

# Time Resolved Luminescence Spectroscopic Analysis in Plasma Switching by Laser Ablation of the Gaseous Cu-CF<sub>4</sub> System

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**Abstract** Plasma switching by laser ablation (PLASLA) is the phenomenon that, in a lower electric field, laser ablation forms the pulse plasma whose on-off timing completely synchronizes with the laser ablation, discovered by us in the gaseous reaction system of laser ablated Cu and CF<sub>4</sub> and considered promising for materials science, as reported previously. Here we study the chemical processes of PLASLA by measuring the time-resolved luminescence spectra as well as the dc-plasma luminescence spectra. It is found that the PLASLA spectrum at 0.5 μs after the laser ablation is quite different from the spectra at 8 μs and 0.25 ms, which are found to be essentially the same as the CuF chemiluminescence spectrum of the gaseous reaction of CF<sub>4</sub> with laser ablated Cu, suggesting that PLASLA has the specific initial processes and the reaction system changes toward the one rather similar to the chemiluminescent reaction system. The analysis of the complicated spectrum at 0.5 μs finds that it is composed of the bands assigned to C, C<sup>+</sup>, C<sup>2+</sup>, C<sub>2</sub>, CuF, Cu, Cu<sub>2</sub>, N<sub>2</sub>, and N<sub>2</sub><sup>+</sup>, suggesting that the product materials of PLASLA are carbon polymers, which agrees with the conclusion from our previous time-of-flight mass spectrometric study. The fact that the CuF luminescence is due to only the singlet states at 0.5 μs and both the singlet and triplet states at 8 μs and 0.25 ms significantly indicates that CuF is formed by Cu<sup>+</sup> and CF<sub>4</sub> through only the singlet-spin-states reaction coordinates at 0.5 μs by keeping the strict spin conservation, which is broken by the relaxation processes after that. The fact that the spin conservation like this is broken through the spin-states mixing by a magnetic field has already been reported by our previous paper on the CuF-chemiluminescence reaction of CF<sub>4</sub> with laser ablated Cu.

**Keywords:** CuF, laser ablation, plasma, spectroscopy, luminescence, PLASLA, spin chemistry

## 1. Introduction

Plasma is a significant tool for materials science, making plasma etching and preparing various functional films and new materials through CVD (chemical vapour deposition) [1,2,3,4]. The fine control of plasma is consequently becoming more and more important. For instance, while plasma has been generally generated by the direct dc-discharge of sample gases, we recently have reported a new promising method called PLASLA, i.e., plasma switching by laser ablation [5-10], where laser-ablated metals induce the switched plasma in a CF<sub>4</sub> sample gas. In PLASLA, the *pulse* plasma in the CF<sub>4</sub> gas is generated with the complete synchronization with the laser ablation of metals under the *milder condition*, i.e., at the lower potential between the electrodes in comparison with that for the direct dc-discharge. These properties of PLASLA suggest the following potential for controlling the plasma-utilized chemical reactions. First, the appropriate timing assembly between the ablation laser and the laser for photochemical reactions will dramatically enhance the ability of the plasma chemistry to control the preparation of materials. Second, the discharge under the

milder condition is evidently effective for preparing very delicate materials. Furthermore, while the direct discharge is very sensitive to the impurity gas, we can avoid the interference with it in PLASLA, i.e., the reactant gas, e.g. CF<sub>4</sub>, can be discharged in PLASLA even in the reaction system, where the impurity gas with the lower ionization potential, e.g. N<sub>2</sub>, is discharged instead of the reactant CF<sub>4</sub> gas in the directly discharged plasma [5]. Thus PLASLA can be regarded as the promising, new metal catalytic reaction for preparing the new interesting functional materials, and hence the basic study on PLASLA is of great interest.

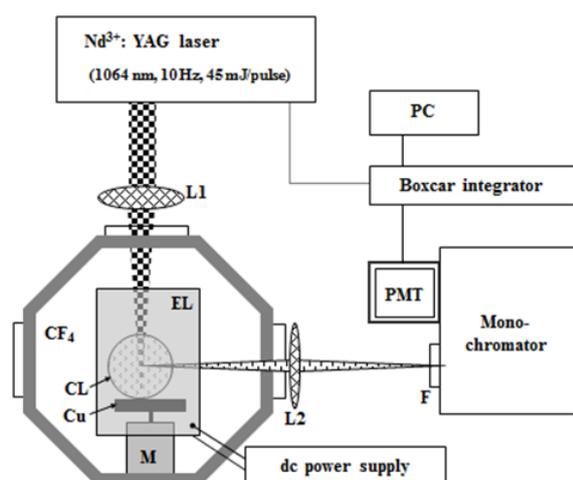
Since the discovery of PLASLA, we have studied the properties and the mechanism of PLASLA in the CF<sub>4</sub> gas system with various laser-ablation target metals [5,9]. As a result, it is found that the metals can be classified into three groups by their electronic configurations. For instance, it is found that the stability of PLASLA depends on the groups of metals. Namely, for instance, the PLASLA potential, at which the stable PLASLA is formed and which is in the very narrow range, i.e., typically ±1 V, depends on the groups of metals [5]. The PLASLA formation rate and the extinction time also depend on the groups of metals as well [5,9]. The product materials and their amounts also depend on the groups of

metals as well [5,9]. It is also found that the spatial distribution of the PLASLA luminescence around and between electrodes depends on the groups of metals [9]. Furthermore, the study on the temporal waves in PLASLA indicates that the front wave is formed just after the laser ablation, and then the stimulated wave is formed, and finally they become the united wave [9]. Besides, we also studied PLASLA in a magnetic field and found the magnetic field effects on PLASLA, which are due to the effects through MHD (magnetic hydrodynamics) such as  $E \times B$  drifts and cyclotron circulations and the effects on the chemical processes through singlet-triplet mixing [5].

Following these previous investigations, here we study PLASLA in a gaseous Cu-CF<sub>4</sub> reaction system through the spectroscopic analysis of the time-resolved luminescence spectra of PLASLA, focusing on the chemical processes of PLASLA. Using CF<sub>4</sub> as the reactant in the present study is due to the fact that it is regarded as the excellent source for the carbon materials through plasma reactions: Carbon materials are more and more significant for us.

