

Spatial and time resolved analysis of CN bands in the laser induced plasma from graphite

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Abstract. Analysis of the emission bands of the CN molecules in the plasma generated from a graphite target irradiated with $1.06\ \mu\text{m}$ radiation pulses from a Q-switched Nd:YAG laser has been done. Depending on the position of the sampled volume of the plasma plume, the intensity distribution in the emission spectra is found to change drastically. The vibrational temperature and population distribution in the different vibrational levels have been studied as function of distance from the target for different time delays with respect to the incidence of the laser pulse. The translational temperature calculated from time of flight is found to be higher than the observed vibrational temperature for CN molecules and the reason for this is explained.

Keywords. Laser induced plasma; emission spectroscopy.

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1. Introduction

Irradiation of a target material with a high power laser pulse generates intense plasma emission from the target surface. Such laser generated plasma is a rich source for atomic, ionic and molecular species in various states of excitations [1, 2]. The abundance of molecular, atomic and ionic species in the plasma will depend on various parameters like nature of the target, laser power and pressure of the residual gas in the plasma chamber [3–6]. Different types of studies of laser induced plasma such as charge and velocity distribution of ablated species, second harmonic generation, X-ray emission, etc. using high power laser pulses have been carried out in detail by many workers [7–9]. The composition of the plasma will also depend on the spatial distance of the point of observation from the target. The detailed studies of composition and temperature in terms of distance from target have great importance with regard to certain practical applications of laser ablation process like deposition of diamond like carbon films [10, 11].

Laser induced plasma from graphite target will contain, in addition to different clusters, atomic and ionic species of carbon and transient species like CN in a partially evacuated plasma chamber. Even though a few studies are available in the literature related to CN species in the plasma, a systematic investigation of the spatial and temporal variations of the characteristics of the plasma plume have not been reported

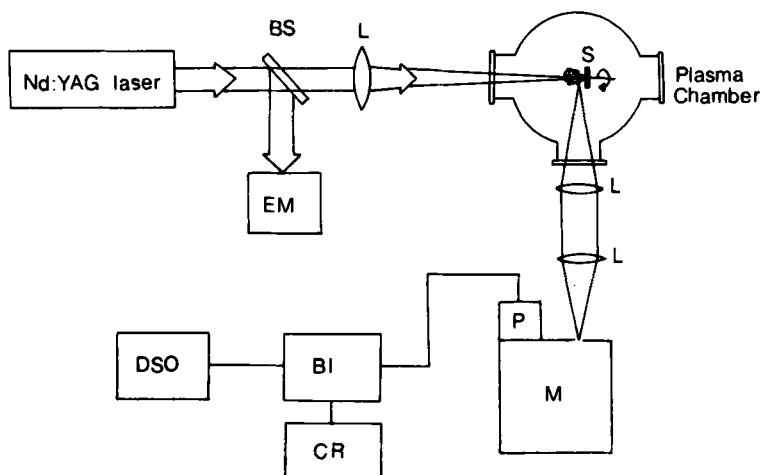


Figure 1. Schematic diagram of the experimental set up. BS, beam splitter; EM, energy meter; L, lens; S, sample; M, monochromator; P, PMT; BI, boxcar averager/gated integrator; CR, chart recorder; DSO, digital storage oscilloscope.

yet. In the present paper the spatial variation of the vibrational temperature of CN molecules at different points of time during the evolution of the plasma is studied using a Q-switched Nd:YAG laser as the pump source by analyzing the emission spectrum of the violet system of CN molecule corresponding to the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition. This will provide information regarding the vibrational distribution of CN molecules in the plasma.

2. Experimental technique

The schematic diagram for the experimental set up is shown in figure 1. Plasma was produced by the irradiation of a high purity graphite target with $1.06 \mu\text{m}$ laser radiation (pulse width 9 ns and $1.1 \times 10^{11} \text{ W cm}^{-2}$ maximum power density) from a Q-switched Nd:YAG laser (Quanta Ray DCR II) at a pulse repetition frequency of 10 Hz. The target was placed in a partially evacuated chamber (20 mTorr) with quartz windows. The target was mechanically rotated so as to minimize the surface etching and after every five minutes' scan the focal spot was laterally shifted to different positions on the target surface in order to provide fresh surface for ablation. In the absence of this arrangement, emission line intensities tend to fade due to etching of the target surface.

