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Gas-phase Chemical Reaction of Laser Ablated Copper Atom with Carbon Tetrafluoride in Electric and Magnetic Fields

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It is of great interest, from a viewpoint of the electric and magnetic field control of a metal catalyst reaction, to study the chemical reaction of the metal atom generated by laser ablation with gaseous phase molecule. The system, in which CuF molecules in various excited states are formed by the reaction of Cu generated by laser ablation with CF_4, is studied here. Since this system was not studied in the past, the molecular dynamics of this reaction system is first clarified as the basic research in the present study. The analysis of the spectrum of chemiluminescence of the reaction product CuF gives the vibrational and rotation temperatures in B, C, b, and c excited states. The time-of-flight experiment gives the translational temperatures of Cu and CuF. Moreover, the spectroscopic analysis gives the temperature of the blackbody radiation from the bulk site of a Cu target. Since, in this way, the data about the energy budget of this reaction system is obtained, the molecular dynamics process is discussed. Moreover, the electric and magnetic field effects expected in this reaction system are discussed. Furthermore, the observation of plasma switching by laser ablation (PLASLA) in an electric field is first reported.
Key words: CuF, Cu, CF_4, laser ablation, electric field, magnetic field

1. INTRODUCTION

The laser ablation method is widely adopted as a simple method of obtaining the gaseous phase atoms of various metals and widely applied in material chemistry. In this research, it is inquiring from a viewpoint of electric and magnetic field control of a metal catalyst reaction of the metal atom generated by laser ablation with gaseous phase molecules. In the present paper, the system, in which CuF in various excited states is generated by the reaction of Cu emitted by laser ablation with CF_4, is studied. Since this reaction system did not have an example of research in the past, in this paper, the molecular dynamics of the reaction system is first clarified as the basic research.

The spectroscopic analysis of the chemiluminescence of the product CuF gives the rotational and vibrational temperatures of B, C and b, and c states. The time-of-flight type experiments do the translational temperatures of CuF and Cu. On basis of the information, the molecular dynamics process is discussed. Furthermore, we first observe plasma switching by laser ablation (PLASLA) in the reaction system in an electric field.

Finally, the electric and magnetic field effects expected in this reaction system are discussed in view of spin chemistry and MHD (magnetic hydrodynamics).

2. EXPERIMENTAL

The schematic diagram of the present experimental system is shown in Fig.1. A fundamental beam (1.065 μm in wavelength, 45 mJ/pulse in power, 10 Hz in a repetition rate) of a Nd^{3+}: YAG laser (Quanta-Ray DCR-2) was focused on the surface of a Cu substrate (Nilaco, 10 mm x 10 mm x 1 mm, better than 99% in purity) in a reaction chamber (aluminum, octagon with 70 mm in side and 200 mm in height) with use of a quartz lens (50 mmϕ, f=300 mm). A copper target was rotated with a motor for homogeneous ablation. In the reaction chamber, a reactant CF_4 gas (Nihon Sanso, 99.999 % in purity) was slowly flowed by keeping its pressure at 0.2 Torr. The luminescence of CuF and Cu in the reaction chamber was introduced into a monochromator (Jobin Yvon HR-1000 with a 2000-lines/mm holographic grating or Nikon G-250 with a 1200-lines/mm grating) with use of a quartz lens (50 mmϕ, f=62.5 mm), which was able to be displaced in the direction parallel to the normal direction to the surface of the Cu target in the time of flight experiment. The output of the monochromator was detected with a photomultiplier (Hamamatsu Photonics 1P28). The signal

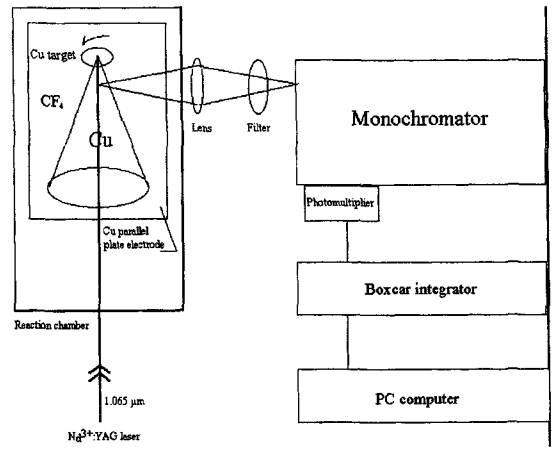

Fig.1 The schematic diagram of the present experimental system.

from the photomultiplier was detected with use of a boxcar integrator (Princeton Applied Research model 162).

