Spectral Characteristics of Laser-Induced Graphite Plasma in Ambient Air*

WANG Jinmei (王金梅)1,3, ZHENG Peichao (郑培超)2,3, LIU Hongdi (刘红弟)3, FANG Liang (方亮)1

1State Key Laboratory of Mechanical Transmission, College of Physics, Chongqing University, Chongqing 400044, China
2State Key Laboratory of Power Transmission Equipment & System Security and New Technology, Chongqing University, Chongqing 400044, China
3College of Optoelectronic Engineering, Chongqing University of Posts and Telecommunications, Chongqing 400065, China

Abstract An experimental setup of laser-induced graphite plasma was built and the spectral characteristics and properties of graphite plasma were studied. From the temporal behavior of graphite plasma, the duration of CN partials (B^2∑_u^+ → X^2∑_g^+) emission was two times longer than that of atomic carbon, and all intensities reached the maximum during the early stage from 0.2 µs to 0.8 µs. The electron temperature decreased from 11807 K to 8755 K, the vibration temperature decreased from 8973 K to 6472 K, and the rotational temperature decreased from 7288 K to 4491 K with the delay time, respectively. The effect of the laser energy was also studied, and it was found that the thresholds and spectral characteristics of CN molecular and C atomic spectroscopy presented great differences. At lower laser energies, the electron excited temperature, the electron density, the vibrational temperature and rotational temperature of CN partials increased rapidly. At higher laser energies, the increasing of electron excited temperature and electron density slow down, and the vibrational temperature and rotational temperature even trend to saturation due to plasma shielding and dissociation of CN molecules. The relationship among the three kinds of temperatures was \( T_{\text{elec}} > T_{\text{vib}} > T_{\text{rot}} \) at the same time. The electron density of the graphite plasma was in the order of \( 10^{17} \text{ cm}^{-3} \) and \( 10^{18} \text{ cm}^{-3} \).

Keywords: laser induced plasma, graphite, plasma parameters, emission spectroscopy

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(Some figures may appear in colour only in the online journal)

1 Introduction

In the pass several decays, laser-induced plasma has attracted a great deal of interest of the researchers in the world [1–3]. A sample is focused by a pulsed laser, and heated by the laser energy and a small portion in the sample is evaporated, and then a plasma is produced [4–7].

In the material science, the thin film preparation using a laser-induced plasma is a well-established technique, and some researchers have engaged in the corresponding research and have made some achievements [8,9]. Ablation of graphite by a pulsed laser is deemed to be an effective method for the deposition of the diamond-like carbon (DLC) thin films. Ruiz et al. presented observed results of time-resolved and space-resolved spectroscopy in the laser-induced graphite plasma under the background of argon [10]. By filtering the emission wavelength of graphite plasma, and the imaging with 20 ns time resolution was used to investigate the dynamic behavior of the expanding plasma. It was found that the graphite emission evolves from the carbon atom to C_2 and C_3 molecular bands dominated, and the temporal evolution and spatial features of the molecular carbon species depend on the argon pressure. Dong et al. analyzed the characteristics of laser induced plasma for the four solid materials (including the graphite, urea, coal and P-Aminobenzene sulfonic acid anhydrous) under air and argon [11]. It was found that the characteristics of C_2 emission and C I (the neutral atomic carbon emission) was similar. However, the emission behavior of CN

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bands had a big relation with CN partials. Al-Shboul et al. investigated the influence of helium on the behavior of \( \text{C}_2 \) formation \cite{12}. The results indicated that the pressure of the helium had a great influence on the formation of \( \text{C}_2 \). In a vacuum, the \( \text{C}_2 \) emission was located near the target. With increasing the pressure of the helium, the intensities of \( \text{C}_2 \) emissions were observed in axial and radial directions. Obviously, current researches about diamond-like carbon film deposited are focused on the formation mechanism of carbon molecular and its influencing factors.