## 2. Experimental

The present experimental system is schematically shown in Figure 1. A fundamental beam (1.064 μm in wavelength, 45 mJ/pulse in power, 10 Hz in repetition rate) of a Nd<sup>3+</sup>:YAG laser (Quanta-Ray DCR-2) was focused onto a Cu target (Nilaco, 10 mm x 10 mm x 1 mm, 99.9 % in purity), which is denoted by Cu in Figure 1 and was set as a target for laser ablation in a reaction chamber (the octagonal aluminum one with 70 mm in side and 200 mm in height), with use of a quartz lens (50 mmφ,  $f=300$  mm), which is denoted by L1 in Figure 1. The target was spun with a motor (M in Figure 1) for constant ablation. In the reaction chamber, a reactant CF<sub>4</sub> gas (Nihon Sanso, 99.999 % in purity) slowly flowed at a pressure of 0.2-0.5 Torr.



**Figure 1.** Experimental system. L1 and L2: lenses, EL: Cu-plate electrodes, CL: chemiluminescence, M: motor, Cu: Cu target, PC: personal computer, PMT: photomultiplier, F: filters.

Two copper plates (50 mm x 18 mm x 1 mm for each), which are denoted by EL in Figure 1, were placed in parallel at a distance of 35 mm at the reaction site in the reaction chamber. Potential of 0-500 V was supplied

between the electrodes with a power supplier (FLUKE 408B-874).

The PLASLA luminescence and the chemiluminescence, which is indicated by a shaded circle denoted by C.L. in Figure 1, in the reaction chamber were focused into a monochromator (JobinYvon HR-1000 with a 2000-lines/mm holographic grating) with use of a quartz lens (denoted by L2 in Figure 1, 50 mmφ,  $f=62.5$  mm). The output of the monochromator was detected with a μ-metal shielded photomultiplier (Hamamatsu Photonics 1P28), which is denoted by PMT in Figure 1. The signal from the photomultiplier was processed with use of a boxcar integrator (Princeton Applied Research model 162) for measuring the time-resolved luminescence spectra. The output signal from the instrument was processed with a personal computer system.

The observed spectral lines and bands were assigned by calculating the theoretical line and band positions [11,12]:

$$\begin{aligned} \nu &= \nu' - \nu'' \\ &= T' - T'' + \left\{ \omega'(v' + \frac{1}{2}) - \omega'\chi'(v' + \frac{1}{2})^2 \right\} \\ &\quad - \left\{ \omega''(v'' + \frac{1}{2}) - \omega''\chi''(v'' + \frac{1}{2})^2 \right\} \end{aligned} \quad (1)$$

For molecules, Equation (1) was used with vibrational quantum numbers  $v'$  and  $v''$ . In the equation,  $\nu$  denotes the line and band positions and equals the energy differences between the excited vibronic states and the ground vibronic states, i.e.,  $\nu = \nu' - \nu''$ . The prime and the double prime indicate the excited state and the ground state, respectively. The electronic energy, the harmonic vibrational constants, and the anharmonic vibrational constants are denoted by  $T$ ,  $\omega$ , and  $\omega\chi$ , respectively. We referred to Herzberg's books for these constants of species for the assignment [11,12]. We also referred to Moore's book for calculating the atomic line positions [13].

## 3. Results and Discussion

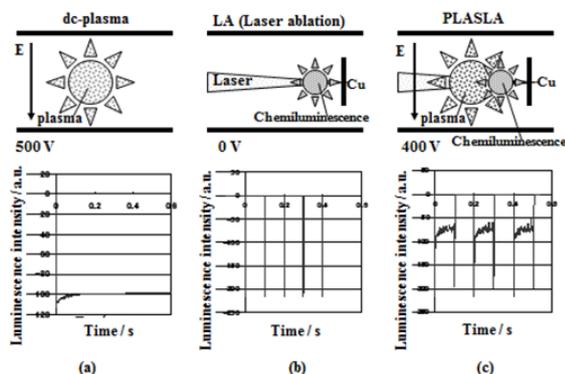
### 3.1. PLASLA, dc-Plasma, LA (Laser Ablation)

As schematically shown on the upper panel in Figure 2a, the direct-current electric field supplied between the parallel Cu plate electrodes generates dc-plasma (direct-current plasma) at a potential of 500 V in a reaction chamber filled with CF<sub>4</sub> at a pressure of 0.2 Torr. In dc-plasma, as the oscilloscope trace on the lower panel in Figure 2a shows, the plasma luminescence intensity continues invariably in the presence of the constant electric field.

In the absence of an electric field, the irradiation of a spinning Cu target with the fundamental beam of a Nd<sup>3+</sup>:YAG laser (1.064 μm in wavelength, 45 mJ/pulse in power, 10 Hz in repetition rate) brings about the laser ablation of Cu, as schematically shown on the upper panel in Figure 2b, generating the pulsing luminescence of CuF and Cu, as the oscilloscope trace on the lower panel in Figure 2b shows.

As schematically shown on the upper panel in Figure 2c, with the laser ablation, after increasing a direct-current electric field between the parallel Cu plates, stable PLASLA is formed at an electric field of 400 V, which is inadequate to generate dc-plasma. The oscilloscope trace of PLASLA on the lower panel in Figure 2c indicates that

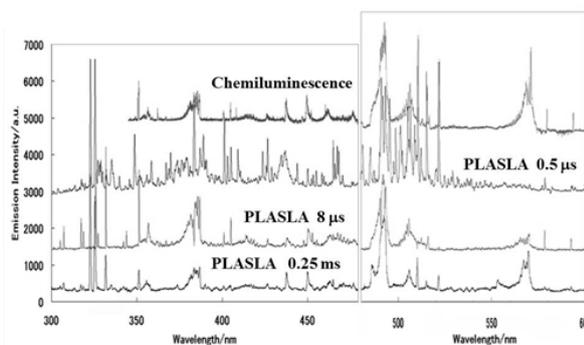
plasma is formed by the first laser ablation, quenched by the next ablation, formed again by the third ablation, quenched again by the fourth ablation, and so on, indicating that the PLASLA formation and quenching completely synchronizes with the laser ablation.



