J. Phys. D: Appl. Phys. **30** (1997) 1703–1709. Printed in the UK PII: S0022-3727(97)81246-6

Optical emission studies of C_2 species in laser-produced plasma from carbon

S S Harilal, Riju C Issac, C V Bindhu, V P N Nampoori and C P G Vallabhan

Laser Division, International School of Photonics, Cochin University of Science and Technology, Cochin 682 022, India

Received 24 January 1997

Abstract. Optical emission studies of C_2 molecules in plasma obtained by Nd:YAG laser ablation of graphite in a helium atmosphere are reported for irradiances in the range (1–9.2) $\times 10^{10}$ W cm^{-2}. The characteristics of the spectral emission intensity from the C_2 (Swan band) species have been investigated as functions of the distance from the target, ambient pressure and laser irradiance. Estimates of vibrational temperatures of C_2 species under various irradiance conditions are made. Results of measurements performed under different ambient helium gas pressures are also discussed.

1. Introduction

Laser-ablated plasmas are currently a topic of considerable interest [1–3]. In addition to applications in basic research, pulsed-laser ablation has well-established uses in materials technology such as deposition of diamond-like carbon thin films [4–6] and high-T_c superconducting films [7–9]. Diamond-like carbon (DLC) thin films which have successfully been prepared using laser ablation have wide applications owing to their interesting characteristics such as extreme hardness, electrical insulation, high thermal conductivity and optical transparency [10]. Laser ablation is a convenient method for the production of stable carbon clusters such as C_{60} and higher fullerenes [11, 12]. When a graphite surface is vapourized by intense laser pulses in a helium atmosphere of moderate pressure, remarkably stable carbon clusters are produced. Carbon molecules (C_n) are particularly interesting due to their unique and fascinating structural and spectroscopic properties, their importance in astrophysical processes and their role in combustion and soot formation. Laser ablation has the unique advantage that most of these molecules are formed in their excited states and hence spectroscopic measurements offer an excellent means to investigate their evolution and dynamics.

The general nature and outcome of the interaction of intense laser radiation with solid matter depends very much on the parameters of the incident laser beam, material properties and environmental conditions. Laser–solid interaction causes several processes to occur simultaneously and these include energy transfer, evaporation of solid material, generation of a dense plasma and formation of charged and neutral particles. There are several techniques for characterizing laser-induced plasmas and they have been reviewed extensively [13, 14]. Time-resolved measurements have recently been made of graphite with laser irradiance [15, 16] and ambient helium pressure [17] as the varying parameters and these studies have yielded many interesting results.

It has been reported that the dominant mechanism for the production of C_2 molecules at low laser irradiance is likely to be the collison of electrons with clusters of higher numbers of carbon atoms followed by photofragmentation whereby one of the emitted product species is an excited C_2 molecule, whereas at higher irradiance Swan band emission is mainly due to excitation resulting from electron–ion and ion–ion recombination [15, 18]. In the context of laser deposition of DLC films, it has been reported that high-quality DLC films are obtained at moderate laser irradiances under which molecular C_2 formation is prominent, as revealed by its emission spectrum [19, 20]. It may in this connection be noted that high-quality DLC films are obtained at laser irradiance about 10^{10} W cm^{-2} for 1.06 μm pulsed-laser deposition [5]. Thus, for the production of DLC films, it is necessary to understand the formation and dominance of C_2 species and their dependence on various parameters such as the laser irradiance, pressure of the ambient gas and concentration of the species at different distances normal to the target. We describe here the results of a series of experiments carried out on a laser-induced plasma produced from graphite in a helium atmosphere. We have here studied the features of C_2 emission spectra under various conditions specifically. The C_2 Swan band system was analysed in the range 465–590 nm as a function of the laser irradiance, helium pressure and time after the

0022-3727/97/121703+07$19.50

initiation of plasma in different regions of the plasma. The variations in the vibrational temperature of C_2 species were also studied as functions of the laser irradiance, ambient helium pressure and time elapsed after initiation of the plasma.