In addition, for the ability to synthesis carbon nanotubes and carbon nanowire structure material, researches on laser-induced carbon plasmas attract a great deal of attention. For example, laser ablated graphite plasmas have been extensively studied for the production of carbon clusters. Furthermore, laser ablation is used as a convenient method to produce \( \text{C}_{60} \) and higher fullerenes. Despite considerable experimental and theoretical progress, the characteristics of laser-induced graphite plasma do not clear on the cluster formation, many factors greatly affect the characteristics, which have not been understood yet. Rusak et al. employed a Nd:YAG laser at 1064 nm and a XeCl laser at 308 nm to form laser-induced graphite plasma, and the vibrational, rotational and excitation temperatures were determined \cite{13}, while the electron number density and the total atomic numbers are not presented. Though some achievements have been made, there are still some inherent mechanisms and the influencing factors still need further study. Much more efforts should be paid to further investigate the characteristics of the laser-induced graphite plasmas in order to obtain carbon nano-materials with high quality.

In this paper, a spectrometer with high resolution and a Nd:YAG laser were employed to study the spectral characteristics and plasma parameters of laser-induced graphite plasma. The plasma properties including electron number density, electron excited temperature, vibrational temperature, rotational temperature and total atomic numbers were described on the temporal behavior. Besides, the effects of laser energy were also evaluated.

### 3 Results and discussion

#### 3.1 Spectral characteristics of atomic and molecular carbon

Fig. 2 shows the ultraviolet and visible band emission spectrum. The spectral lines of Fe, Mg and Ca, etc. appeared for the primary element of C emission, which are from the impurities in the graphite samples. Although there is no CN radical in the target, the emission spectrum of the CN violet band can be obviously observed. Some references have reported the formation of CN molecules in laser ablation of graphite and the CN emission would be formed from the following recombination reactions \cite{15-17}:

\[
\begin{align*}
\text{C} + \text{N}_2 & \rightarrow \text{CN} + \text{N} \quad (1) \\
\text{C}_2 + \text{N}_2 & \rightarrow 2\text{CN} \quad (2)
\end{align*}
\]

![Fig.2 Emission spectrum of laser induced graphite plasma (240 nm to 520 nm)](image)

The atomic, ionic and molecular species of the carbon eject from the target resulting in the formation of CN molecules. Among the emission spectra, the molecular \( \text{C}_2 \) emission from the Swan system (\( \text{d}^3\Pi_g \rightarrow \text{a}^3\Pi_u \)) and CN from the violet system (\( B^2 \sum^+ \rightarrow X^2 \sum^+ \)) is significant. The 2400 grooves/mm grating (0.03 nm resolution) was employed detector. An ICCD gate width of 200 ns was selected to obtain all spectra. Ambient gas is very important for the atomic and molecular emission \cite{14}, and the open air was selected as the working gas in this experiments. The sample was also polished in the experiment.
for collecting the scattering light, and the vibrational and rotational spectra of the CN violet band were resolved. Fig. 3 offers a typical CN molecular emission spectrum of $B^2 \Sigma^+ \rightarrow X^2 \Sigma^+$ for the $\Delta \nu = 0$ sequence. It shows that the emission band heads of CN including $0-0$ (388.43 nm), $1-1$ (387.14 nm), $2-2$ (386.19 nm), $3-3$ (385.47 nm) and $4-4$ (385.09 nm) are relatively significant in the spectra.

Fig.3 ECN($B^2 \Sigma^+ \rightarrow X^2 \Sigma^+$) emission for $\Delta \nu = 0$

### 3.2 Time-resolved analysis of emission spectra and properties of graphite plasma

Actually, there are many differences between atomic spectroscopy and molecular spectroscopy. In order to understand the differences, the temporal evolutions of emission intensities for atomic carbon and molecular CN were investigated from 200 ns with a step of 200 ns for the delay time. The laser energy of 50 mJ was selected, and the intensities of five transitions of CN and one transition of atomic carbon versus delay time are illustrated in Fig. 4 and Fig. 5.

