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# Laser spectroscopy of jet-cooled CuF in visible region*

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The laser-induced fluorescence excitation spectra of jet-cooled CuF have been recorded in the range of 19000–21470cm$^{-1}$, in which the CuF radicals were produced by the reaction of $SF_6$ with copper atoms from a dc discharge-sputtering source under supersonic jet conditions. Eight observed vibronic transition bands have been assigned as the transition from the ground state $X(^1\Sigma^+)$ to $B(^1\Sigma^+)$, $C(^1\Pi)$ and an unreported upper state. The rotational structure of all observed bands has been analysed at the estimated rotational temperature 80K. We determined the newly observed band to be the $(^1\Pi, v = 1)$–$X(^1\Sigma^+ v = 0)$ transition according to the character of the rotational structure and the isotopic shift analysis. In addition, the lifetimes of the states involved in these bands were measured.

**Keywords:** CuF, visible spectra, fluorescence
**PACC:** 3320K, 3350D, 3150

## 1. Introduction

The spectra of diatomic molecules containing copper atoms, such as CuO, CuH, and monohalides, have been studied extensively for its involvement of d orbital electron in chemical bonding.[1] Among these, the transition of copper monofluoride has been continuously investigated theoretically.[2–4] In previous experimental studies, some bands have been observed in chemiluminescence. In 1970, the rotational analysis of CuF spectrum was reported by Hoeft *et al.*[5] Then, Honerjager *et al*[6] studied the microwave spectrum of CuF and confirmed that the CuF ground state is $^1\Sigma^+$. Some reliable rotational constants of the ground state were provided. The laser-induced fluorescence was first studied, leading to an analysis of $B^1\Sigma^+$–$X^1\Sigma^+$ transition by Steele *et al*[7] in 1978. Then Brazier *et al*[8,9] reported an analysis of $^{63}$CuF magnetic hyperfine splitting at Doppler-limited resolution by laser-induced fluorescence in the $b^3\Pi$–$X^1\Sigma^+$ yellow system and $a^3\Sigma^+$–$X^1\Sigma^+$ red system.[10] However, the main contribution to the CuF spectrum was made by Ahmed *et al*[11] who recorded the electronic spectra of CuF over the range 250–850nm. They performed the analysis of the transitions to $a^3\Sigma^+$, $A(^1\Pi,^1\Sigma)$, $B^1\Sigma^+$, $C^1\Pi$, and $D^1\Pi$ states from ground state $X^1\Sigma^+$. Recently, Jakob *et al*[12,13] studied the hyperfine structure of $C$–$X$ transition of CuF by LIF technique in the sub-Doppler regime and reported the hyperfine parameters of the $C$ state of CuF.

In this paper, we study the excitation spectrum of CuF in the region 19000–21470cm$^{-1}$ by laser-induced fluorescence. The CuF radical was produced by the reaction of $SF_6$ with copper atoms from a dc discharge sputtering source under supersonic-jet conditions. Eight observed vibronic transition bands belonging to the transitions from the ground state $X(^1\Sigma^+)$ to $B(^1\Sigma^+)$, $C(^1\Pi)$, as well as an unreported upper state was observed and analysed at the estimated 80K rotational temperature.

## 2. Experiment

The experimental apparatus have been described in detail elsewhere.[14,15] The $SF_6$ gas was premixed with argon. The mixture at a stagnation pressure of ∼500Pa passed through a pulsed nozzle (General

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valve) of 0.5mm diameter into the vacuum chamber. A pair of pure copper pins with 1-mm spacing was set for discharge at 1.5mm downstream from the nozzle. The CuF molecules were produced by the reaction of the copper atoms with the $SF_6$ molecules under a discharge condition. The pressures of the vacuum chamber were $\sim 4\times10^{-2}$ and $\sim 2.7\times10^{-3}$Pa with and without the jet running, respectively.

