Chapter 6

Spectroscopic Studies on Cyanogen Bands from Laser Produced Carbon Plasma

Time and space resolved studies of emission from CN molecules have been carried out in the plasma produced from graphite target by 1.06 μm pulses from a Q-switched Nd:YAG laser. Depending on the laser pulse energy, 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 have been studied as functions of distance, time, laser irradiance and ambient gas pressure. Evidences for nonlinear effects of the plasma medium like self-focusing which exhibits threshold-like behaviour are also obtained. 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.
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6.1 Introduction

The Cyanogen (CN) system is of considerable astrophysical interest because of its use in determining the nitrogen abundance in stellar atmospheres [1]. The CN radical occurs in a wide variety of sources. It can be observed through either the red \( \left(A^2\Pi \rightarrow X^2\Sigma^+\right) \) or violet \( \left(B^2\Sigma^+ \rightarrow X^2\Sigma^+\right) \) emission systems [2]. In the laboratory, CN is abundant in flames, electrical discharges of all types, plasma produced during laser ablation of any carbon containing material in air or under partial vacuum conditions etc. CN is also detected in a wide variety of extraterrestrial sources including sun, stellar atmosphere, comets, red giants, interstellar clouds by techniques of microwave, infrared and ultraviolet spectroscopy [3-7]. In principle the two CN band systems should be an excellent probe of the chemistry under these conditions, where direct measurements are difficult or impossible. If the dissociation energy and transition probability of CN were known, the observed emission intensity in the stellar atmosphere could be converted into elemental abundance. Theoretical studies of the dissociation energy of the red and violet band systems of CN were carried out by Bauschlicher et al [8]. They reported that dissociation energy of CN molecules to be 7.65 ± 0.1 eV and the life time of the \( v' = 0 \) level of the violet system to be 62.4 ns. Fluorescence from the CN radical in both the \( A^2\Pi \) and \( B^2\Sigma^+ \) states has been extensively studied [9,10] as a probe of primary photochemical processes in cyanide-containing polyatomic molecules such as HCN, CH\(_3\)CN and ICN. This has led to detailed information of final energy distributions in the photofragments [9]. Much effort has therefore been devoted to determine reliable radiative transition probabilities and life times for the CN system. Knowels et al [11] reported Einstein coefficients of spontaneous emission and oscillator strengths for CN molecules.

CN molecules have been the subject of numerous laboratory investigations. It is reported that CN molecules produced by ablation using excimer laser are due to photochemical processes whereas if they are obtained by NIR (Nd:YAG) laser, thermal processes might be expected to be more relevant [12]. Rotational and vibrational temperatures of CN molecules produced during laser ablation of graphite target in air have been reported by Hatem et al [13]. Atoms or ions of carbon ejected during laser ablation of graphite target combine with the ambient nitrogen inside the plasma chamber producing the excited CN molecules through recombination processes. Characteristic spectral emission of CN bands were obtained due to \( B^2\Sigma^+ \rightarrow X^2\Sigma^+ \) for violet system.
and $A^2\Pi \rightarrow X^2\Sigma^+$ for red system.

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 [14, 15]. 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 [16-18]. Laser induced plasma (LIP) 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 [19-21].

Depending on the time of observation and position of the sampled volume the features of the plasma emission change as the plasma expands. In the case of LIP from graphite target, the emission contain molecular band systems from different species like $C_2$, CN etc.. It has been pointed out that the excited diatomic species, which are sources of band emission in the different regions of plasma, may be formed by a secondary photolysis of the initial products. The CN violet system ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$) has been studied by a variety of techniques [22-24] since it is an important free radial occurring in many emission sources. Even though a few studies are available in the literature related to CN species in the plasma, a systematic investigation of spatial and temporal variations of the characteristics of the plasma has not been reported yet. This chapter describes the spatial, temporal, laser irradiance and ambient gas pressure dependence of the CN species generated in graphite plasma by 1.06 $\mu$m pulsed laser irradiation under partial vacuum using optical emission diagnostics technique. Optical spectroscopy is an effective as well as convenient tool to detect various transient species such as excited atoms, ions and diatomic/polyatomic molecules, all of which are produced during laser ablation. The vibrational temperature and its variations under different conditions have been evaluated from the emission spectrum of CN violet band.