The emission spectrum from the plasma was viewed normal to its expansion direction by imaging the plasma plume using appropriate collimating and focussing lenses onto the slit of a one meter Spex monochromator (1200 grooves/mm, 100 mm by 100 mm grating blazed at 500 nm). The scan rate of the monochromator was adjusted by using Spex CD2A compudrive arrangement. The recording was done using a thermoelectrically cooled Thorn EMI Photo Multiplier Tube (PMT, model KQB 9863) which was coupled to a boxcar averager/gated integrator (Stanford Research Systems, SR 250). The total extension of the plasma in the present set up was about

25 mm beyond which the light emission become very weak for effective detection. For spatially resolved observations, different regions of the plume was focussed onto the monochromator slit. In these studies, accuracy in spatial dimensions was better than 0.2 mm. The output from the gated integrator (gate width 100 ns), which averaged out emission intensities from ten consecutive pulses, was fed to a chart recorder. The spectrum in the region 355–475 nm was normalized using the optical response curves of the monochromator-PMT assembly. For temporal studies the PMT output was fed to a 200 MHz digital storage oscilloscope (Iwatsu, DS 8621) with 50 Ω input impedance. This set up essentially provides velocity as well as decay times of the constituent species [12] at a specific point within the plasma and these are extremely important parameters related to the evolution of laser ablated materials in a direction normal to the target surface.

3. Results and discussion

The spectrum of the graphite plasma contains different vibrational bands of CN molecules along with emission lines from atomic and ionic species of carbon. Atoms and ions of carbon ejected from the target due to laser ablation combine with the ambient nitrogen inside the plasma chamber producing CN molecules through recombination process. Characteristic spectral emission of CN molecule was obtained

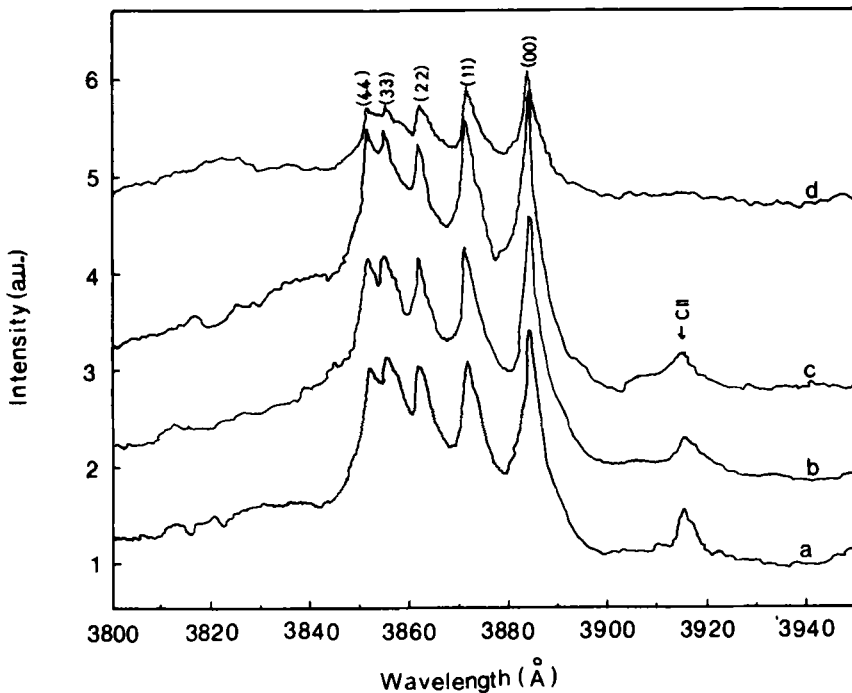


Figure 2. CN violet band for $\Delta v = 0$ sequence at different spatial distances from the target (laser irradiance $7.3 \times 10^9 \text{ W cm}^{-2}$, time delay $5 \mu\text{s}$) (a) 2 mm, (b) 6 mm, (c) 10 mm, (d) 14 mm.