In order to confirm that no charged particles such as ions and electrons affected the present chemiluminescent reaction, we did the experiments with the reaction system in an electric field. For the experiment, two copper plates (50 mm x 18 mm for each) are placed in parallel with a distance of 35 mm at a reaction site. Potential of 0-500 V was supplied between the plates with a power supplier (FLUKE 408B-874). In the experiment of the electric field effect, the photo-multiplier was covered with a μ-metal shield.

3. RESULTS AND DISCUSSION

3.1 Chemiluminescence and Reaction Equation of the Present Reaction System

In the reaction of laser-ablated copper with carbon tetrafluoride, greenish luminescence is observed. As shown in Fig.2, the luminescence is due to neutral copper and copper fluoride. No luminescence that can be assigned to copper fluoride ions or copper ions is observed. In fact, we confirm that no charged species such as ions or electrons concerns the present reaction, since the luminescence spectra are invariant in an electric field of 0-500 V.

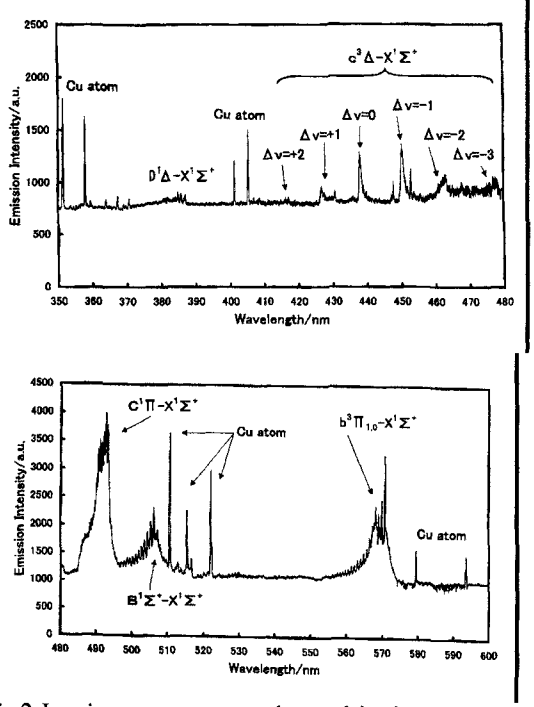

Fig.2 Luminescence spectra observed in the reaction of laser ablated copper with carbon tetrafluoride.

Therefore the present reaction is expressed in terms of Eq.(1).

$$Cu^* + CF_4 \rightarrow CuF^* + CF_3 \qquad (1)$$

where Cu* is the laser-ablated copper in various excited states and CuF* is copper fluoride in various excited states.

3.2 Electronic States of CuF

The luminescence spectra in Fig.2 indicate that CuF in b, B, C, c, and D excited states [1-6] are formed in the reaction. As shown in Table I, the band positions calculated by a method of Single Configuration Interaction (Gaussian 98M) with the basis sets of 6-311+G(2d,p) that agree well with the experimental results after the normalization with a scaling factor of 1.504. The results indicate that the lowest excited singlet state is B state. While the state should be called A state that is the lowest singlet excited, it is called B state, since b state was incorrectly called A state in the past.

Table 1 Low lying electronic states of CuF†

Bands	Transitions	λ_{calc} / nm	f_{calc}
D	$^1\Delta - ^1\Sigma^+$	386.5	0.0000
c	$^3\Delta - ^1\Sigma^+$	432.9	0.0000
C	$^1\Pi - ^1\Sigma^+$	429.0	0.0115
B	$^1\Sigma^+ - ^1\Sigma^+$	504.5	0.0001
b	$^3\Pi - ^1\Sigma^+$	495.8	0.0000

† λ_{calc} and f_{calc} indicate the band position and the band intensity (frequency factor), respectively, obtained in the present calculation.