As indicated in Fig. 4 and Fig. 5, the emissions of the transitions of CN and carbon present a similar trend, firstly increase to a maximum during the early stage from 0.2 $\mu$s to 0.8 $\mu$s, and decrease rapidly afterwards. While the durations of the molecular CN emission and atomic carbon emission are different, the former (30 $\mu$s) is almost three times of the latter (10 $\mu$s). One possible reason for this behavior is that the lifetime for CN molecular emission is longer than carbon atomic emission due to the molecular vibration and rotation relaxation. In addition, the wavelength of the carbon (C I 247.85 nm) is in the ultraviolet band, and the absorption effect by the ambient air is stronger than the CN emission, which is near the visible bands.

Plasma temperature is very important for understanding the plasma excitation characteristics. The atomic emission intensity $I_{mn}$ is associated with the population of the element. Local thermodynamic equilibrium (LTE) was assumed when measuring the electron temperature, the population of an excited level related to a neutral atom or ion according to Boltzmann’s law [14]:

$$I_{mn} = \frac{hc}{4\pi \lambda_{mn}} \frac{N(T)}{U(T)} g_m A_{mn} \exp \left(-\frac{E_m}{kT}\right), \quad (3)$$

where $k$ is the Boltzmann constant, and $h$ is the Plank constant. $N(T)$ and $U(T)$ mean the total density and partition function. $I_{mn}$ is the intensity of the transition from the upper level ($m$) to lower level ($n$), $\lambda_{mn}$ and $A_{mn}$ are the transition wavelength and transition probability, respectively. $g_m$ and $E_m$ are the statistical weight of level ($m$) and the energy of the upper level, respectively. $T$ is the electron temperature, which can be calculated from the intensities of spectral lines [18–20], as shown in the following formula:

$$\ln \frac{I_{mn} \lambda_{mn}}{g_m A_{mn}} = \frac{-E_m}{kT} + \ln \left(\frac{hc}{4\pi} \frac{N(T)}{U(T)}\right). \quad (4)$$

Eq. (4) leads to a liner plot of $\ln \left[\frac{\lambda_{mn}I_{mn}}{(A_m g_m)}\right]$ versus the term energy $E_m$, and the electron temperature can be calculated from the slope of the fitting line.

In this work, the five Ca II lines were used to calculate the electron temperature. A typical spectrum of laser-induced graphite plasma is illustrated in Fig. 6, and the spectroscopic data for electron temperature calculation are listed in Table 1 [21]. The Boltzmann plot obtained from Ca ionic lines is shown in Fig. 7.
Table 1. Spectroscopic parameters of Ca II lines

<table>
<thead>
<tr>
<th>Wavelength $\lambda_{mn}$ (nm)</th>
<th>Transition</th>
<th>Statistical weight $g_m$</th>
<th>Transition probability $A_{mn}$ (s$^{-1}$)</th>
<th>Energy (eV) $E_m$, $E_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 317.93</td>
<td>$3p^54d^2D_{3/2} \rightarrow 3p^54p^2P^0_{1/2}$</td>
<td>6</td>
<td>$3.60 \times 10^9$</td>
<td>7.049150, 3.150984</td>
</tr>
<tr>
<td>2 370.60</td>
<td>$3p^65s^2S_{1/2} \rightarrow 3p^64p^2P^0_{1/2}$</td>
<td>2</td>
<td>$8.80 \times 10^9$</td>
<td>6.467875, 3.123349</td>
</tr>
<tr>
<td>3 373.69</td>
<td>$3p^65p^2S_{1/2} \rightarrow 3p^64s^2P^0_{1/2}$</td>
<td>2</td>
<td>$1.70 \times 10^9$</td>
<td>6.150984, 0</td>
</tr>
<tr>
<td>4 393.37</td>
<td>$3p^64p^2P^0_{1/2} \rightarrow 3p^64s^2S_{1/2}$</td>
<td>4</td>
<td>$1.47 \times 10^9$</td>
<td>3.150984, 0</td>
</tr>
<tr>
<td>5 396.85</td>
<td>$3p^64p^2P^0_{1/2} \rightarrow 3p^64s^2S_{1/2}$</td>
<td>2</td>
<td>$1.40 \times 10^9$</td>
<td>3.123349, 0</td>
</tr>
</tbody>
</table>