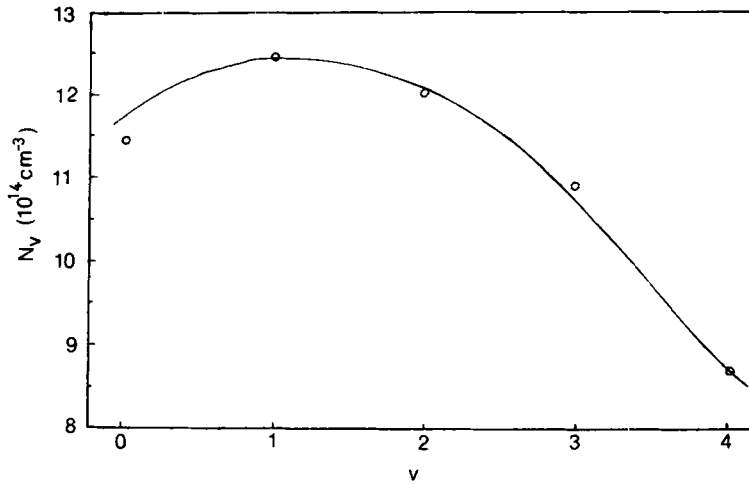


Figure 3. The vibrational distribution of CN violet band (distance 10 mm, laser irradiance $7.3 \times 10^9 \text{ W cm}^{-2}$).

in the violet region due to the $\text{B}^2\Sigma^+ \rightarrow \text{X}^2\Sigma^+$ transition [13]. Depending on the laser fluence, time of observation and position of the sampled volume of plasma, the intensity distribution of the emission spectra change drastically as the plume expands. Spectra for sequences $\Delta v = 1, 0, -1, -2$ are recorded where, $\Delta v = v' - v''$ is the difference between the vibrational quantum numbers of the upper ($\text{B}^2\Sigma^+$) and lower ($\text{X}^2\Sigma^+$) electronic states. Figure 2, gives the typical CN-violet band ($\Delta v = 0$) for different distances from the target at a laser irradiance $7.3 \times 10^9 \text{ W cm}^{-2}$ (estimated laser spot size being $\approx 200 \mu\text{m}$ in radius). Spectrum show a gradual increase in the emission intensity up to a distance 10 mm away from the target and beyond this distance the intensity decreases rapidly. Contrary to this, the singly ionized carbon (CII) line intensity decreases continuously as we move away from the target. It has also been observed that the intensity of CN bands increases up to a laser irradiance of $7.3 \times 10^9 \text{ W cm}^{-2}$ and it levels off above this power density.

The band emission intensities were used to calculate molecular vibrational temperature T_{vib} , details of which are available in the literature [14]. The vibrational distribution in the excited states of CN molecules at distance 10 mm away from the target is shown in figure 3 at a laser irradiance $7.3 \times 10^9 \text{ W cm}^{-2}$. The inverse distribution observed for $v < 2$ is in accordance with the Frank-Condon principle. Similar inverse distributions were also observed in certain other molecules [15, 16].

The spatial variation of the vibrational temperature for $2 \mu\text{s}$ and $5 \mu\text{s}$ delay times after the onset of the plasma is given in figure 4. It was found that at a particular laser fluence, depending on the time of observation and the position of the sampled volume, the vibrational temperature of CN molecules varies. Spatial variation of vibrational temperature after $2 \mu\text{s}$ from the onset of the plasma peaks ($2.14 \times 10^4 \text{ K}$) at a distance 3 mm away from the target. For $5 \mu\text{s}$ delay time, the vibrational temperature was maximum ($1.96 \times 10^4 \text{ K}$) at 8 mm from the target surface. This is because of the fact that near the target surface the temperature is so high that collision induced processes

Laser induced plasma

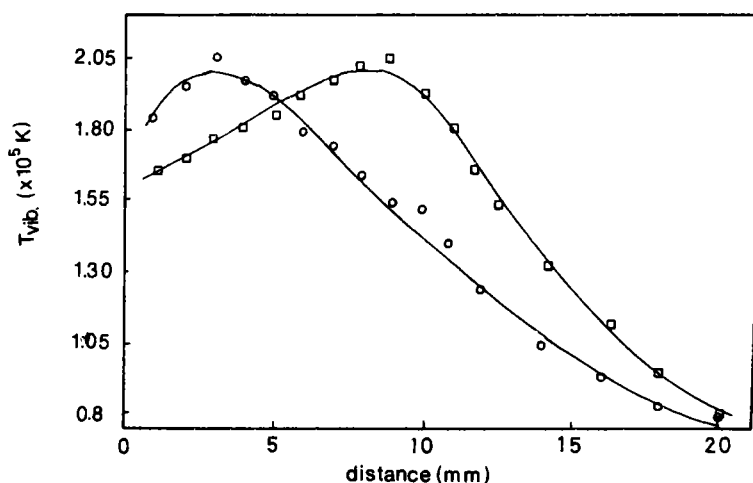


Figure 4. The variation of vibrational temperature of the CN violet band with distance from the target for 2 μs (○) and 5 μs (□) delay time.

