quanta ray DCR II) with pulse width 9 ns and pulse repetition rate 10 Hz. The target is kept in a chamber [23] (having quartz windows) in which a helium gas atmosphere is maintained. The target is mechanically rotated so as to minimize the surface etching.

The emission spectrum from the plasma is viewed normal to its expansion direction by imaging the plasma plume using appropriate collimating ($f = 22$ cm) and focusing ($f = 20$ cm) lenses onto the slit of a 1 m Spex monochromator (1200 grooves mm^{-1}, 100 mm by 100 mm grating, blazed at 500 nm). The scan rate of the monochromator is adjusted by using a Spex CD2A compudrive arrangement. The recording is done by using a thermoelectrically cooled Thorn EMI photo multiplier tube (PMT, model KQB 9863) which is coupled to a boxcar averager/gated integrator (SR250, Stanford Research Systems). For spatially resolved studies, different regions of the plume are focused on to the monochromator slit. In our studies, accuracy in spatial dimensions is better than 0.2 mm. The output from the boxcar which for the present study averaged out intensities for ten pulses is fed to a chart recorder. The gate width is kept at 100 ns for recording the space resolved spectra. The helium ambient pressure is kept at 50 mTorr during the above measurements. Studies have been made at distances up to 15 mm away from the target surface for two different time delays, viz 2 μs and 5 μs after the incidence of the laser pulse onto the target.

3. Results and discussion

The plasma represents a heated high-pressure gas kept in a region of small dimensions which, later on, is allowed sudden expansion into the surrounding vacuum. In a laser produced plasma the preferential vaporization of the evaporated material is always found to be in a direction perpendicular to the target surface, irrespective of the angle of incidence of laser beam. Spectral measurements were performed in graphite plasma generated in these experiments at different distances from the target surface. The electron temperature and density of the plasma have been evaluated using the relative intensities of successive ionization states of the carbon atom and the Stark broadening method respectively [24]. Various parameters for electron temperature and electron density are available in the literature [25, 26]. The temperature and density show a decreasing behaviour with distance. With increasing distance from the target the electron temperature falls from 2.43 eV at 1 mm to 1.6 eV at 11 mm while the electron density decreases from 2.5×10^{17} cm^{-3} at 1 mm to 1×10^{17} cm^{-3} at 11 mm. These results are consistent with recently reported values of such quantities [27, 28]. The variation of electron temperature and density with distance (z) perpendicular to the target surface shows a $z^{-0.1}$ and z^{-1} dependence respectively [29].

The Swan bands arise from transition between the $d^3\Pi_g$ and $a^3\Pi_u$ electronic states of the C_2 molecules. Swan band emission is a likely result when intense laser pulses of almost any wavelength which span the 400 to 700 nm region are focused onto carbon containing solids or gases. The spectrum in the region 400–670 nm is recorded and is intensity normalized using the optical response curves of the monochromator–PMT assembly. The emission spectrum is found to contain different vibrational bands of C_2 molecules along with atomic and ionic species. Bands are identified by comparing the wavelength with literature data [30] as well as by carrying out vibrational analysis of the spectrum.

For spatial studies, as indicated earlier, different parts of the plasma are imaged onto the slit of the monochromator. The continuum emission intensity in the plasma emission is greatest in the region close to the target surface and decreases within a few millimetres away from the target. This continuum arises as a result of free–free bremsstrahlung and electron–ion recombination. In the region close to the target surface, the density in the plasma core is fairly high so that much of the broadened line emission cannot be separated from the background. In the case of excited carbon, the lines become narrower and weaker with increasing separation from the target. The broadening of such lines close to the target surface can be attributed to collisional broadening.

The emission spectrum in the presence of helium gas contained well defined Swan band heads in the $\Delta v = -2$, -1, 0, 1, 2 sequences. In addition to C_2 bands there are some neutral and lower ionic carbon species which are very prominent at points closer to the target surface at lower laser irradiance. But at higher laser irradiance the multiply ionized species up to C IV have been observed. At low laser irradiances, the emission spectrum is dominated by C_2 bands. Swan band heads (0,0), (1,1), (2,2), (3,3) and (4,4) are seen for the $\Delta v = 0$ sequence, and for the $\Delta v = -1$ sequence Swan band heads up to (4,5) are observed. The bands (0,2), (1,3), (2,4), (3,5), (4,6) which are very weak at lower laser irradiance levels are also observed. All the band heads corresponding to $\Delta v = 1$ (up to (6,5) at 467 nm) and for $\Delta v = 2$ (up to (4,2) at 437 nm) are also seen. At low irradiances we also observed the high-pressure band of the Swan band system which originates from the $v' = 6$ level at 589.9 nm. The presence of C_2 high-pressure bands would be due to the possibility that the upper levels of these bands are populated via a potential-energy curve crossing by the metastable state which is populated preferentially during the formation of C_2 from free carbon atoms [31]. We did not observe any cometary band centred around 405 nm. Typical C_2 Swan band emission ($\Delta v = -1$) at different distances from the target surface is given in figure 2.