During the temporal evolution of graphite plasma, the electron density is a crucial parameter for the plasma physical condition. The electron density can be determined from the Stark broadening of an isolated line. The full width at half maximum (FWHM) $\Delta \lambda_{1/2}$ of a line is as follows \cite{22}:

$$\Delta \lambda_{1/2} = 2\omega \left( \frac{N_e}{10^{16}} \right) ,$$

where $N_e$ is the electron number density. The electron number density ($N_e$) can be obtained from the FWHM of Stark broadening of the spectral line. In our work, Ca II 393.37 nm was selected for the calculation. The values of $\omega$ corresponding to different electron temperatures are shown in Ref. \cite{23}.

Fig. 6 shows the temporal evolutions of the electron temperature and electron density. The electron temperature decreases from 11807 K to 8757 K when the delay time ranges from 200 ns to 6 $\mu$s, and then decreases rapidly at the early stage and slows down afterwards. Electron density is in the order of $10^{18}$ cm$^{-3}$, and decreasing with the delay time to $10^{17}$ cm$^{-3}$. The results indicate that the expansion velocity and the rate of temperature change are different at different stages during the lifetime of the plasma. At the early stage, the temperature decreases rapidly due to the expansion of the plasma.

According to the theory of molecular spectroscopy, the distribution of molecular emission intensity is determined by the molecular structure and the degrees of freedom for temperature. For a specific molecule, the distribution of molecular emission intensity is merely determined by the degree of freedom for each temperature. Therefore, the vibrational temperature and rotational temperature can be obtained through analyzing the distribution of molecular emission intensity \cite{24}. The emission intensity of the molecular band is obtained by the formula:

$$I_{\nu',J'}^{\nu,J} = A_{\nu',J',\nu,J}^\nu N_{\nu',J'} h c \nu_{\nu',J'} ,$$

where $\nu'$ and $\nu$ represent high and low energy level, respectively. $A_{\nu',J',\nu,J}^\nu$ is the Einstein transition probability, $N_{\nu',J'}$ is the number of molecules at the high energy level, $\nu_{\nu',J'}$ is the wave number of transition, $c$ is the velocity of light in a vacuum and $h$ is the Plank constant. The population of the energy levels for a particular species is governed by the Boltzmann
distribution, and the \( N_{\nu', J'} \) can be expressed as:

\[
N_{\nu', J'} = \frac{N_0 g_e}{Q_{\text{elec}}(T_{\text{elec}}) Q_{\text{vib}}(T_{\text{vib}}) Q_{\text{rot}}(T_{\text{rot}})} \times \exp \left( \frac{-E_{\text{elec}}}{kT_{\text{elec}}} \right) \times \exp \left( \frac{-E_{\text{vib}}}{kT_{\text{vib}}} \right) \times (2J' + 1) \times \exp \left( \frac{-E_{\text{rot}}}{kT_{\text{rot}}} \right),
\]

where \( Q_{\text{elec}}(T_{\text{elec}}) \), \( Q_{\text{vib}}(T_{\text{vib}}) \) and \( Q_{\text{rot}}(T_{\text{rot}}) \) are the electronic, vibrational and rotational partition functions, respectively. \( N_0 \) is the total number of molecules, \( g_e \) is the degeneracy of electron, \( T_{\text{elec}}, T_{\text{vib}} \) and \( T_{\text{rot}} \) are electron temperature, vibrational temperature and rotational temperature, respectively. \( E_{\text{elec}}, E_{\text{vib}} \) and \( E_{\text{rot}} \) are electronic, vibrational and rotational energy, respectively.