**Figure 2.** Schematic diagrams of experimental systems and oscilloscope trace signals of (a) dc-plasma, (b) LA (laser ablation), and (c) PLASLA

### 3.2. Time-Resolved Spectra of PLASLA

The time-resolved luminescence spectra of PLASLA at delays of 0.5  $\mu$ s, 8  $\mu$ s, and 0.25 ms in a wavelength range of 300-600 nm are shown in Figure 3, as well as the chemiluminescence spectrum, which was observed by the gaseous reaction of  $\text{CF}_4$  with laser-ablated Cu, on the top of the figure. While the spectra at the delays of 8  $\mu$ s and 0.25 ms are similar to the chemiluminescence spectrum, the spectrum at 0.5  $\mu$ s is fairly different from them. Furthermore, all these spectra are found to be quite different from that of the dc-plasma, which was observed with the present experimental system, as discussed in Sec. 3.4.



**Figure 3.** The time-resolved luminescence spectra of PLASLA at 0.5  $\mu$ s, 8  $\mu$ s, and 0.25 ms of delay with the chemiluminescence spectrum

Figure 3 indicates that the spectra at 8  $\mu$ s and 0.25 ms, as similarly in the chemiluminescence spectrum, consist of the CuF luminescence bands, which are assigned to the sequences of  $c^3\Delta-X^1\Sigma^+$  at 390 nm,  $C^1\Pi-X^1\Sigma^+$  at 490 nm,  $B^1\Sigma^+-X^1\Sigma^+$  at 510 nm, and  $b^3\Pi-X^1\Sigma^+$  at 570 nm and to the  $D^1\Delta-X^1\Sigma^+$  band around 450 nm, and Cu luminescence lines. While the spectra at 8  $\mu$ s and 0.25 ms are similar to each other and to the chemiluminescence spectrum thus, some small differences can be found in these spectra. First, the intensity of the Cu luminescence lines in the spectrum at 8  $\mu$ s is rather stronger than that at 0.25 ms: This fact will be due to the fact that the Cu atoms in the excited states are generated by laser ablation. Furthermore, the relative intensity among the CuF luminescence bands in the spectrum at 8  $\mu$ s is different from that at 0.25 ms. For instance, the  $c^3\Delta-X^1\Sigma^+$  band at 390 nm and the  $B^1\Sigma^+-X^1\Sigma^+$  band at 510 nm are strong

rather in the spectrum at 8  $\mu$ s, while the  $C^1\Pi-X^1\Sigma^+$  band at 490 nm, the  $b^3\Pi-X^1\Sigma^+$  band, and the  $D^1\Delta-X^1\Sigma^+$  band around 450 nm are strong rather in the spectrum at 0.25 ms. These facts indicate that the CuF molecules in the c-state and the B-state are more formed rather in the early stage and the ones in the C-state, the D-state, and the b-state are more formed rather in the late stage. Hence it is suggested that CuF in the higher triplet state is initially formed and relaxes to the lower triplet state, while CuF in the lower singlet state is initially formed and CuF in the higher singlet states is formed after that, probably through the reactions. Furthermore, it is found that the CuF chemiluminescence spectrum is rather closer to the spectrum at 8  $\mu$ s than the spectrum at 0.25 ms.

### 3.3. Analysis of PLASLA Luminescence Spectrum at 0.5 $\mu$ s

#### 3.3.1. $D^1\Delta-X^1\Sigma^+$ Band of CuF in PLASLA Spectrum

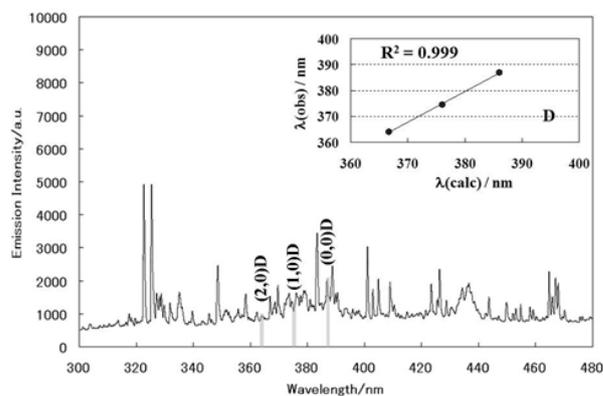
As shown in Figure 4, the luminescence bands assigned to the  $D^1\Delta-X^1\Sigma^+$  transition of CuF are confirmed. Hence it is found that the CuF molecules in the vibrational levels of quantum numbers of 0-2 in the  $D^1\Delta$  excited state are formed in the early stage of PLASLA, i.e., until 0.5  $\mu$ s.

#### 3.3.2. $B^1\Sigma^+-X^1\Sigma^+$ and $C^1\Pi-X^1\Sigma^+$ Bands of CuF in PLASLA Spectrum

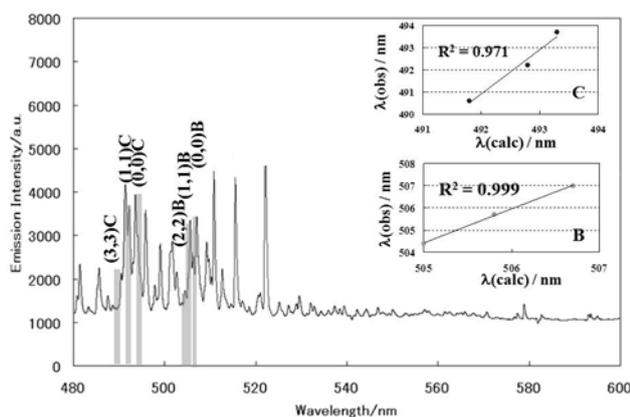
Besides the luminescence bands assigned to the  $D^1\Delta-X^1\Sigma^+$  transition of CuF, as shown in Figure 5, the luminescence bands assigned to the sequences of the  $B^1\Sigma^+-X^1\Sigma^+$  and  $C^1\Pi-X^1\Sigma^+$  transitions of CuF are confirmed. The assignments indicate that the CuF molecules in the vibrational levels of quantum numbers of 0-2 in the  $B^1\Sigma^+$  excited state and 0-3 in the  $C^1\Pi$  excited state are formed in the early stage of PLASLA, i.e., up until 0.5  $\mu$ s. Unfortunately, we cannot confirm whether the CuF molecules in the vibrational level of the quantum number of 2 are formed in the  $C^1\Pi$  excited state because of the overlap by the  $\text{Cu}_2$  luminescence bands.