3.3 Vibrational, Rotational, and Translational Temperatures of the Product CuF

Detailed analysis of the luminescence bands assigned to b-X, B-X, C-X, and c-X transitions give the vibrational and rotational temperatures. The analysis indicates that the populations in the lower vibrational levels in C and b states are discrepant from Boltzmann distributions, while those in the higher vibrational levels agree well with Boltzmann distributions. On the other hand, the rotational populations in b, B, C, and c states are confirmed to be Boltzmann distributions. These results are schematically shown in Fig.3.

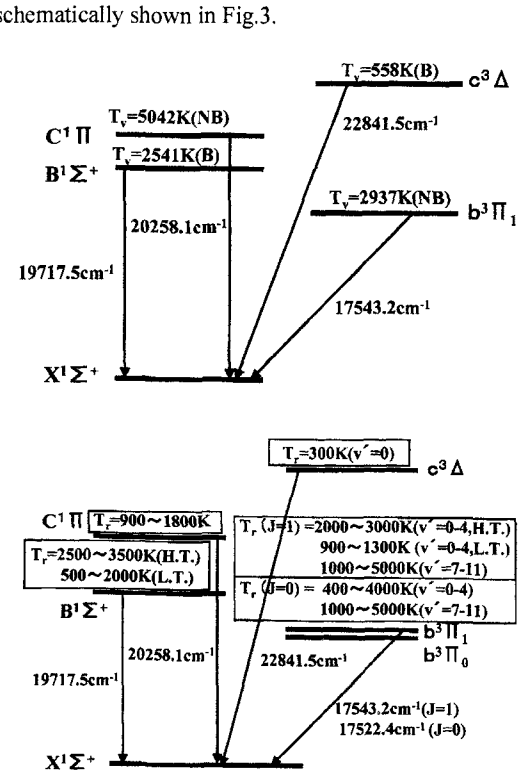

Fig.3 Vibrational (upper) and rotational (lower) temperatures. B and NB denote Boltzmann and non-Boltzmann distributions, respectively. HT and LT are the high and low temperature components, respectively.

In Fig.4, these rotational and vibrational temperatures of CuF are plotted as a function of the excitation energy of the excited states from the ground state. The figure indicates that both rotational and vibrational temperatures decrease with the excitation energy of the states. Hence the use of more reaction energy for the excitation of an electronic state decreases the rotational and vibrational temperatures of the states. Furthermore the populations over wide rotational temperatures in lower excited states, as shown in this figure, indicate the relaxation from higher excited states to lower states.

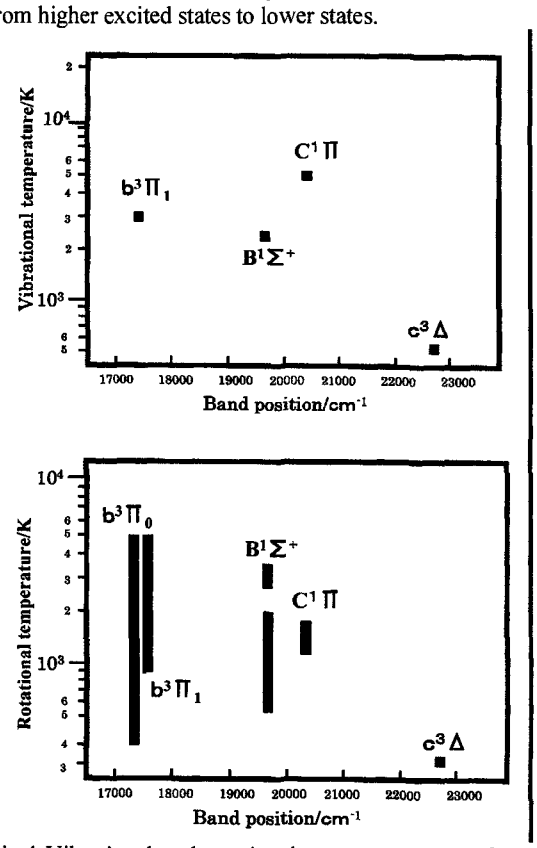

Fig.4 Vibrational and rotational temperatures as a function of excitation energy of excited states from the ground state of CuF.