![Simulation of CN violet system (\( B^2 \Sigma^+ \rightarrow X^2 \Sigma^+ \)) by LIFBASE software package](image)

Fig.9 Simulation of CN violet system (\( B^2 \Sigma^+ \rightarrow X^2 \Sigma^+ \)) by LIFBASE software package

![Temporal evolution of molecular CN band vibrational temperature and rotational temperature](image)

Fig.10 Temporal evolution of molecular CN band vibrational temperature and rotational temperature

In our work, the vibrational temperature and rotational temperature were measured by the simulation of the CN violet system (\( B^2 \Sigma^+ \rightarrow X^2 \Sigma^+ \)) under the assistance of the LIFBASE software package. The software package provides the parameters such as the Einstein emission and absorption coefficients, lifetime, transition probability, frequency and Hönl–London factors etc. The other parameters for the simulation were set according to the actual situation. Fig. 9 shows the simulation result of the CN violet system (\( B^2 \Sigma^+ \rightarrow X^2 \Sigma^+ \)) at the delay time of 2 \( \mu \)s and 50 mJ laser energy. The vibrational temperature and rotational temperature are 6914 K and 6130 K, respectively. By the simulation of the CN violet system (\( B^2 \Sigma^+ \rightarrow X^2 \Sigma^+ \)) at different delay times, it is easy to obtain the temporal variation of the vibration temperature and rotational temperature. As indicated in Fig. 10, the vibrational temperature decreases from 9873 K to 6472 K, and the rotational temperature decreases from 7288 K to 4491 K with the delay time, which are similar with the trend of the electron temperature. While the order of the three temperatures is \( T_{\text{elec}} > T_{\text{vib}} > T_{\text{rot}} \) at the same time. According to the theory of molecular spectra, if the ultraviolet and visible emission is significant, the transitions between the electronic states of the molecules dominate.

Meanwhile there are some vibrational energy levels on each electronic energy level, therefore the vibrational states transitions exist in the electronic energy levels. Meanwhile the rotational energy levels exist due to the rotation of the molecule all the time [25].

### 3.3 Effects of the energy of laser

The energy of laser is provided directly by the pulsed laser, and it undoubtedly affects the properties of the graphite plasma. It is essential to study the properties of the carbon plasma effected by the laser energy. In order to obtain an excellent signal to background ratio, the experiment was carried out at the delay time of 2 \( \mu \)s with different laser energy. Fig. 9 and Fig. 10 depict the emission intensities of the CN (\( B^2 \Sigma^+ \rightarrow X^2 \Sigma^+ \)) band and C I 247.85 nm dependence on the energy of the laser. As shown in Fig. 11, the energy of the laser threshold of molecular CN emission is about 5 mJ. When increasing the energy of laser from 5 mJ to 10 mJ, the emission intensity of the CN (\( B^2 \Sigma^+ \rightarrow X^2 \Sigma^+ \)) band for \( \Delta \nu=0 \) increases rapidly. Further increasing the laser energy, the emission intensity changes slowly, and decreases afterwards when it is above 90 mJ. The results may essentially be due to the fact that comparative numbers of molecules are excited to higher vibrational and rotational levels with increasing laser energy when it is below 10 mJ, and a higher laser energy input in the plasma plume disassociates some of the CN molecules and prevents the formation of stable CN molecules. While Fig. 12 shows that the laser energy threshold of C I 247.85 nm is almost 12 mJ, and the emission intensity keeps growing in the whole laser energy range. By increasing the laser energy from 12 mJ to 100 mJ, more and more atomic carbons are excited to higher electronic levels, which lead to almost linear increasing of the emission intensity.