#### 3.3.3. Luminescence Lines of Cu in PLASLA Spectrum

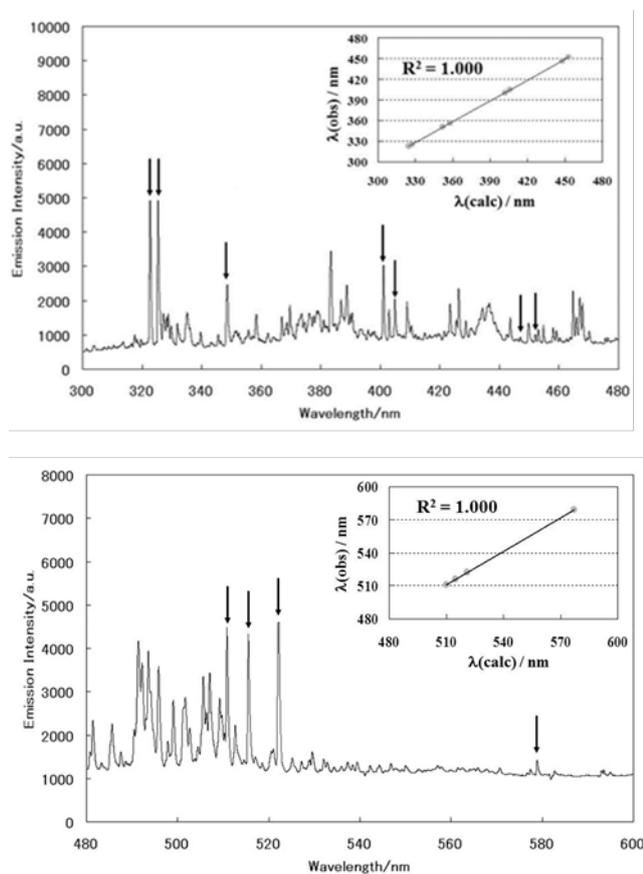
Figure 6 shows the lines assigned to the luminescence of Cu in wavelength regions of 300-480 nm and 480-600 nm. The Cu luminescence of the  $4^2S_{1/2} - 4^2P_{3/2}$  and  $4^2S_{1/2} - 4^2P_{1/2}$  transitions at 324 and 327 nm is observed, respectively, as well as the Cu luminescence lines observed in the chemiluminescent reaction of the  $\text{Cu-CF}_4$  system [14].



**Figure 4.** The luminescence spectrum of PLASLA at a delay of 0.5  $\mu$ s and the assignment to CuF ( $D^1\Delta-X^1\Sigma^+$ ) bands (marked with D) with correlation coefficients  $R^2$  between observed and calculated band positions in wavelengths,  $\lambda(\text{obs.})$  and  $\lambda(\text{calc.})$



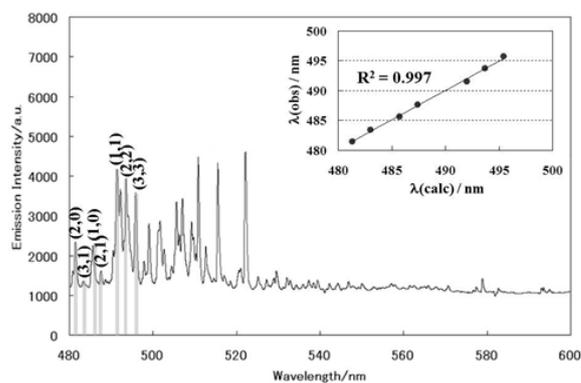
**Figure 5.** The luminescence spectrum of PLASLA at 0.5  $\mu\text{s}$  of delay and the assignment to CuF ( $B^1\Sigma^+-X^1\Sigma^+$ ) bands (marked with B) and CuF ( $C^1\Pi-X^1\Sigma^+$ ) bands (marked with C) with correlation coefficients  $R^2$  between observed and calculated wavelengths,  $\lambda(\text{obs.})$  and  $\lambda(\text{calc.})$



**Figure 6.** The luminescence spectrum of PLASLA at 0.5  $\mu\text{s}$  of delay and the assignment to Cu lines with correlation coefficients  $R^2$  between observed and calculated wavelengths,  $\lambda(\text{obs.})$  and  $\lambda(\text{calc.})$

### 3.3.4. $A^1\Pi_u-X^1\Sigma_g^+$ Band of $\text{Cu}_2$ in PLASLA Spectrum

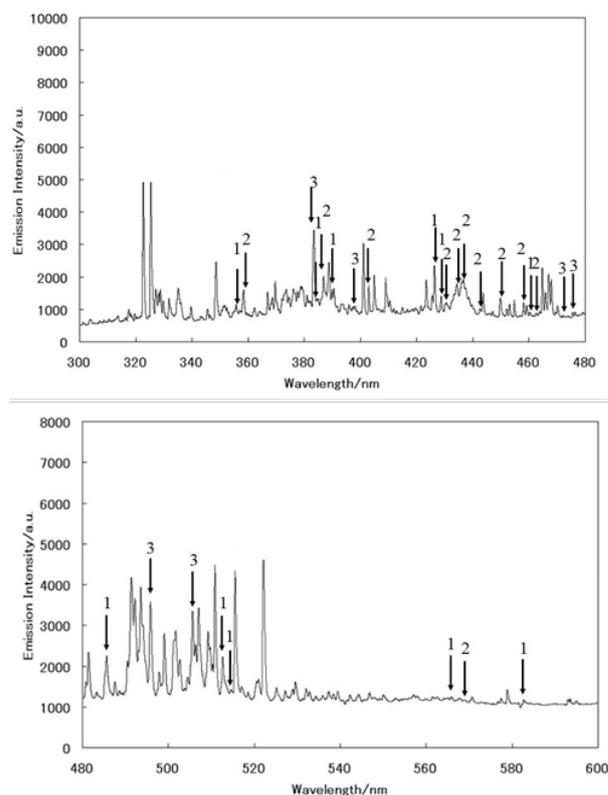
Besides the luminescence lines of Cu, the luminescence bands assigned to the  $A^1\Pi_u-X^1\Sigma_g^+$  transition of  $\text{Cu}_2$  are observed [15], as shown in Figure 7. The figure indicates that the  $\text{Cu}_2$  molecules in the vibrational levels of quantum numbers of 1-3 in the  $A^1\Pi_u$  excited state are formed in the early stage of PLASLA, until 0.5  $\mu\text{s}$ . It is of great interest that an appreciable amount of  $\text{Cu}_2$  molecules are formed in PLASLA, while they are not observed in the luminescence spectrum of the chemiluminescent reaction of the gaseous Cu- $\text{CF}_4$  system.