The band emission intensities can be used to calculate the molecular vibrational temperature T_{vib} under the assumption that the plasma is in local thermodynamic equilibrium (LTE). In a transient system, such as the plasma formed by a pulsed laser beam, for LTE to hold good, the electron–atom and electron–ion collision processes must be extremely rapid and must dominate the radiative processes [25, 32, 33]. In a system that is at LTE, particles will have Maxwellian velocity distributions, populations of

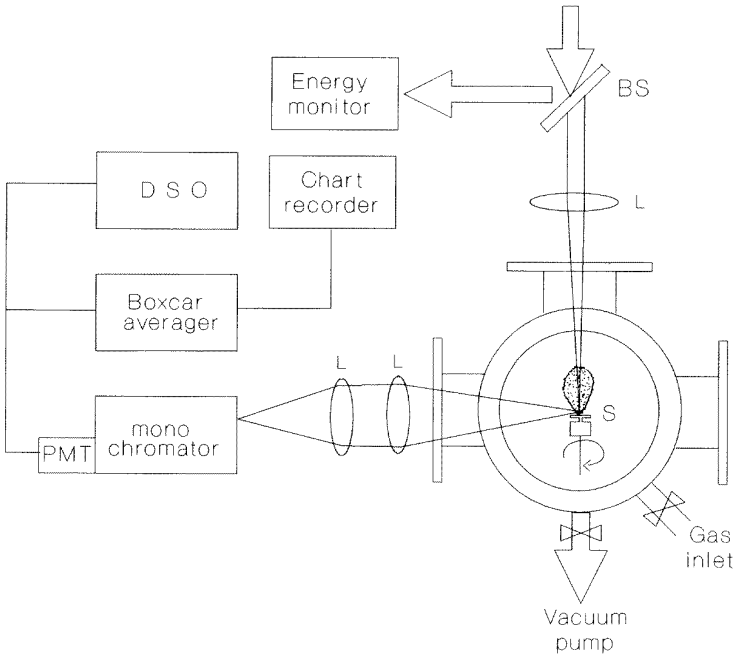

Figure 1. Schematic diagram of the experimental set-up. BS, beam splitter; L, lens; S, sample; PMT, photomultiplier tube; and DSO, digital storage oscilloscope.

the species in their energy levels will follow Boltzmann statistics, the ionization processes will be described by Saha's equation and radiation density will obey Planck's law. Along the boundary of the plasma, the number densities are low and movement of the boundary region is rapid, the LTE is probably not a good assumption. However slightly deeper into the plasma volume, where conditions change more slowly and collisions occur more frequently, this assumption is valid. In our experiment the apparent length of the plasma is ~25 mm and studies were made for distances up to 15 mm from the target surface. Since for our analysis of T_{vib}, we have assumed the plasma is in LTE, it is worthwhile to check in these experiments the condition for LTE. Clearly for LTE to hold the electron density must be sufficiently high. Befki [32] and McWhirter [34] has derived a necessary (but not sufficient) criterion for LTE:

$$n_e \geq 1.4 \times 10^{14} T_e^{1/2} (\Delta E_{mn})^3 \text{ cm}^{-3} \tag{1}$$

where T_e is the electron temperature in eV, ΔE_{mn} is the energy difference between the upper and lower energy levels (in eV). Substituting values for T_e (2 eV) and ΔE (3.16 eV) [24] in (1) the lowest limit for n_e is 6.3×10^{15} cm^{-3}. Our calculated values of n_e are much greater than this limit implying that LTE approximation for these analyses is valid.

According to the vibrational sum rule for the intensities of different bands in a progression the sums of the band strengths of all bands with the same upper or lower state are proportional to the number of molecules in the respective states [35], i.e.

$$\sum_{v''} \frac{I(v', v'')}{\nu^4} \propto N_{v'} \tag{2}$$

$$\sum_{v'} \frac{I(v', v'')}{\nu^4} \propto N_{v''} \tag{3}$$

where $I(v', v'')$ is the emission intensity from vibrational level v' of the upper electronic state to the vibrational level v'' of the lower electronic state, ν is the frequency in cm^{-1}, $N_{v'}$ and $N_{v''}$ the number densities of the C_2 molecules in the vibrational levels of the upper and lower electronic state respectively. Molecules in a certain vibrational level v' of the upper electronic state can decay to different vibrational levels v'' of the lower electronic states giving the emission intensities $I(v', v'')$.