The translational temperatures of CuF and Cu are obtained by time-of-flight experiments. The translational temperature of Cu indicates a clear double layer structure; the temperature is $100x10^3$-$1340x10^3$ K in the inside layer and is $20x10^3$-$75x10^3$ K in the outside layer. On the other hand, the translational temperature of CuF is found to be $31x10^3$ K in C state, $4x10^3$ K in B state, and $7x10^3$ K in b state.

In the time-of-flight experiments, another luminescence is observed and assigned to the blackbody emission from the bulk site of the copper target. The temperature of the emission is obtained to be 9000 K.

3.4 Energy Budget in the Present Reaction

All temperatures obtained in the present experimental study are shown in Fig.5. Among the temperatures, the translational temperature of Cu is highest. On the other hand, the energy necessary for the reaction in Eq.(1) corresponds to (125-250) $x10^3$ K, which is estimated from bonding energies of the reactant and product molecules. Thus it is found that the energy necessary for the present reaction is found to be equal to the lower part of the translational temperature of Cu in the inner layer. Thus the present study confirm that the translational energy of laser ablated copper has adequate kinetic energy for the reaction in Eq.(1). Probably, the collisional cooling mechanism of the product CuF with CF_4 is significant for the formation of the stable product CuF.

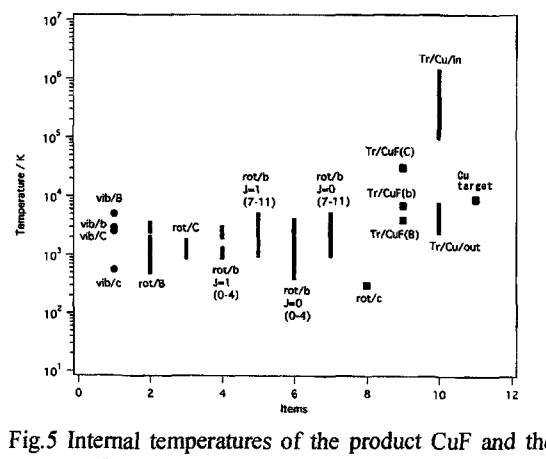

Fig.5 Internal temperatures of the product CuF and the reactant Cu. In notations, e.g., "vib/B" indicates the vibrational temperature of B state, "rot/b J=1 (0-4)" does the rotational temperatures of v'=0-4 levels in b($^3\Pi_1$) state, "Tr/CuF(C)" does the translational temperature of CuF in C state, "Tr/Cu/in" does the translational temperature of Cu in the inner layer, and "Cu target" does the temperature of the bulk site of the Cu target.

The translational temperature of CuF is rather similar in magnitude to the rotational and vibrational temperatures, while it is highest in these internal temperatures of CuF. This indicates that the reaction rather equally provides the translational, rotational, and vibrational energies in CuF; that the collisional energy transfer mechanism is significant in the distribution of theses temperatures. In general, the equal distribution of these internal energies indicates that the reaction is essentially thermal and has an early barrier, which is placed on the early site of the reaction coordinate and generally known popular in an exothermal reaction. In the reaction with the early barrier, the translational energy of Cu is used to go over the reaction barrier in the reactant site and the exothermal reaction energy is converted to the vibrational and rotational energy rather than the translational energy of the products in the product site beyond the barrier.

3.5 Plasma Switching by Laser Ablation (PLASLA)

While the luminescence spectra do not change in an electric field less than 500 V, DC discharged plasma is formed in an electric field greater than 500 V. As a result, the redish purple luminescence is predominant instead of the green luminescence, which is due to Cu emission and CuF chemiluminescence, by the plasma formation. The intensity of the redish purple luminescence oscillates with a period of 3 s.

The plasma luminescence is stable and does not oscillate without laser ablation. This indicates that the

oscillation of the plasma luminescence is due to the laser ablation. Furthermore, since the plasma luminescence is not observed without CF_4, the luminescence is due to the plasma formed by the DC discharge of CF_4.

Figure 6 shows the time chart of the total luminescence of the plasma switched by the laser ablation. In this figure, the irregularity in the switching of the plasma luminescence by the laser ablation is due to the contamination of the electrode.