**Figure 7.** The luminescence spectrum of PLASLA at 0.5  $\mu\text{s}$  of delay and the assignment to  $\text{Cu}_2$  ( $A^1\Pi_u-X^1\Sigma_g^+$ ) bands with correlation coefficients  $R^2$  between observed and calculated wavelengths,  $\lambda(\text{obs.})$  and  $\lambda(\text{calc.})$

### 3.3.5. Luminescence bands of C, $\text{C}^+$ , and $\text{C}^{2+}$ in PLASLA spectrum

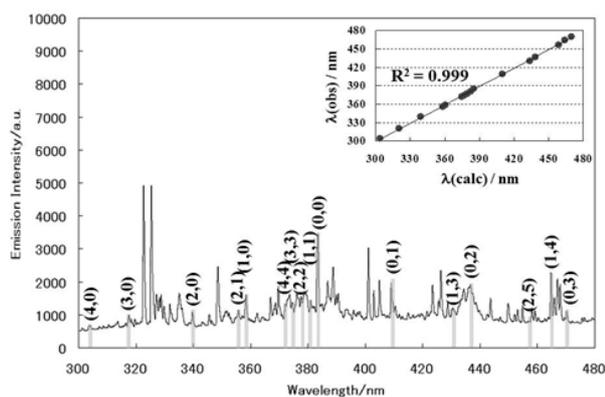
The present reactant gas  $\text{CF}_4$  is known as a good carbon source in plasma. In fact, the luminescence lines of C,  $\text{C}^+$ , and  $\text{C}^{2+}$  are assigned [16,17,18], as shown in Figure 8.



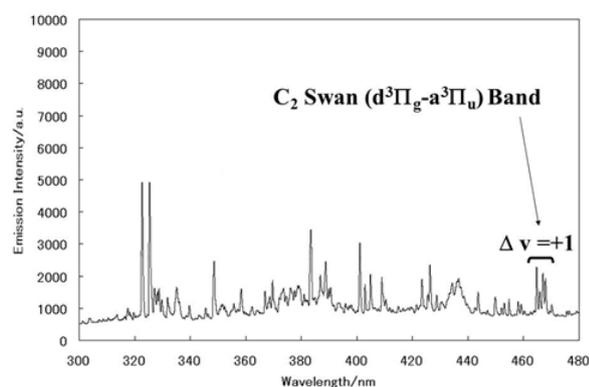
**Figure 8.** The luminescence spectrum of PLASLA at 0.5  $\mu\text{s}$  of delay and the assignment to  $\text{C}^+$ ,  $\text{C}^{2+}$ , and C lines (numbered with 1, 2, and 3, respectively)

### 3.3.6. Luminescence Bands of $\text{C}_2$ in PLASLA Spectrum

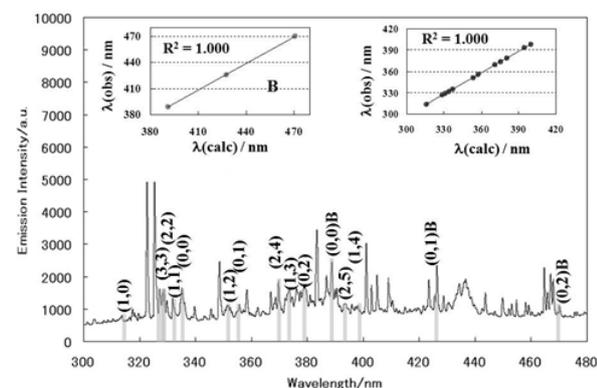
As the good carbon source of the present reactant gas  $\text{CF}_4$  in plasma, the luminescence bands of carbon molecules  $\text{C}_2$  are expected in the luminescence spectrum, as well as the luminescence bands of carbon atoms and atomic ions, i.e., C,  $\text{C}^+$ , and  $\text{C}^{2+}$ . In fact, the Deslandres-d'Azambuja band of the  $C^1\Pi_g-A^1\Pi_u$  transition [19,20] and the Swan band of the  $d^3\Pi_g-a^3\Pi_u$  transition [18,21,22] of  $\text{C}_2$  are observed, as shown in Figure 9 and Figure 10, respectively [23,24].



**Figure 9.** The luminescence spectrum of PLASLA at 0.5  $\mu$ s of delay and the assignment to  $C_2$  Deslandres-d'Azambuja ( $C^1\Pi_g-A^1\Pi_g$ ) bands with correlation coefficients  $R^2$  between observed and calculated wavelengths,  $\lambda(\text{obs.})$  and  $\lambda(\text{calc.})$



**Figure 10.** The luminescence spectrum of PLASLA at 0.5  $\mu$ s of delay and the assignment to  $C_2$  Swan ( $d^3\Pi_g-a^3\Pi_u$ ) bands