2. Experimental details

The experimental set-up used in this work was similar to that described earlier [21]. A Q-switched Nd:YAG laser (Quanta Ray DCR 11, maximum energy 300 mJ) at its fundamental wavelength (1.06 μm) with a pulse repetition frequency of 10 Hz and pulse width 9 ns was used to produce the carbon plasma. A lens of focal length 20 cm was used to focus the laser beam onto the rotating graphite target. The estimated spot size at the target surface was 200 μm. The plasma chamber was evacuated to a pressure of less than 1 mTorr and then filled with helium gas at desired pressures. Under these experimental conditions intense emission from the plasma appeared in the visible region. This bright optical emission from the laser-produced carbon plasma was imaged at right angles to the expansion direction to produce a 1:1 image on the entrance slit of a calibrated 1 m Spex scanning monochromator equipped with a thermoelectrically cooled Thorn EMI photomultiplier tube (PMT, KQB 9863). The output from the PMT was then fed to a boxcar averager/gated integrator (Standford Research Systems, model SRS 250) coupled to a chart recorder and this arrangement averaged the emission intensities for ten consecutive pulses. A microprocessor-controlled scanning system was used to control the scanning speed of the monochromator. By using a series of slits and apertures it was possible to record the emission spectrum from a segment of the plasma plume situated a definite distance from the target. The spatial resolution available here was better than 0.2 mm. Except for the time-resolved studies, the spectra were recorded with a time integration gate width of 3 μs. For the time-resolved studies, the gate width was set at 100 ns.

3. Results and discussion

The experimental arrangement described above allowed us to obtain the spectra from different vertical slices of the plasma plume generated by laser irradiation of a target. Just like had been seen in many earlier studies, beyond a threshold laser irradiance, the target becomes ablated with the emission of light caused by a variety of processes occurring in the ablated products. However, the various features of the emission spectra depended strongly on the laser irradiance incident on the target surface.

In the present case, the emission spectra of the laser-generated carbon plasma were recorded at low as well as at high levels of laser irradiances in a helium ambient atmosphere from sections at various distances from the target. The intensities of the spectral lines from the plasma plume were found to be sensitive to various experimental parameters. The apparent length of the plasma plume was around 25 mm in vacuum and reduced considerably with increasing pressure of the helium gas. The presence of helium gas helped faster cooling of the plasma, thus reducing the plume length and causing changes in the colour of the plasma. Under low irradiance conditions the recorded spectra were found to be dominated by band emission from C_2 molecules (Swan bands), whereas at high irradiance, strong line emission from atomic and ionic species occurred. In these experiments, emission from multiply ionized species up to C IV (triply ionized carbon) was recorded together with emission from the molecular C_2 species. Since Swan bands are a clear signature of C_2 species, a detailed study of these bands offered the best method to trace the evolutionary history of C_2 molecules generated in the laser ablation of graphite.

3.1. Spectroscopy of the Swan band emission

The Swan bands arise from transitions between the $d\,^3\Pi_g$ and $a\,^3\Pi_u$ electronic states of the C_2 molecules [22]. Swan band emission is a likely result when intense laser pulses of almost any wavelength are focused onto carbon-containing solids or gases.

In the present case in which a graphite target was irradiated with a Q-switched Nd:YAG laser beam at 1.06 μm wavelength the emission spectrum in the presence of helium gas contained well-defined Swan band heads in the $\Delta v = -2$, -1, 0, 1 and 2 sequences [23]. In addition to C_2 bands there were lines from some neutral and less ionized carbon species which were very prominent at points closer to the target surface, even at low levels of laser irradiance. However, at higher laser irradiance the multiply ionized species up to C IV were observed. Swan band heads corresponding to (0, 0), (1, 1), (2, 2), (3, 3) and (4, 4) were seen for the $\Delta v = 0$ sequence (figure 1) and for the $\Delta v = -1$ sequence (figure 2); Swan band heads up to (4, 5) were observed at low laser irradiances. The bands (0, 2), (1, 3), (2, 4), (3, 5) and (4, 6) were also observed at low laser irradiances for $\Delta v = -2$, albeit very weakly. All the band heads corresponding to $\Delta v = 1$ (up to (6, 5) at 467 nm, figure 3) and for $\Delta v = 2$ (up to (4, 2) at 437 nm) were recorded (figure 4). The overall uncertainty expected in the intensity tabulation is expected to be less than 10%. At low irradiances we further observed the high pressure band of the Swan system which corresponds to the $v' = 6$ level to $v'' = 8$ centred at 589.9 nm. Little and Brown [24] reported recently that these C_2 high-pressure bands could 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. The cometary band centred at around 405 nm was not identifiable in the recorded spectra.