For a plasma at local thermodynamic equilibrium (LTE), the number densities at various vibrational levels of the molecule in the excited state can be evaluated using the Boltzmann distribution [35],

$$\ln \sum_{v''} (\lambda^4 I(v', v'')) = C_1 - G(v') \left[\frac{hc}{kT_{vib}} \right] \tag{4}$$

where λ is the wavelength corresponding to the emission, h the Planck constant, c the velocity of light, C_1 a constant, and $G(v')$ is the term value corresponding to the vibrational level in the upper electronic state. The vibrational temperature for C_2 bands is obtained from the plot of the sums of the band strengths measured in various v' or v'' progressions against the vibrational term values $G(v)$. Since the intercept C_1 has no significance, the slope is a direct measure of the vibrational temperature [15, 31]. The advantage of using the Boltzmann distribution is that the information regarding the transition probability is not essential in this case. We have also evaluated the vibrational temperature of C_2 species by taking the ratio of the relative population of each vibrational level:

$$\frac{N_{v'}}{N_{v'=0}} = \exp\left(-\frac{G(v') - G(v'=0)hc}{kT_{vib}} \right) \tag{5}$$

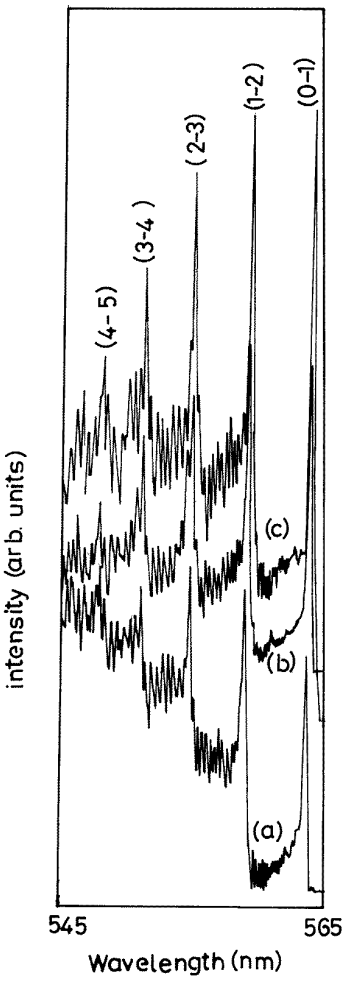

Figure 2. C_2 Swan band for the $\Delta v = -1$ sequence at different spatial distances from the target surface, (a) 1 mm, (b) 3 mm and (c) 5 mm.

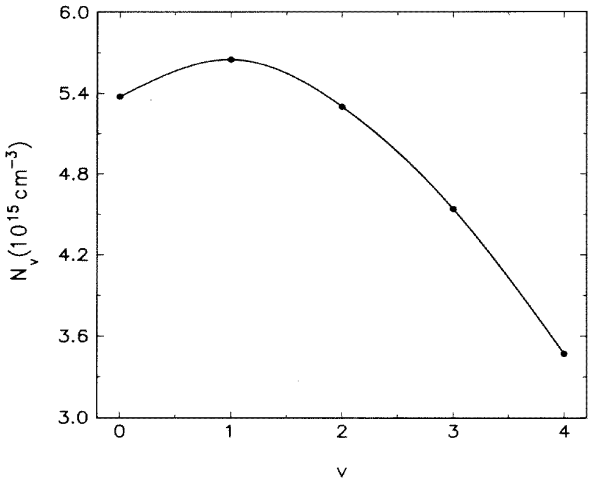

Figure 3. The vibrational distribution of C_2 molecules (distance 5 mm, laser irradiance 70 GW cm^{-2}).