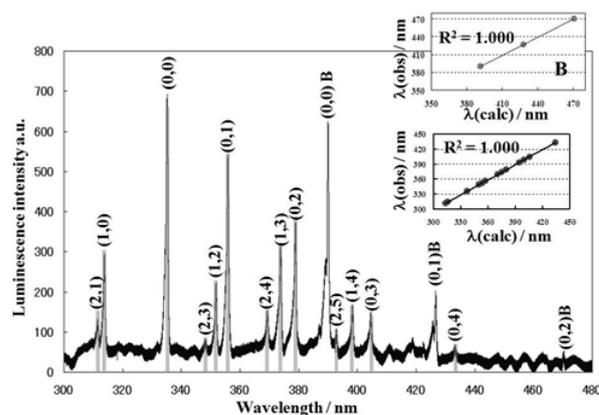
**Figure 11.** The luminescence spectrum of PLASLA at 0.5  $\mu$ s of delay and the assignment to  $N_2$  second positive ( $C^3\Pi_u-B^3\Pi_g$ ) bands and  $N_2^+$  ( $B^2\Sigma_u^+-X^2\Sigma_g^+$ ) bands (marked with B) with correlation coefficients  $R^2$  between observed and calculated wavelengths,  $\lambda(\text{obs.})$  and  $\lambda(\text{calc.})$

### 3.3.7. $N_2$ and $N_2^+$ Bands in PLASLA spectrum

As it will be discussed in section 3.4, all the luminescence bands of the dc-plasma are found to be assigned to  $N_2$  and  $N_2^+$ , which have their origins in the impurity  $N_2$  gas of the present experimental system. Hence let us find these bands in the time-resolved luminescence spectrum of PLASLA at 0.5  $\mu$ s. As a result, as shown in Figure 11, we can find these bands also in the PLASLA spectrum at 0.5  $\mu$ s. However, the intensity of these bands is found to be very weak.

## 3.4. Spectrum of dc-Plasma

The spectrum of dc-plasma in a wavelength range of 300–480 nm is shown in Figure 12. As shown in the figure, in spite of the fact that the present dc-plasma was formed by the discharge with a  $CF_4$  sample gas and the Cu electrodes, the analysis of the spectrum finds that all the bands of the spectrum can be assigned to  $N_2$  and  $N_2^+$  with the complete correlation coefficients, i.e.,  $R^2=1.000$  both for  $N_2$  and  $N_2^+$ . The three bands marked with B are due to the  $B^2\Sigma_u^+-X^2\Sigma_g^+$  transition of  $N_2^+$  and others are due to the  $C^3\Pi_u-B^3\Pi_g$  transition of  $N_2$  [11]. We suppose that these  $N_2$  and  $N_2^+$  have their origins in the minor impurity of  $N_2$  in the reaction chamber. In the dc-plasma, while the minor impurity  $N_2$  amounts to  $c1/20$  of the reactant  $CF_4$  at most, which is estimated by the fact that the pressure of  $CF_4$  is 0.2 torr under a background pressure of  $10^{-2}$  torr in the reaction chamber; it discharges by collisions with electrons instead of  $CF_4$ , which has the ionization potential much higher than that of  $N_2$ . As a result, neither C atom nor  $C_2$  molecule nor their ions are formed in the dc-plasma. Hence we need to correct the previous tentative estimation on the dc-plasma species [7, 8].



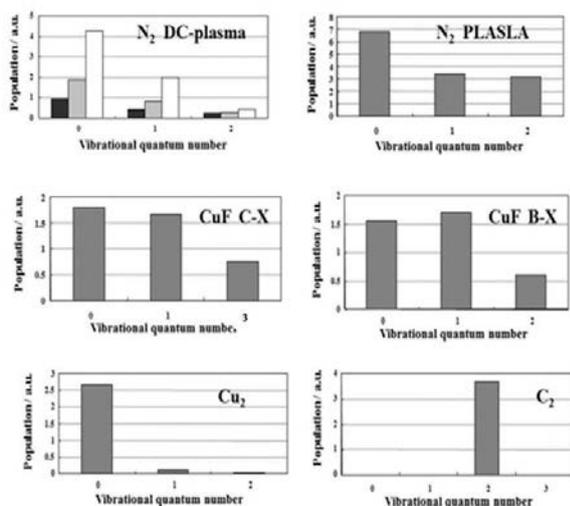
**Figure 12.** The luminescence spectrum of dc-plasma and the assignment to  $N_2$  second positive ( $C^3\Pi_u-B^3\Pi_g$ ) bands and  $N_2^+$  ( $B^2\Sigma_u^+-X^2\Sigma_g^+$ ) bands (marked with B) with correlation coefficients  $R^2$  between observed and calculated wavelengths,  $\lambda(\text{obs.})$  and  $\lambda(\text{calc.})$ , respectively

## 3.5. Vibrational Distribution

The distribution over the vibrational quantum levels, i.e. the vibrational distribution, of various species generated in PLASLA and dc-plasma was investigated by using the time-resolved spectra of PLASLA at a delay of 0.5  $\mu$ s and the luminescence spectrum of dc-plasma, as shown in Figure 13. In this figure, the vibrational distribution of  $N_2$  in the dc-plasma and of  $N_2$ , CuF,  $Cu_2$ , and  $C_2$  in the PLASLA is shown. As a result, the Maxwell-Boltzmann distribution can be fitted only to the distribution of  $N_2$  in the dc-plasma, giving  $34000\pm 10000$  K for the vibrational temperature of  $N_2$  in the dc-plasma. Thus, it is found that the Maxwell-Boltzmann distribution is formed in the dc-plasma and not at a delay of 0.5  $\mu$ s in the PLASLA.

The fact that the Maxwell-Boltzmann distribution is not available in the vibrational distribution of  $N_2$ , CuF,  $Cu_2$ , and  $C_2$  in the PLASLA suggests the active, complicated, non-equilibrium chemical reactions at a delay of 0.5  $\mu$ s in the PLASLA. In fact, the suggestion agrees with the fact that the distribution deviates from the Maxwell-Boltzmann distribution rather in the higher vibrational

levels. As the most characteristic case for that, for instance, as shown in the distribution marked with “CuF B-X” on the right-middle panel in Figure 13, the population of the vibrational level of  $v=1$  is rather higher than that of the  $v=0$  level in the B-state of CuF in the PLASLA, causing the discrepancy between the vibrational distribution and the Maxwell-Boltzmann distribution. Furthermore, as compared with the Maxwell-Boltzmann distribution, the populations of the vibrational level of  $v=1$  and 3 are evidently high in the distribution of the C-states of CuF in the PLASLA, as shown on the left-middle panel in Figure 13, as well as the distribution of  $N_2$  in the PLASLA, as shown on the right-top panel in Figure 13. Besides, the population only of the vibrational level of  $v=2$  is observed in  $C_2$  in the PLASLA, as shown on the right-bottom panel in Figure 13, suggesting that  $C_2$  is formed through this vibrational level. On the other hand, the population of  $Cu_2$  in the PLASLA is large especially in the vibrational level of  $v=0$ , as shown on the left-bottom panel in Figure 13, indicating that the excess energy is small in the  $Cu_2$  formation reaction in the PLASLA and suggesting that  $Cu_2$  will be formed predominantly through the  $v=0$  vibrational level.