The electron temperature and electron density at different laser energy are displayed in Fig. 13. When the energy of the laser is less than 30 mJ, the electron temperature increases almost linearly with the
laser energy. At higher laser energies, the electron temperature and electron density increase very slowly and even trend to saturation. As shown in Fig. 13, the electron temperature varies from 7462 K to 10124 K, and the electron density varies between $8.9 \times 10^{17} \text{ cm}^{-3}$ and $9.65 \times 10^{17} \text{ cm}^{-3}$ for the energy of laser range from 10 mJ to 100 mJ.

![Fig.11 Variation of the emission intensity of the CN(B2∑+ → X2∑+) band for ∆ν=0 with the laser energy](image1)

![Fig.12 Variation of the emission intensity of CI 247.85 nm with the laser energy](image2)

![Fig.13 Dependence of the electron temperature and electron density on the energy of the laser](image3)

Since the vibrational and rotational energies of CN molecules are directly supplied by the laser energy, the vibrational and rotational states will undoubtedly change under different laser energy. The variations of the vibrational and rotational temperatures with laser energy are shown in Fig. 14. The vibrational and rotational temperatures increase rapidly for the laser energy from 6.5 mJ to 10 mJ due to the larger number of molecules stimulated by the higher energy of laser. When further increasing the laser energy, they increase extremely slow and even trend to saturation. The order of the temperatures is also $T_{\text{elec}} > T_{\text{vib}} > T_{\text{rot}}$ at the same time. Combine these results with those of Fig. 11, it is reasonable to refer that reactions (1) and (2) are energetic for the energy of laser from 6.5 mJ to 10 mJ, and the vibrational and rotational temperatures increase rapidly. When the energy of laser is above 10 mJ, the CN molecules is beginning to disassociate, and the plasma needs more energy to be sustained. Besides the amount of nitrogen, contact with the plasma is limited, the emission intensity, vibrational and rotational temperature increase slowly and even trend to saturation.

![Fig.14 Behavior of the vibrational temperature and rotational temperature of molecular CN band with the laser energy](image4)

### 3.4 Total atomic carbon number

In the plasma system, the effect of the plasma parameters on the spectral emission can be estimated by the total atomic number $N(T)$. According to Eq. (1), the qualitative formula of $N(T)$ is obtained by:

$$N(T) \propto I_{\text{mn}} U(T) / \exp\left(-\frac{E_m}{kT}\right).$$

The $U(T)$ of C I can be obtained from Ref. [26].

The temporal behavior and the influence of the energy of the laser for the total atomic number of carbon are illustrated in Fig. 15 and Fig. 16. The total atomic carbon number grows to the maximum at the early stage and decreases rapidly afterwards with a different delay time. Fig. 16 displays that the total atomic carbon number increases with the energy of the laser range. Again, these data support the phenomena and conclusions discussed above.
4 Conclusion

Spectral characteristics have been carried out on the laser induced graphite plasma. It was found that the properties of the graphite plasma are sensitive to the energy of the laser and the time after elapse of the energy of the laser. The duration of CN partials \((B^2 \sum^+ \rightarrow X^2 \sum^+)\) emission was two times longer than that of the carbon atom during the temporal evolution of carbon plasma, and all the emission intensities reached the maximum during the early stage from 0.2 \(\mu\)s to 0.8 \(\mu\)s. The electron temperature decreased from 11807 K to 8755 K, the vibration temperature decreased from 8973 K to 6472 K, and the rotational temperature decreased from 7288 K to 4491 K with the delay time, respectively. The influence of the energy of laser indicated that the thresholds and spectral characteristics of CN molecular and C atomic spectroscopy presented great differences. At lower laser energies, the plasma parameters of CN partials increased rapidly. While at higher laser energies, the plasma parameters almost trend to saturation due to the disassociation of CN molecules. The order among the three kinds of temperature was \(T_{\text{elec}} > T_{\text{vib}} > T_{\text{rot}}\) at the same time. The electron density was in the order of \(10^{17} \text{ cm}^{-3}\) and \(10^{18} \text{ cm}^{-3}\).

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E-mail address of corresponding author Fang Liang: lfang@cqu.edu.cn