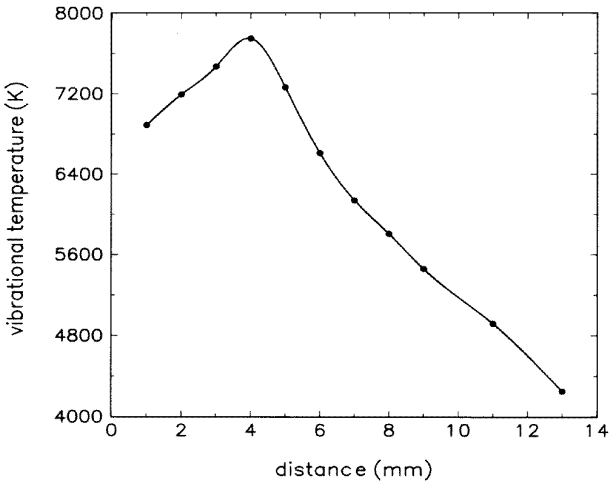

Figure 4. The variation of vibrational temperature of the C_2 molecules with distance from the target for 5 μs delay time (laser irradiance 21 GW cm^{-2}).

where $N_{v'} = C\lambda^4 I(v', v'')/F_{v'v''}$; C, a constant and $F_{v'v''}$, the Franck–Condon factor [36]. The calculated values of vibrational temperature of C_2 molecules using (5) show good agreement with calculated values of the same using (4). The uncertainty observed in the values of T_{vib} calculated using these methods is $\pm 10\%$.

The vibrational distribution in the excited states of C_2 molecules at distance 5 mm away from the target is shown in figure 3 at a laser irradiance 70 GW cm^{-2}. The inverse distribution observed for $v < 1$ is in accordance with the Franck–Condon principle. Similar inverse distributions are also observed in certain other molecules [38–40]. Please note that these values of N_v are to be regarded as relative values and not as absolute values. However, the calculated orders of magnitude are in good agreement with those of the reported values [15].

Figure 4 shows the spatial variation of vibrational temperature for 5 μs delay after the laser pulse at an incident laser irradiance 21 GW cm^{-2}. The curve peaks at a distance 4 mm away from the target (7800 K). It is clear that the relative spectral intensities depend on the position and the boxcar gate width that detects the PMT signal. The spatial variation of vibrational temperature can be explained as follows. 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 irradiances, graphite will be ablated layer by layer producing large particles which in turn are dissociated due to high temperature to form C_2 molecules near the target surface [7]. The dissociative mechanism can be further supported by the observation of the long duration of Swan band emission [12, 13]. Near the target surface the temperature is so high that collisional dissociation predominates and this causes a net decrease of de-excitation of higher vibrational levels with consequent reduction in band intensity. At distances farther than an optimal distance the decrease in plasma temperature will cause a reduction in vibrational temperature.

The spatial dependences of vibrational temperature of C_2 molecules at higher irradiance of 70 GW cm^{-2} for 2 and 5 μs delays after the evolution of plasma are given in figure 5. The vibrational temperature decreases steadily with increasing separation from the target surface. This

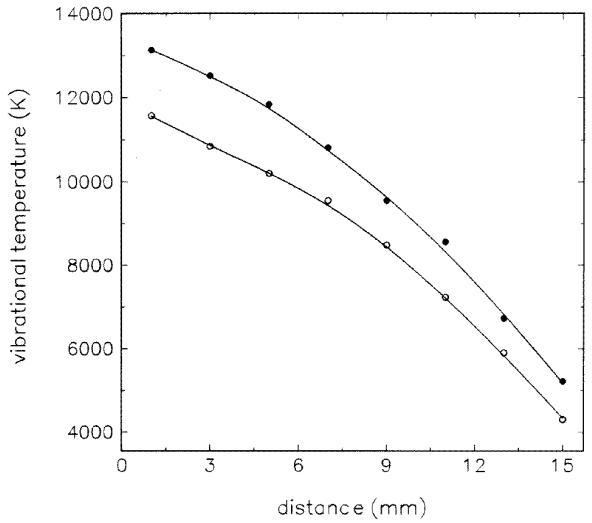

Figure 5. Spatial dependence of vibrational temperature of the C_2 molecules for different time delays (•) 2 μs and (○) 5 μs after the laser pulse (laser irradiance 71 GW cm^{-2}).

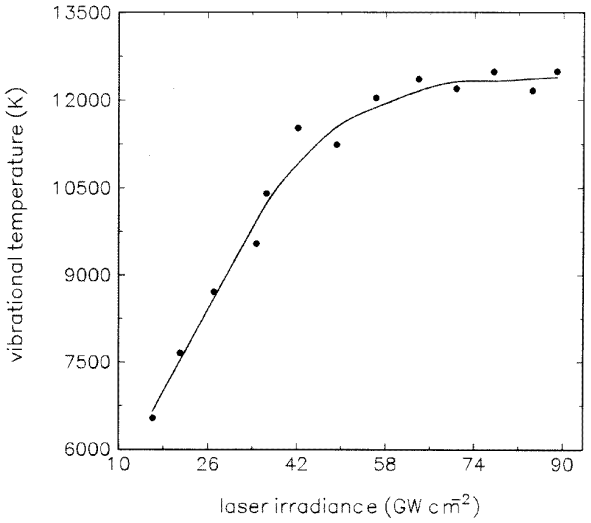

Figure 6. The variation of vibrational temperature of the C_2 molecules with laser irradiance at a distance 5 mm from the target.