6.2 Experimental Details

The schematic experimental set-up is shown in chapter 2. Plasma was produced by the irradiation of a high purity graphite target with 1.06 $\mu$m laser radiation from a Q-switched Nd:YAG laser at a pulse repetition frequency of 10 Hz. The target was placed in a partially evacuated chamber (0.05 mbar) 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 focusing lenses onto the slit of a one meter Spex monochromator. The recording was done by a thermoelectrically cooled PMT which was coupled to a boxcar averager/gated integrator. The total extension of the plasma in the present set-up was about 25 mm beyond which the light emission became very weak for effective detection. For spatially resolved observations, different regions of the plume were focused on to 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. For temporal studies the PMT output was fed to a 200 MHz digital storage oscilloscope with 50 Ω input impedance.

6.3 Results and Discussion

6.3.1 Emission Spectra

The CN emission spectra of the LIP from graphite target were recorded in the region λλ 355 - 475 nm. All the emission intensities are corrected for the detector spectral response which was predetermined through use of a standard lamp. The emission spectrum is found to contain different vibrational bands of CN molecules in addition to atomic and ionized species of carbon. The intensities of the band emission have been found to depend on the delay time and distance from the target surface. Near the target surface atomic as well as ionic species predominate while in regions away from the target, molecular species like CN and C₂ dominate. In the present experiment the emission from the CN system arises from the outer region of the plasma that surrounds the laser beam. The atomic, ionic and molecular carbon ejected from the target due to laser ablation combines with the ambient nitrogen resulting in the formation of CN molecules. Characteristic spectral emission of CN molecule in the violet region is obtained due to \( B^2Σ^+ \rightarrow X^2Σ^+ \) transition. Well defined bands in 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 \( (B^2Σ^+) \)
and lower ($X^2\Sigma^+$) electronic states. The CN ($B \rightarrow X$) $\Delta v = 0$ violet band sequence (fig. 6.1) consisted of band heads (0-0) at 388.3 nm, (1-1) at 387.1 nm, (2-2) at 386.2 nm, (3-3) at 385.5 nm and (4-4) at 385.1 nm. For $\Delta v = -1$ (fig. 6.2) band heads from (0-1) at 421.6 nm to (5-6) at 415.2 nm are found to be predominant. We also observed the $\Delta v = 1$ CN violet sequence (fig. 6.3) with band heads of (1-0) at 359 nm, (2-1) at 358.6 nm and (3-2) at 358.4 nm. Fig. 6.4 shows the $\Delta v = -2$ violet band system with band heads of (0-2) at 460.6 nm, (1-3) at 457.8, (2-4) at 455.3 nm, (3-5) at 453.2 nm, (4-6) 451.5 nm and (5-7) at 450.2 nm.

### 6.3.2 Spatial Dependence

One of the results in the present series of studies is that the spectral features are distinctly different for the emission from different sections of the plasma plume. For spatial studies, different parts of the plasma were imaged onto the slit of the monochromator. Fig. 6.5 gives the typical CN violet band ($\Delta v = 0$) for different distances along the plasma expansion direction at a laser power density of 35 GW cm$^{-2}$ (pressure 0.05 mbar). The continuum emission intensity in the plasma emission is greatest in the region close to the
Figure 6.2: Spectrum of the resolved CN violet band emission for $\Delta v = -1$