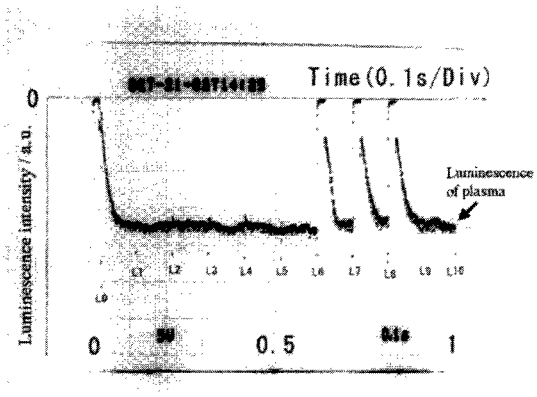

Fig.6 Total emission time chart recorded on an oscilloscope in the experiment of plasma switching by laser ablation (PLASLA). L0-L10: emission of laser ablation.

In this time chart, two kinds of luminescence are observed: luminescence of plasma and the emission of laser ablation marked with L0-L10. The chart indicates that the plasma luminescence intensity rapidly falls to zero simultaneously with the emission of laser ablation. Yet the rapid fall of the plasma luminescence intensity does not occur for laser ablations L1-L5 and L9, while it does for L0, L6-L8. After the rapid fall, the plasma luminescence recovers again. Thus the plasma switching turns out to be a nonlinear process. Since we confirmed that the plasma switching does not occur without laser ablation, it is evident that the laser ablation switches the plasma luminescence; hence we call it plasma switching by laser ablation (PLASLA).

In the further experiments, we find another type of PLASLA. While the laser ablation turns off the plasma in the previous PLASLA, the laser ablation turns on the plasma in this type of PLASA. That is, just under and very close to the threshold of DC discharge without laser ablation, the laser ablation turns on and off the plasma periodically. The induction of the plasma will be due to the ionization of the ablated copper by the impact of electrons formed in the DC discharge. The quenching of the plasma will be caused by the decrease in the concentration of charged species such as ions and electrons by their reaction with laser ablated copper.

The induction of the plasma will be due to the following processes:

$$Cu + e \rightarrow Cu^+ + e \quad (2)$$

$$Cu^+ + CF_4 \rightarrow Cu + CF_4^+ \quad (3)$$

The electrons with kinetic energy less than the ionization potential of CF_4 ionize the laser ablated copper in Eq.(2). The product copper cations react with CF_4 and form carbon tetrafluoride cations. These carbon tetrafluoride cations react with other carbon tetrafluorides to ignite the plasma.

The quenching of the plasma will be due to the following process:

$$Cu + CF_4^+ \rightarrow Cu^+ + CF_4 \quad (4)$$

This process decreases the concentration of cations such as CF_4^+, CF_3^+, CF_2^+, CF^+, C_2^+ etc. As a result, the plasma is quenched.

Another mechamism for the qenching of the plasma may be due to the processes in Eqs.(2) and (3). Although it is a paradoxical way of speaking, an extremely superfluous increase in the concentration of cations such as CF_4^+, CF_3^+, CF_2^+, CF^+, C_2^+ etc., and anions such F^- and F_2^- might finally quench the plasma.

3.6 Magnetic Field and Electric Field Effects on the Present Reaction

In the present reaction, as seen in Eq.(1), laser ablated copper in doublet states reacts with carbon tetrafluoride in the singlet ground state to form copper fluoride in singlet and triplet states and carbon trifluoride in doublet states. In view of spin chemistry, it is of great interest to study the spin exchange in the reaction and its control by a magnetic field [7]. The present study gives the significant basic information for the objective. It is noticeable that no charged species concerns the present reaction, since we can do the experiments of the magnetic field effect without a magnetic hydrodynamic (MHD) effect.

Furthermore, PLASLA observed first in the present study is of great interest in view of laser CVD. In particular, the cooperative electric and magnetic control of the macroscopic structure of the reaction system will open a new technique in material science.

4. CONCLUSION

In the present paper, we first study the reaction of laser ablated copper with carbon tetrafluoride to form chemiluminescent product copper fluoride. All the internal energies of reaction species are experimentally obtained and the reaction mechanism is discussed in view of energy budget.

We first observe plasma switching by laser ablation (PLASLA) in the present study.

Finally we discuss the magnetic and electric field effects on the present reaction in view of spin chemistry and MHD.

The present results will be very significant for the future study on magnetic and electric control of metal catalyst laser CVD.

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