**Figure 13.** Vibrational distribution of  $N_2$  in dc-plasma and  $N_2$ , CuF (C-X, B-X),  $Cu_2$ , and  $C_2$  in PLASLA at 0.5  $\mu$ s delay from laser ablation

### 3.6. Species Absent from the Luminescence Spectra

In the present spectroscopic analysis, almost all the spectra bands and lines in the time-resolved luminescence spectrum of PLASLA at 0.5  $\mu$ s can be assigned. Then, we consider that the contributions from other species will be negligibly small. By taking into account of the possibility of the contributions by species, which include C, Cu, F, N, O and H, we have also calculated the band positions of  $O_2$ ,  $F_2$ , CH, CN, and CuH and confirmed that the calculated band positions of these species disagree with those of any bands in the observed luminescence spectra. Hence, at least, it is found that these species are not in the excited states in the present reaction system.

### 3.7. Remarks on CuF Luminescence Spectra

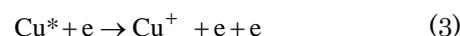
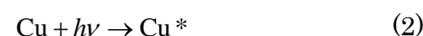
In the present study, we have confirmed the  $D^1\Delta-X^1\Sigma^+$ ,  $B^1\Sigma^+-X^1\Sigma^+$ , and  $C^1\Pi-X^1\Sigma^+$  bands of CuF in the PLASLA

spectrum at 0.5  $\mu$ s, while we can observe neither  $c^3\Delta-X^1\Sigma^+$  nor  $b^3\Pi-X^1\Sigma^+$  bands of CuF in the spectrum, indicating that CuF molecules in the singlet excited states are formed but any ones in the triplet excited states are still not at 0.5  $\mu$ s after the laser ablation. This significant result indicates that the CuF formation until 0.5  $\mu$ s after the laser ablation is on the singlet reaction coordinates, suggesting that the CuF formation is due to the ionic reactions with  $Cu^+$ , i.e., for instance,  $Cu^+$  (singlet) +  $CF_4$  (singlet)  $\rightarrow$  CuF (singlet) +  $CF_3^+$  (singlet). On the other hand, the luminescence from CuF both in the singlet and triplet excited states are observed in the CuFchemiluminescent reaction, i.e.,  $Cu$ (doublet) +  $CF_4$  (singlet)  $\rightarrow$  CuF (singlet/triplet) +  $CF_3$ (doublet). The mixing between the singlet and triplet paths is due to a spin-orbit interaction and has been confirmed to be enhanced in a magnetic field [5].

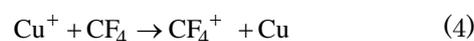
As described in Section 3.2, the relative intensity among the CuF luminescence bands in the spectrum at 8  $\mu$ s is different to that in the spectrum at 0.25 ms. For instance, the  $c^3\Delta-X^1\Sigma^+$  and  $B^1\Sigma^+-X^1\Sigma^+$  bands are rather strong in the spectrum at 8  $\mu$ s, while the  $C^1\Pi-X^1\Sigma^+$ ,  $b^3\Pi-X^1\Sigma^+$ , and  $D^1\Delta-X^1\Sigma^+$  bands are rather strong in the spectrum at 0.25 ms. This fact and the fact that CuF molecules in the c- and b-states are not formed at 0.5  $\mu$ s indicate that CuF molecules in the c-state are formed rather earlier and the ones in the b-state are formed rather later. Hence suggested the following scheme: since the energy of the c-state is closer to those of the D, C, B-states, in which CuF molecules formed until 0.5  $\mu$ s populate, than the b-state is, CuF in the c-state is formed first through the intersystem crossing from the D, C, B-states and then CuF in the b-state is formed through the internal conversion from the c-state. On the other hand, the fact that more CuF molecules in the B state are formed at 8  $\mu$ s and more CuF molecules in the D and C states are formed at 0.25 ms suggests that the formation of CuF in its excited states occur through the chemical processes, not through the internal conversion among these singlet states. Namely, the relaxation processes will be irrelevant, since CuF in the lowest excited state is formed earlier than CuF in the higher excited states.

### 3.8. Chemical Reactions and Product Materials

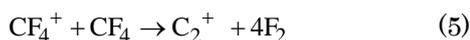
The present spectroscopic study confirms the luminescence of C,  $C^+$ ,  $C^{2+}$ ,  $C_2$ , CuF, Cu,  $Cu_2$ ,  $N_2$ ,  $N_2^+$  in the PLASLA of the present Cu- $CF_4$  system. Let us investigate the chemical reactions concerning these species. After the laser ablation, Cu atoms are emitted from the Cu target and ionized by the electron impact, as shown in Equations (2) and (3), respectively.



On the other hand, while the kinetic energy of electrons is inadequate to ionize  $CF_4$  by the electron impact, it can be ionized through the collision with  $Cu^+$ , as shown in Equation (4).



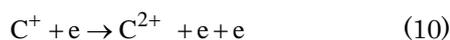
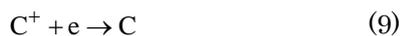
Following the ionization of  $CF_4$ , the reaction between  $CF_4^+$  and  $CF_4$  occurs to form  $C_2^+$ , as shown in Equation (5).



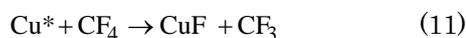
The collision of  $\text{C}_2^+$  with electrons forms the neutral  $\text{C}_2$  molecule, as shown in Equation (6).