3.2. The calculation of the vibrational temperature

The detection of band emission originating from C_2 is of particular interest since it provides an estimation of the plume temperature. The Swan band emission intensities were analysed in order to calculate the molecular vibrational temperature T_{vib}. According to the vibrational sum rule for the intensities of different bands in a progression, the

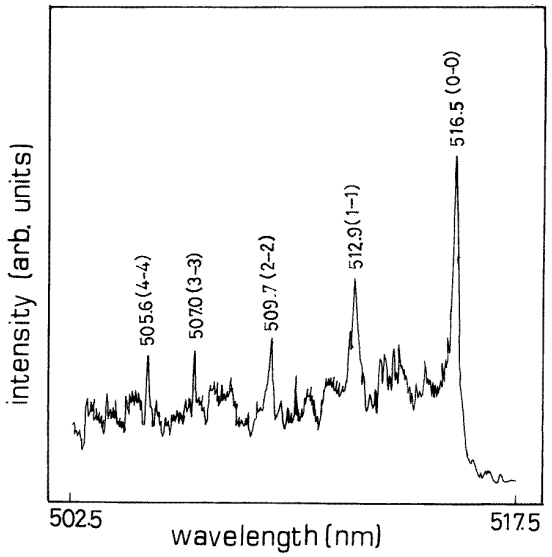

Figure 1. The spectrum of the resolved C_2 Swan band emission for $\Delta v = 0$.

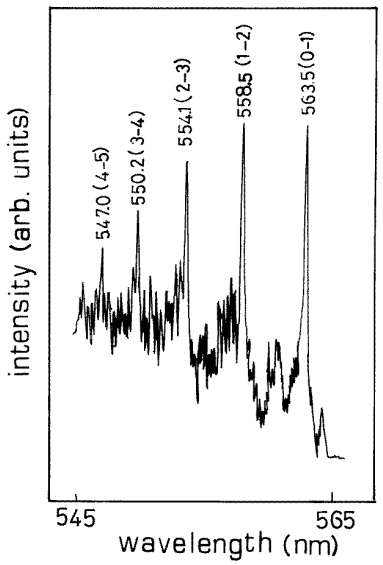

Figure 2. The spectrum of the resolved C_2 Swan band emission for $\Delta v = -1$.

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. For a plasma in 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 [25, 26]:

$$\ln\left(\sum_{v''}(\lambda^4 I_{v'v''})\right) = C_1 - G(v')\frac{hc}{kT_{vib}} \qquad (1)$$

where λ is the wavelength corresponding to the emission, h Planck's constant, c the velocity of light, C_1 a constant, $G(v')$ the term value corresponding to the vibrational level in the upper electronic state and T_{vib} the vibrational