variation is quadratic in separation (z) from the target surface and can be written as $T_{vib}(z) = T_0 - az^2$ with T_0 as the vibrational temperature at $z = 0$. At higher irradiance levels, the temperature is so high that the breakage of intra-layer and the inter-layer carbon bonds takes place. The presence of the ambient helium atmosphere creates a denser plasma which improves the dissociative mechanism. This causes a decrease in particle size at higher irradiance. This may be the reason for the quadratic dependence of the vibrational temperature at higher laser irradiance.

We have also carried out measurements of the laser intensity dependence of vibrational temperature at a distance 5 mm from the target which is given in figure 6. It is found that the intensity of C_2 band heads increases with laser intensity up to 42 GW cm^{-2} beyond which it is almost constant. The dominant mechanism for the production of C_2 Swan band emission at low irradiance is the electron collision with C_n cations ($n > 2$) and neutrals ($n > 2$) followed by dissociation where one of the fragments is an emitted C_2 molecule while at higher irradiances Swan band formation is mainly due to electron–ion, ion–ion recombination [7]. The presence of helium ambient atmosphere cools the hot electrons by collisions leading to a more efficient electron impact excitation and plasma recombination, leading also to plasma confinement near the target which enhances the emission from this region [42]. This is also demonstrated by the fact that the increase in helium pressure decreases the vibrational temperature (figure 7). The saturation which is observed beyond a threshold laser irradiance of 42 GW cm^{-2} (figure 6) is mainly due to two factors: (1) at high laser irradiance levels, the depletion of the excited state could occur not only because of the excitation to higher levels which leads to consequent dissociation and ionization but also by de-excitation to lower levels by quenching and this causes a net depletion of the excited state population in the higher vibrational levels and, (2) plasma shielding i.e. the change in the efficiency of laser coupling to the

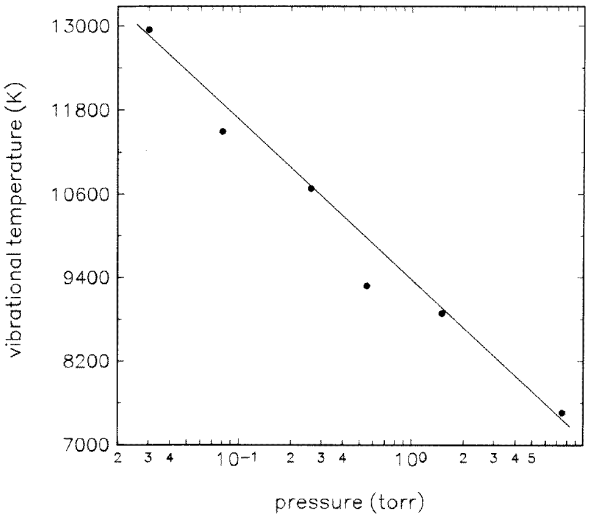

Figure 7. The change in vibrational temperature for C_2 molecules with respect to ambient helium gas pressure inside the plasma chamber (distance 5 mm, 71 GW cm^{-2}).

target by increased absorption by the laser produced plasma. When the laser intensity is high, the plasma absorbs the incoming laser radiation and prevents light from reaching the target surface. Therefore, most of the energy in the laser pulse will be absorbed by plasma in front of the target surface and a relatively small fraction will actually reach the surface. The surface is effectively cut off from the incoming radiation for a large fraction of the laser pulse.

4. Conclusion

We have made the spatially resolved analysis of C_2 bands in the spectrum of laser induced plasma from graphite target in helium ambient atmosphere. At low incident energies the emission bands due to C_2 predominate while at higher

laser irradiance the multiply ionized species of carbon up to C IV have been observed. From the spectroscopic studies of the emission bands, the population distribution and vibrational temperature in different regions of plasma have been deduced. The change in vibrational temperature with distance for low and high laser irradiances reveal the change in the mechanisms involved in the formation of the C_2 species. At low irradiances C_2 formation is predominantly due to dissociation of higher clusters of carbon whereas at high laser irradiance C_2 formation is due to two-body or three-body recombination.

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