As for the formation processes of carbon atoms and their ions, besides the decomposition of  $\text{C}_2$  and  $\text{C}_2^+$ , we suppose the following processes:



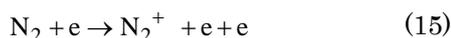
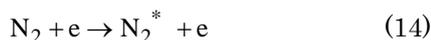
On the other hand, while  $\text{CuF}$  is formed by the process in Equation (8), it will be also formed through the chemiluminescent reaction, as shown in Equation (11).



Besides the formation of  $\text{Cu}$  in the excited states through the laser ablation in Equation (2), the following minor processes will occur: the process in Equation (4), the decomposition of  $\text{CuF}$ , or the extraction of  $\text{F}$  from  $\text{CuF}$  by the reactions with  $\text{CF}$ ,  $\text{CF}_2$ , and  $\text{CF}_3$ . Furthermore, for the formation process of  $\text{Cu}_2$ , we suppose the reactions in Equations (12) and (13).



On the other hand, in the dc-plasma, we suppose the following processes for the formation of  $\text{N}_2$  and  $\text{N}_2^+$  in the excited states:



However, since the electric potential is low in the PLASLA,  $\text{N}_2$  cannot be ionized directly by the electron impact in the PLASLA, as expressed in terms of Equation (15). Instead,  $\text{N}_2^+$  will be formed by the collisions of  $\text{N}_2$  with  $\text{Cu}^+$ , as shown in Equation (16).



As for the product materials in the PLASLA of the present  $\text{Cu-CF}_4$  system, carbon polymers are suggested by the fact that  $\text{C}$ ,  $\text{C}^+$ ,  $\text{C}^{2+}$ , and  $\text{C}_2$  are formed as the main products in the initial processes of the chemical reactions in the PLASLA. On the other hand, in the previous studies, we found that the color of the product materials on the electrodes is black and our experiments with time-of-flight mass-spectrometry suggest carbon polymers as the product materials in the present PLASLA [5, 9, 10]. Furthermore, our previous experiments found that *pure* carbon polymers are yielded in a magnetic field in the PLASLA [5].

## 4. Conclusion

The time-resolved spectra of PLASLA luminescence have been studied for the gaseous  $\text{Cu-CF}_4$  system in the present study. As a result, they have got the significant information especially on the initial processes of the chemical reactions in the PLASLA.

First, it is found that the luminescence spectrum at 0.5  $\mu\text{s}$  is quite different from those at 8  $\mu\text{s}$  and 0.25 ms. The spectra at 8  $\mu\text{s}$  and 0.25 ms are very close to the luminescence spectra of the chemiluminescent reaction of the  $\text{Cu-CF}_4$  system: while these spectra are similar, the spectrum at 8  $\mu\text{s}$  is found to be closer to the chemiluminescence spectrum. These facts indicate that the PLASLA reaction system is fairly different from the chemiluminescent reaction system just after the laser ablation and then becomes similar to it, proceeding further, with time.

Second, we have assigned almost all the lines and bands in the complicated PLASLA luminescence spectrum at 0.5  $\mu\text{s}$ . As a result, the presence of  $\text{C}$ ,  $\text{C}^+$ ,  $\text{C}^{2+}$ , and  $\text{C}_2$  has been confirmed, as well as  $\text{CuF}$ ,  $\text{Cu}$ ,  $\text{Cu}_2$ ,  $\text{N}_2$ , and  $\text{N}_2^+$ . Thus, the carbon species turns out to be formed, as atoms, ions, and molecules, at the early stage of the PLASLA reaction system, suggesting that carbon polymers are the product materials in the present PLASLA, which agrees well with the results from the time-of-flight mass spectrometric analysis, which indicates that carbon clusters are the main species emitted from the product materials by laser ablation.

Third, the luminescence spectrum of dc-plasma is found to disagree with the luminescence spectra of neither PLASLA nor chemiluminescence. All the bands of the luminescence spectrum of the dc-plasma have been assigned to  $\text{N}_2$  and  $\text{N}_2^+$ , indicating that the minor impurity  $\text{N}_2$  gas, which has the lower ionization potential than that of the reactant  $\text{CF}_4$  gas, is discharged and the reactant  $\text{CF}_4$  gas is not in the dc-plasma in the present experimental system. On the other hand, the luminescence bands of  $\text{N}_2$  and  $\text{N}_2^+$  are very weak in the PLASLA luminescence spectrum, indicating that the reactant gas is discharged in PLASLA, excluding the interference from the impurity gas with the lower ionization potential.

Fourth, as for  $\text{CuF}$ , the comparison of the time-resolved PLASLA luminescence with the  $\text{CuF}$  chemiluminescence of the laser-ablated  $\text{Cu}$  and a  $\text{CF}_4$  gas system turns out to be of great interest. In the PLASLA,  $\text{CuF}$  is generated through the process;  $\text{Cu}^+$  (singlet) +  $\text{CF}_4$  (singlet)  $\rightarrow$   $\text{CuF}$  (singlet) +  $\text{CF}_3^+$  (singlet), where only  $\text{CuF}$  in the singlet excited states is formed until 0.5  $\mu\text{s}$ . On the other hand, in the  $\text{CuF}$  chemiluminescent reaction,  $\text{CuF}$  is generated through the process:  $\text{Cu}$  (doublet) +  $\text{CF}_4$  (singlet)  $\rightarrow$   $\text{CuF}$  (singlet/triplet) +  $\text{CF}_3$  (doublet), where the mixing between the singlet and triplet paths is due to a spin-orbit interaction and has been confirmed to be enhanced in a magnetic field.

Thus, the present results doubtless indicate that PLASLA is promising for preparing the carbon materials. Since we have confirmed that the PLASLA reaction system changes with time after laser ablation, the appropriate assembly of the timing between the ablation laser and the laser for photochemical reactions is the significant factor for controlling the chemical reactions and the product materials. Furthermore, we also consider that the aid of a magnetic field is of great interest: For instance, since our previous study indicates that PLASLA

in a magnetic field can prepare the *purer* carbon materials, which include neither metals nor fluorine impurities. Besides, the present results point out the significance of switching the chemical reactions through the singlet and triplet mixing by a magnetic field.

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