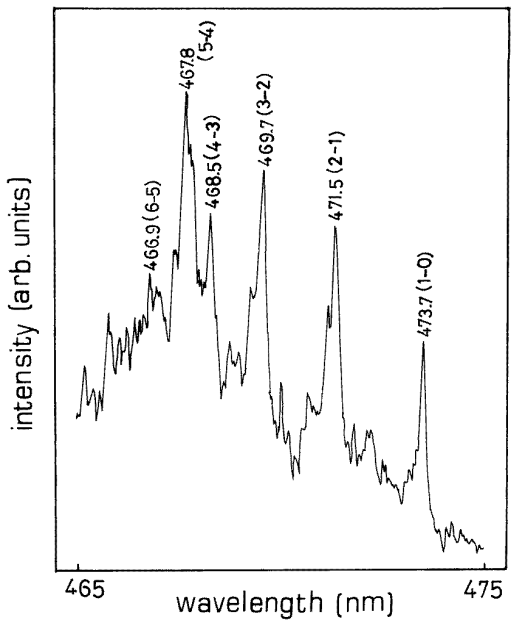

Figure 3. The spectrum of the resolved C_2 Swan band emission for $\Delta v = 1$.

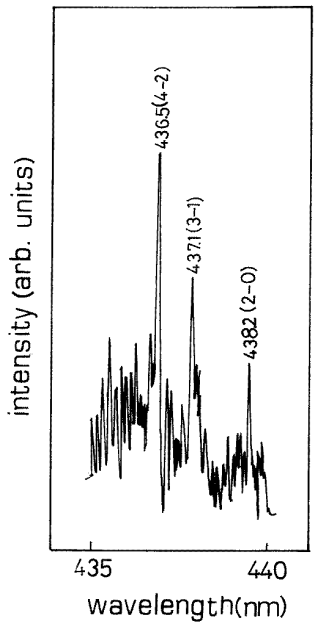

Figure 4. The spectrum of the resolved C_2 Swan band emission for $\Delta v = 2$.

temperature. The vibrational temperature for C_2 bands was obtained from a plot of the sums of the band-head 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. The advantage of using the Boltzmann distribution is that the information regarding the transition probability is not essential in this case. Boltzmann plots of the band intensities against vibrational energy were drawn for different laser irradiances and are given in figure 5.

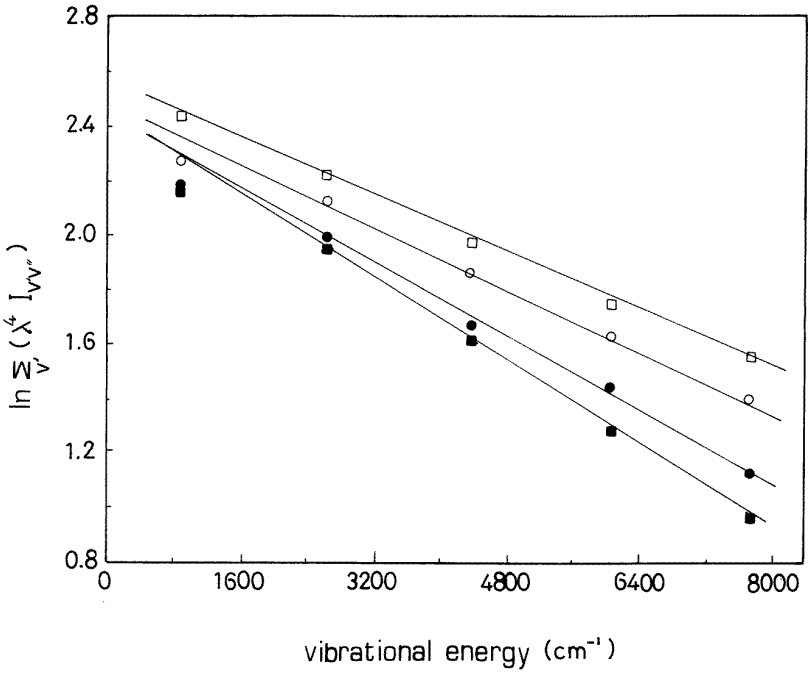

Figure 5. Boltzmann plots of the vibrational band intensity versus the vibrational energy for various laser irradiances 10 mm from the target: (□), 4.5×10^{10} W cm^{-2}; (○), 4.25×10^{10} W cm^{-2}; (●), 3.5×10^{10} W cm^{-2}; and (■), 2.5×10^{10} W cm^{-2}). The slope of the fitted line was used to calculate the vibrational temperature.