Figure 6.3: Spectrum of the resolved CN violet band emission for $\Delta v = 1$
target surface and decreases sharply within a few millimeters from the target surface. The spectral emission intensity is very bright during the initial stages (up to \( \sim 100 \) ns) of plume expansion due to Bremsstrahlung emission (free-free transition) from the hot plasma. In the region very close to the target surface, density in the plasma core is so high that much of the broadened line emission cannot be separated from the background. Farther away from the target surface, in the case of excited carbon species, the lines become narrower and weaker with increasing separation from the target. Spectrum show a gradual increase in the CN 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 (C II) line intensity decreases continuously as we move away from the target. From this it can be inferred that CN emission arises from the outer region of the plasma as was already mentioned. For these studies the gate width was set at 100 ns. The average velocity being \( 6 \times 10^5 \text{cm/sec} \) [25], for an integration time of 100 ns, the spatial distance travelled by CN molecules is 0.6 mm, which is smaller than the successive spatial steps of 1 mm. In our present work the spatial resolution was better than 0.2 mm. Hence there will not be any significant mixing of spatial and temporal aspects of plasma. The vibrational distribution in the excited states of CN molecules at distance
Figure 6.5: CN violet band for $\Delta v = 0$ sequence at different spatial distances from the target (laser irradiance 7.3 GW cm$^{-2}$, time delay 5 $\mu$s) (a) 2 mm, (b) 6 mm, (c) 10 mm, (d) 14 mm

10 mm away from the target is shown in fig. 6.6 at a laser irradiance 73 GW cm$^{-2}$. The inverse distribution observed for $v < 1$ is in accordance with the Frank-Condon principle. Similar inverse distributions were also observed in certain other molecules [27, 28].

The band emission intensities were used to calculate molecular vibrational temperature $T_{vib}$, details of which are given in section (3.3.1) [26]. The vibrational temperature is obtained from the slope of the Boltzmann plot between $\ln \Sigma_{v'}(\lambda^4 I_{v'v})$ and $G(v')$. Typical Boltzmann plot of the band intensities against vibrational energy are given in fig. 6.7 for various distances from the target surface. The spatial variation of the vibrational temperature for 2 $\mu$s and 5 $\mu$s delay times after the onset of the plasma is given in fig. 6.8.

It was found that at a particular laser irradiance, 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 $\mu$s from the onset of plasma formation was found to peak ($2.05 \times 10^4$ K) at a distance 3 mm away from the target. For 5 $\mu$s delay time, the vibrational temperature was maximum ($1.96 \times 10^4$ K) at 8 mm from the target surface. The expected experimental error was $\pm 10\%$. These results are also consistent with earlier reports on vibrational temperature of CN species [13, 29, 30].
Figure 6.6: The vibrational distribution of CN violet band (distance 10 mm, laser fluence 73 W cm\(^{-2}\))

Figure 6.7: Typical Boltzmann plots of vibrational band intensity vs vibrational energy for different distances from the target
Figure 6.8: The variation of vibrational temperature of the CN violet band with distance from the target for 2 \( \mu s \) (\( \bigcirc \)) and 5\( \mu s \) (\( \square \)) delay time

The observed spatial variation of vibrational temperature can be explained as follows. Near the target surface the temperature is so high that collisional dissociation predominates and this causes a net decrease of de-excitation of the higher vibrational levels with corresponding reduction in band intensity. As we move away from the target, the collisional effects are reduced so that effectively the vibrational temperature is found to be high. At distances beyond an optimal value the decrease in plasma temperature [31] will cause a reduction in vibrational temperature. The location at which maximum occurs for vibrational temperature was different for 2 \( \mu s \) and 5 \( \mu s \) delays (for 2 \( \mu s \) maximum is at 3 mm and for 5 \( \mu s \) 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.
Figure 6.9: CN violet band for $\Delta v = 0$ sequence at different time delays after the onset of plasma (laser irradiance 35 W cm$^{-2}$, distance 7 mm) Time delays (a) 20 $\mu$s, (b) 10 $\mu$s, (c) 4 $\mu$s, (d) 2 $\mu$s (e) 1 $\mu$s and (f) 500 ns