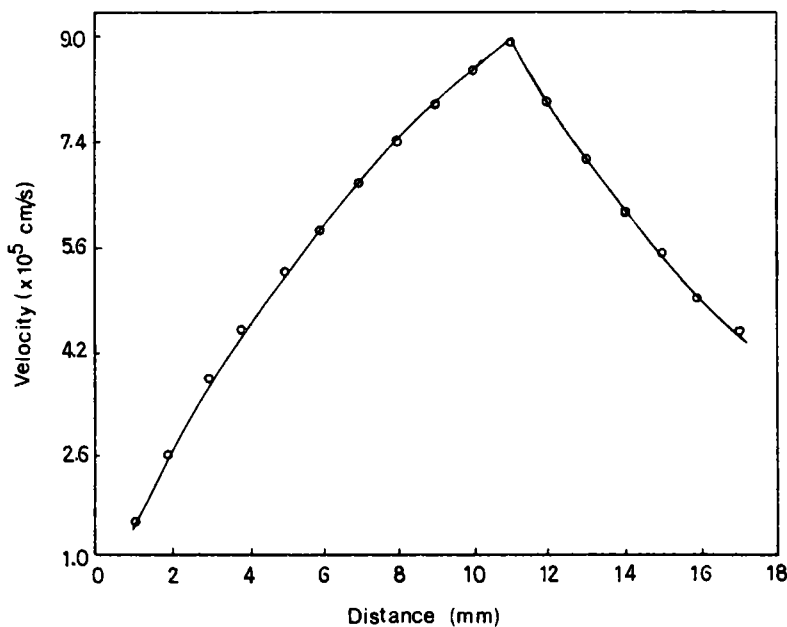


Figure 5. The change in the expansion velocity of CN molecules (388.3 nm) as a function of distance from the target (laser irradiance $7.3 \times 10^9 \text{ W cm}^{-2}$).

predominate and cause a decrease in vibrational temperature due to de-excitation of the higher vibrational levels. As we move away from the target, the collisional effects are reduced so that effectively vibrational temperature was found to be high. At distances farther than this optimal distance, the decrease in plasma temperature will cause

a reduction in vibrational temperature. The location at which maximum occurs for vibrational temperature was different for $2 \mu\text{s}$ and $5 \mu\text{s}$ delays (for $2 \mu\text{s}$ maximum is at 3 mm and for $5 \mu\text{s}$ at 8 mm). Such an effect takes place because different physical processes like collision between neutrals, ions or electron capture by CN^- etc. predominate at different times within the plasma and the evolutionary history of CN is fairly complex. This causes the CN number densities to vary with respect to time as well as space in the laser generated plasma from graphite.

From the observed time delays, one can evaluate expansion velocities of these transient species. Figure 5 shows the change in the expansion velocity of CN molecules as a function of distance from the target at laser irradiance $7.3 \times 10^9 \text{ W cm}^{-2}$. It is found that the expansion velocity of CN molecules was increasing up to a certain distance from the target (8 mm) and thereafter they slow down rapidly attaining a much smaller expansion velocity, which corresponds to plasma cooling.

The maximum molecular vibrational temperature for CN molecules was found to be around $2.14 \times 10^4 \text{ K}$, which is much higher than the melting point of graphite ($4 \times 10^3 \text{ K}$). This large vibrational temperature may arise due to the direct heating of the plasma plume. This is supported by the measurement of the temperature equivalent of translational energy which varies from $2 \times 10^4 \text{ K}$ to $7 \times 10^4 \text{ K}$ at a laser irradiance of $7.3 \times 10^9 \text{ W cm}^{-2}$. The large variation in the translational temperature implies that, the observed time delays are not only due to time of flight (TOF) phenomenon alone but also due to those arising from other processes like recombination/dissociation of the species, collisional excitation process etc. Further experiments like mass spectral measurements may shed some light on these aspects.

In conclusion, laser irradiation of graphite in a low pressure air chamber generates plasma containing CN molecules. From the spectroscopic studies of the emission bands of the CN molecules, the population distribution and vibrational temperature at different regions of the plasma plume have been obtained. It is found that the vibrational temperature of the CN molecules varies with the position of the sampled volume within the plasma plume.

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