It has already been reported that the diamond-like character of the films deposited on substrates is strongly dependent upon the variation of temperature in the laser plasma which in turn depends upon the laser irradiance [18]. The variations in vibrational temperature with laser irradiance corresponding to C_2 molecules at distances 5 and 10 mm are given in figure 6. At 5 mm radial distance from the target surface, the vibrational temperature increased rapidly until the optimal irradiance had been attained and after that there was a saturation effect. The saturation effect at high laser irradiances may be due to two reasons. (i) At high irradiance due to a high plasma temperature, 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. This would cause a net depletion of the excited state population in the higher vibrational levels. (ii) Plasma shielding, namely the change in efficiency of laser coupling to the target caused by increased absorption and/or reflection from the laser-induced plasma could cause saturation. The absorption by the fragments heats the plume to higher temperatures by which further fragmentation into small components, including atoms and ions, occurs. The particular nature of the vibrational temperature at different distances (5 and 10 mm) results from the fact that excited-state C_2 formation is controlled by various interaction processes such as electron capture, collisional excitation and ionization, recombination processes and fragmentation of higher clusters, which vary greatly with the spatial separation from the target.

The emission characteristics of a laser-produced plasma are influenced to a large extent by the nature and composition of the surrounding atmosphere. The increase in helium ambient pressure gave rise to an enhancement in the emission intensity from all the species due to collisions on the expansion front and subsequent intra-plume collisions, sharpening of the plume boundary and slowing down of the plume relative to the propagation in vacuum, all leading to spatial confinement of the plasma. The dependence of the vibrational temperature of C_2 molecules on the helium ambient pressure is given in figure 7. It can be seen that the increase in helium

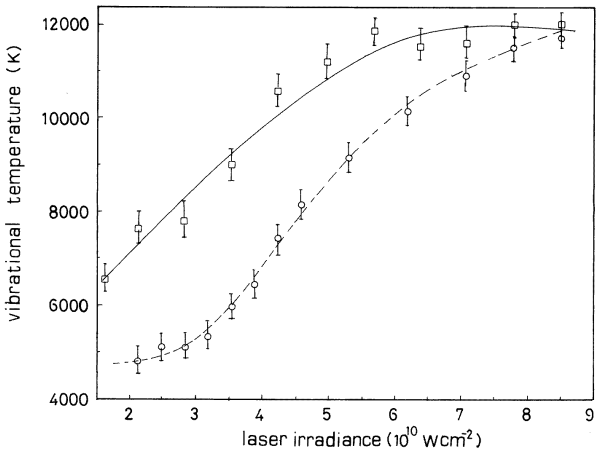

Figure 6. The vibrational temperature calculated from C_2 Swan bands as a function of the laser irradiance at (□) 5 mm and (○) 10 mm, with a helium pressure of 50 mTorr. The error bars were assigned by assuming 10% errors in intensities.