6.3.3 Time Dependence

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 $\mu$s with the gate width of the boxcar averager fixed at 100 ns. All the spectra were recorded at a distance of 7 mm away from the target. Fig. 6.9 gives the change in band head intensity of CN molecules ($\Delta v = 0$) at different time delays for a laser power density of 35 GW cm$^{-2}$. The emission characteristics of the plasma varied with time as illustrated in fig. 6.9. Shortly after the plasma initiation, the dominant radiation was a continuum mixed with ionic lines. The continuum emission is due to Bremsstrahlung radiation and radiative recombination. Between 0.1 $\mu$s to 1 $\mu$s, both of these contributions decayed, leaving neutral lines and molecular bands which were seen up to 40 $\mu$s or longer. It has been observed that the individual emission lines from different atomic and ionic species are highly stark broadened [31] during the initial stages of the plasma due to high plasma electron densities. At later times greater than 2 $\mu$s, the spectrum is found to be dominated by CN violet system. It is to be noted that CN molecules are formed as a result of recombination.
Figure 6.10: Time dependence of vibrational temperature of CN molecule (laser irradiance 35 GW cm$^{-2}$, distance 7 mm)

Figure 6.11: Velocity distribution of CN molecules for $v = 0$ ($N_v$ number density)
of excited carbon species with ambient nitrogen present in the chamber as the hot plasma expands and cools. The time dependence of vibrational temperature is shown in fig. 6.10. As it is clear from the figure there is a maximum vibrational temperature \((19 \times 10^3 \text{ K})\) after an elapse of \(5 \mu \text{s}\) at a distance of \(7 \text{ mm}\) away from the target. For time intervals from 1 to \(5 \mu \text{s}\) the intensity of the CN band are found to be increasing and thereafter the intensity of the same decreases. Assuming that average temperature is proportional to vibrational temperature one can evaluate velocity distribution of CN molecules from fig. 6.11. The result of this calculation is given in fig. 6.11 which shows the variation in number density of CN molecules with velocity.

### 6.3.4 Effect of Laser Irradiance

The variation of vibrational temperature of CN molecules with laser irradiance at distances \(5\) and \(10 \text{ mm}\) from the target surface is given in fig. 6.12. Such variation of vibrational temperature with laser power density occurs essentially due to the fact that comparatively large number of molecules are excited into higher vibrational levels with increasing laser irradiance. At \(5 \text{ mm}\) axial distance from the target surface, the vibrational temperature increases rapidly till laser power density reaches \(60 \text{ GW cm}^{-2}\) and after that it shows saturation behaviour. The saturation in vibrational temperature at higher irradiance may be due to following reasons. At higher laser irradiance the plasma temperature is so high that collisional dissociation/ionization predominates over recombination causing a net decrease in de-excitation rate of population in the higher vibrational levels and by plasma shielding which is due to the change in efficiency of laser coupling to the target by increased absorption and/or reflection by the plasma itself [31,32]. At \(10 \text{ mm}\) distance from the target surface, a knee is found to occur in the curve showing variation of vibrational temperature at \(42 \text{ GW cm}^{-2}\). This suggests the onset of possible nonlinear interactions such as self-focusing of the laser beam within the plasma medium.

The self-focusing phenomenon of laser beams in plasma will occur if the Debye length \((\lambda_D)\) is less than the laser beam diameter. The Debye length which is the characteristic screening length of the plasma is given by [33,34],

\[
\lambda_D = \left( \frac{k_B T_e e_0}{n_e e^2} \right)^{1/2}
\]

where \(k_B\) is the Boltzmann constant, \(T_e\) is the equilibrium plasma temperature, \(n_e\) is the
Figure 6.12: The variation of vibrational temperature of the CN molecule with laser energy at distances (□) 5 mm, (○) 10 mm from the target.

equilibrium concentration, \( \epsilon_0 \) is the permittivity and \( e \) is the electron charge. At 10 mm radial distance from the target surface, using the relative line intensity measurements of the successive ionization stages of the carbon species (as mentioned in chapter 5), the estimated \( T_e \) and \( n_e \) are 19700 K and \( 9.6 \times 10^{16} \text{ cm}^{-3} \). Using these data, the Debye length is found to \( \lambda_D = 0.03 \text{ \mu m} \) which is much less than the estimated beam diameter (200 \( \mu \text{m} \)). Such self-focusing in the plasma leads to a higher effective power density resulting in an enhanced emission. Similar threshold like phenomenon is not perceptible at 5 mm radial distance from the target. Apparently this is due to the fact that a greater laser power density resulting from self-focusing due to large plasma density and temperature lead to a much lower value for this threshold.