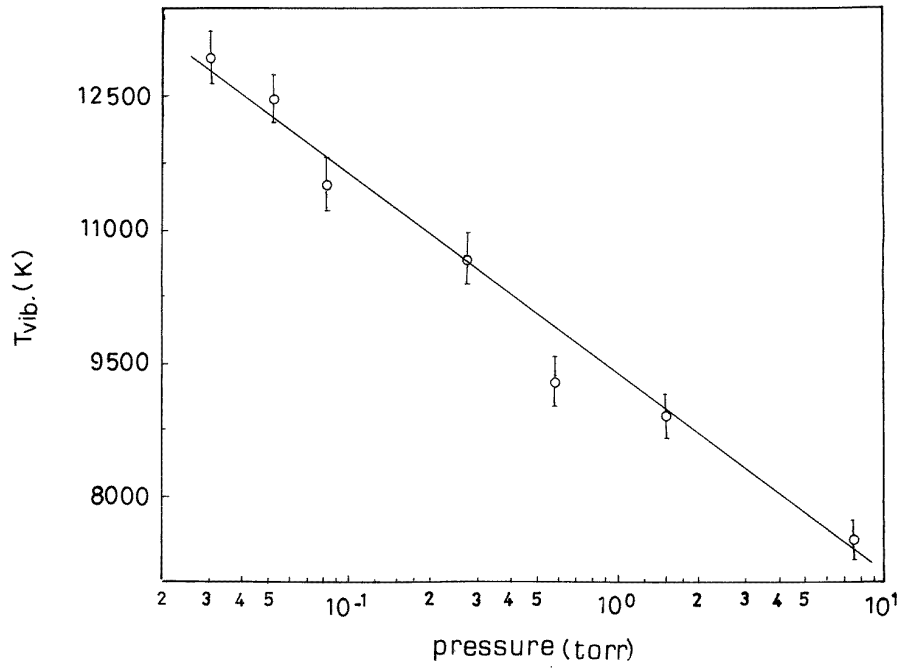

Figure 7. The variation in vibrational temperature with helium ambient pressure (distance 5 mm, laser irradiance 7.3×10^{10} W cm^{-2}). The error bars were assigned by assuming 10% errors in intensities.

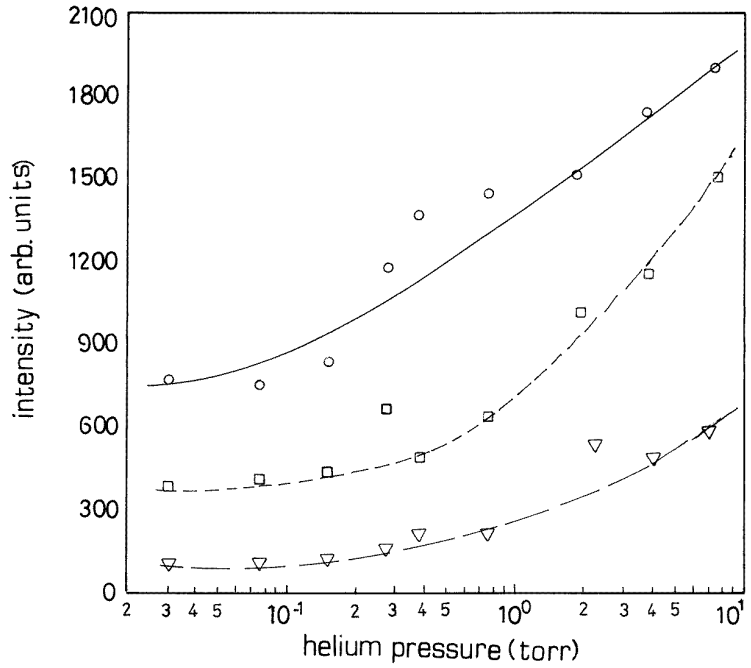

Figure 8. The variation in intensity of C_2 band heads as a function of the helium gas pressure: (○), (0–0) at 516.5 nm; (□), (0–1) at 563.5 nm; and (▽), (1–0) at 473.7 nm (distance 5 mm).

pressure decreased the vibrational temperature of the C_2 species. This was due to the fact that the ambient helium atmosphere cooled the hot electrons as well as excited states of molecules by collisions leading to a more efficient thermalization and thereby decreasing the vibrational temperature. This result also implies that the distribution of vibrationally excited states was not in equilibrium with the plasma at low pressures. The addition of helium improved the confinement of the plasma which in turn enhanced the emission from all species. This is also supported by the observed enhancement in the intensities of C_2 bands on increasing the helium pressure (figure 8).

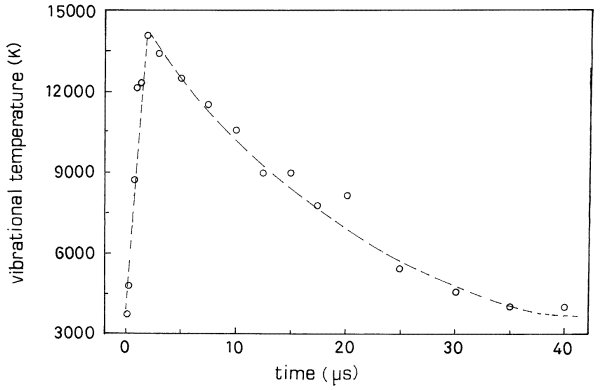

Figure 9. The time dependence of the vibrational temperature of C_2 molecules at 5 mm (laser irradiance 7×10^{10} W cm^{-2}, helium pressure 50 mTorr).

For the time-dependence studies, emission spectra were recorded by varying delay times with respect to the laser pulse in the range 100 ns to 40 μs with the gate width of the boxcar averager fixed at 100 ns. All the spectra were recorded 5 mm away from the target and at a laser irradiance of 7×10^{10} W cm^{-2}. For an integration time of 100 ns, the spatial distance travelled by the C_2 species was 0.4 mm, taking the average expansion velocity to be 4×10^5 cm s^{-1} [27] at a laser irradiance of 7×10^{10} W cm^{-2}, which is much smaller than the successive spatial steps of 1 mm. Hence there could not have been any significant mixing of spatial and temporal aspects of the plasma and an effective separation of spatial and temporal effects must have been achieved. It was observed that the emission characteristics of the plasma varied drastically with time. At shorter times, the dominant radiation was a continuum mixed with ionic lines. The continuum emission was due to Bremsstrahlung radiation and radiative recombination or to incandescence of hot carbon particles [28]. In the period 0.1–2 μs, both of these contributions decayed, leaving neutral species lines and molecular bands which were seen up to 40 μs or longer. It was also observed that, during shorter times, due to the high electron density the individual emission lines from various atomic and ionic lines were highly Stark-broadened [29]. The time dependence of the vibrational temperature of C_2 species is shown in figure 9. It is clear from figure 9 that there was a maximum vibrational temperature (14×10^3 K) after an elapsed time of 2 μs at a distance of 5 mm from the target. At shorter times (<2 μs), due to the high plasma temperature depletion of the excited levels took place because of excitation to higher levels and de-excitation to lower levels.

4. Conclusion

In this paper we describe a detailed spectroscopic study of a laser-produced carbon plasma. We have performed the spatially as well as the temporally resolved analysis of C_2 Swan bands in the emission spectrum of a laser-induced plasma from a graphite target in a helium atmosphere. The emission intensities from C_2 species were sensitive to the laser irradiance, pressure of the background gas, time after the initiation of the plasma and spatial separation from the target. These investigations also demonstrated that there are different possible routes for the formation of C_2 molecules. At a low incident irradiance the emission bands due to C_2 predominate whereas at a higher irradiance multiply ionized carbon species up to C IV were observed together with C_2 species. The C_2 emission observed at a low irradiance could have been due to plasma excitation and that at high irradiance to recombination processes. The presence of an ambient helium atmosphere caused enhancement of the line emission of the band heads of the C_2 species. This enhancement in the emission intensity from C_2 was due to collisions on the expansion front and subsequent intra-plume collisions.

From the spectroscopic studies of the emission bands, the vibrational temperature of the C_2 species in the plasma was estimated. The vibrational temperature was found to increase with increasing laser irradiance and saturated at higher irradiance levels. An increase in laser irradiance caused an increase in the degree of ionization and vibrational temperature of C_2 molecules in the plasma. The saturation at higher laser irradiances occurred mainly due to excitation to higher levels, quenching and plasma shielding. From the time-resolved studies, it was observed that the vibrational temperature peaked after 2 μs of the laser pulse had elapsed at a laser irradiance of 7×10^{10} W cm^{-2}. It was also confirmed that the vibrational temperature of the C_2 molecules decreased with increasing helium pressure. The addition of helium apparently cooled and confined the plasma, causing a reduction in the vibrational temperature. In summary, the present work threw some light on the production and kinetics of C_2 molecules in a laser-generated plasma from a graphite target.