### 6.3.5 Effect of Ambient Nitrogen

The emission characteristics of laser produced plasma are influenced to a large extend by the nature and composition of the surrounding atmosphere. A quantitative study of the effect of pressure on the relative intensities of the lines in the CN bands gives insight into the mechanism of formation of CN in its excited states and the mechanism
Figure 6.13: The change in vibrational temperature for CN molecules with respect to ambient nitrogen gas pressure inside the plasma chamber (distance 3 mm, 35 GW cm\(^{-2}\)) of collisional energy transfer [35-37]. The change in vibrational temperature for CN molecules with respect to ambient nitrogen gas pressure inside the plasma chamber is given in fig. 6.13 at a radial distance 3 mm away from the target and 3 \(\mu s\) after the irradiation at 35 GW cm\(^{-2}\). The vibrational temperature peaks at 0.08 mbar and then falls quickly with increase in pressure and finally levels off at slightly lower value for \(T_{\text{vib}}\). Highest rate of formation of excited CN molecules occur at 0.08 mbar pressure under the above conditions. It can be noted that at higher nitrogen pressure the confinement of the plasma takes place. There can be competing nonradiative de-excitation processes which will be predominant at higher pressure of nitrogen gas in the chamber. Thus competition with collisional de-excitation results in reduced vibrational temperature as seen in fig. 6.13.

6.3.6 Time of Flight Analysis

Time resolved studies on CN molecules were also made. In order to study the time evolution of a particular species produced by laser ablation, the characteristic lines were selected using the monochromator, and the PMT output with 50 \(\Omega\) termination was fed
to a 200 MHz digital storage oscilloscope. The experimental details of the time resolved studies are described in chapter 2. Typical time of flight pattern for CN molecules (selecting 388.3 nm corresponding to (0-0) transition of the CN violet system) is given in fig. 6.14. The CRO trace shows a sharp prompt emission and delayed emission peaking after few nanoseconds. The variation of measured time delay with distance from the target surface is given in fig. 6.15. These time delays can directly be converted into expansion velocities of these transient species and that is given in the right axis of fig. 6.15. From the figure it is clear that the time delays are found to increase with increase in distance from the target surface, while expansion velocities of CN molecules increasing up to a certain distances from the target surface 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 $2.14 \times 10^4$ K, which is much higher than the melting point of graphite ($4 \times 10^3$ K) [38]. 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 $2 \times 10^4$ K to $7 \times 10^4$ K at a laser irradiance.
Figure 6.15: The change in the time delay and expansion velocity of CN molecules (388.3 nm) as a function of distance from the target ($c - 73$ GW cm$^{-2}$) and $\Delta - 35$ GW cm$^{-2}$. The darked symbols correspond to expansion velocity of 73 GW 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.

6.4 Conclusions

Q-switched Nd:YAG laser ablation of graphite target in partial vacuum conditions 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. Extensive studies on the time and space resolved emission characteristics have been carried out. These investigations demonstrate that the emission intensities from CN species are sensitive to laser power density, pressure of the background gas, time after the elapse of laser pulse and spatial separation from the target. At low laser irradiance the emission bands due to $C_2$ and
CN predominates while at higher irradiance the multiply ionized species up to C IV have been observed along with CN and C\textsubscript{2} species.

The vibrational temperature is found to increase with increase in laser power density and saturates at higher power levels. The saturation of vibrational temperature at higher power density is due to depletion of excited state population of CN molecules and by plasma shielding. The nonlinear interactions between the laser and the plasma give rise to phenomenon such as self-focusing which exhibit threshold-like behaviour. It is noted that the vibrational temperature of the CN molecules varies with the position of the sampled volume within the plasma plume, integration time after the elapse of laser pulse and ambient gas pressure inside the plasma chamber.
6.5 References


[31] See Chapter 5.