Acknowledgments

The present work was supported by the Department of Science and Technology, Government of India. One of the authors (SSH) is grateful to the Council of Scientific and Industrial Research, New Delhi for a senior research fellowship. RCI and CVB are grateful to the University Grant Commission, New Delhi for their senior research fellowships.

References

[1] Hughes T P 1975 *Plasmas and Laser Light* (Bristol: Hilger)
[2] Redziemsky 1989 *Laser Induced Plasma and Applications* (New York: Dekker)
[3] Miller J C and Haglund R F (eds) 1991 *Laser Ablation: Mechanisms and Applications* (Berlin: Springer)
[4] Wagal S S, Juengerman E M and Collins C B 1988 *Appl. Phys. Lett.* **53** 187
[5] Voevodin A A, Laube S J P, Walck S D, Solomon J S, Donley M S and Zabinski J S 1995 *J. Appl. Phys.* **78** 4123
[6] Martin J A, Vazquez L, Bernard P, Comin F and Ferrer F 1990 *Appl. Phys. Lett.* **57** 1742
[7] Venkatesan T, Wu X D, Inam A and Wachtman J B 1988 *Appl. Phys. Lett.* **52** 1193
[8] Ashok Kumar and Narayan J 1991 *Appl. Phys. Lett.* **59** 1785

[9] Harilal S S, Radhakrishnan P, Nampoori V P N and Vallabhan C P G 1994 *Appl. Phys. Lett.* **64** 3377
[10] Pappas D L, Saenger K L, Bruley J, Krakow W, Cuomo J J, Gu T and Collins R W 1992 *J. Appl. Phys.* **71** 5675
[11] Rohlfing E A, Cox D M and Kaldor A 1984 *J. Chem. Phys.* **81** 3322
[12] Radi P P, Bunn T L, Kemper P R, Molchan M E and Bowers M T 1988 *J. Chem. Phys.* **88** 2809
[13] Chrisey D B and Hubler G K (eds) 1994 *Pulsed Laser Deposition of Thin Films* (New York: Wiley)
[14] Miller J C and Geohegan D B (eds) 1993 *Laser Ablation: Mechanisms and Applications* (New York: AIP)
[15] Harilal S S, Issac R C, Bindhu C V, Nampoori V P N and Vallabhan C P G 1996 *J. Appl. Phys.* **80** 3561
[16] Harilal S S, Issac R C, Bindhu C V, Nampoori V P N and Vallabhan C P G 1997 *J. Appl. Phys.* **81** at press
[17] Harilal S S, Issac R C, Bindhu C V, Nampoori V P N and Vallabhan C P G 1997 *Japan. J. Appl. Phys.* **36** 134
[18] Iida and Yeung E S 1994 *Appl. Spectrosc.* **48** 945
[19] Dwivedi R K and Thareja R K 1995 *Surf. Coating Technol.* **73** 170
[20] Dwivedi R K and Thareja R K 1995 *Phys. Rev.* B **51** 7160
[21] Harilal S S, Issac R C, Bindhu C V, Nampoori V P N and Vallabhan C P G 1996 *Pramāna J. Phys.* **46** 145
[22] Weltner W Jr and Van Zee R J 1989 *Chem. Rev.* **89** 1713
[23] Pearse R W B and Gaydon A G 1965 *The Identification of Molecular Spectra* (London: Chapman and Hall)
[24] Little C E and Browne P G 1987 *Chem. Phys. Lett.* **134** 560
[25] Herzberg G 1950 *Spectra of Diatomic Molecules* (*Molecular Spectra and Molecular Structure*) (New York: Van Nostrand)
[26] Harilal S S, Issac R C, Bindhu C V, Nampoori V P N and Vallabhan C P G 1997 *Spectrochim. Acta* A at press
[27] Harilal S S 1997 *PhD Diss.* Cochin University of Science and Technology
[28] Rohlfing E A 1988 *J. Chem. Phys.* **89** 6103
[29] Griem H R 1975 *Plasma Spectroscopy* (New York: McGraw-Hill)