The light source system used was a tunable dye laser (Lumonics, HT-500) pumped by a Nd:YAG laser (Spectra Physics GCR-170), where dyes C503,C480 and C460 were used. The output of the pulsed dye laser (with a linewidth about $0.1\text{cm}^{-1}$) traversed the vacuum chamber and perpendicularly crossed the jet flow. The fluorescence from the excited CuF radicals was detected by a photomultiplier (R928, Hamamatsu) at right angles both to the laser beam and the jet flow. The output of the photomultiplier was averaged with a computer data acquisition system for observing the spectra or fed to a transient digitizer (Tektonics TDS 380) for measuring the lifetime. The laser wavelength was calibrated by using optogalvanically active neon lines.

# 3. Result and analysis

The laser induced fluorescence excitation spectra were recorded in the region between 19000 and $21470\text{cm}^{-1}$ in this paper. Eight vibronic bands of CuF radicals in this range have been observed. The observed bands could be divided into three groups: group one is located on 19735, 20384, 21025 and $21659\text{cm}^{-1}$, (506.7, 490.5, 475.6 and 461.7nm); group two on 20270, 20906 and $21535\text{cm}^{-1}$(493.3, 478.3 and 464.3nm), and group three on $19658\text{cm}^{-1}$ (508.7nm). The group one exhibits only $P$ and $R$ branches and has $650\text{cm}^{-1}$ intervals; the group two has $P$, $R$ and $Q$ branches and has $635\text{cm}^{-1}$ intervals; and the group three has only one band with $P$, $R$ and $Q$ branches. All transitions are assumed to originate from the ground state since the CuF molecules in the detection zone have relaxed to the ground state after 3 cm expansion from the discharge zone in the supersonic jet. The ground state of CuF radical was experimentally identified as $a\ ^1\Sigma^+$ symmetry.[5,6] As is well known, when the lower state is $a\ ^1\Sigma^+$ state, only the transition to the upper state $\Pi$ or $\Sigma$ can occur according to the selection rules. For the $\Pi$–$\Sigma$ transition, the spectra have $P$, $R$ and $Q$ branches. The $\Sigma$–$\Sigma$ transition exhibits only $P$ and $R$ branches. Based on the previous work[11] and the character of the rotational structure of the observed bands, the group one belongs to the $B(^1\Sigma^+)$–$X(^1\Sigma^+)$ transition, the group two is the $C(^1\Pi)$–$X(^1\Sigma^+)$ transition, and the $19658\text{cm}^{-1}$ (508.7nm) band is the transition from the ground state $X(^1\Sigma^+)$ to the upper $\Pi$ state.

### 3.1. Rotational analysis and simulation

The line positions of the observed $B(^1\Sigma^+)$–$X(^1\Sigma^+)$ and $C(^1\Pi)$–$X(^1\Sigma^+)$ transitions were used to determine the rotational constants. The rotational constant of the ground state were determined by using all the available combination difference. The energy level expression for the ground state is $F''(J) = B''J(J+1) - D''J^2(J+1)^2$. The maximum $J$ is 35 in the observed bands. The derived rotational constant of the ground state are $B_0''$=0.37773, $D_0''$=$5.0\times10^{-7}$ and $B_0''$=0.37504, $D_0''$=$4.9\times10^{-7}$ for $^{63}$CuF and $^{65}$CuF radicals, respectively. These rotational constants are in good agreement with Ahmed's work.[11] The upper state rotational constants and band origin were determined by the least-squares fit. The rotational analysis shows clearly that all bands belong to Hund's case $b$ transition. The energy level expression for the upper state is the same as the ground state. So the following expressions can be used to fit the spectra.

$$\begin{aligned}P(J) =& T_0 + Bv'J(J-1) - Dv'J^2(J-1)^2\\ &- Bv''J(J+1) + Dv''J^2(J+1)^2,\end{aligned}$$

$$\begin{aligned}R(J) =& T_0 + Bv'(J+1)(J+2) - Dv'(J+1)^2(J+2)^2\\ &- Bv''J(J+1) + Dv''J^2(J+1)^2,\end{aligned}$$

and

$$\begin{aligned}Q(J) =& T_0 + (Bv' - Bv'')J(J+1)\\ &- (Dv' - Dv'')J^2(J+1)^2.\end{aligned}$$

In the simulation, the Lorentzian function was used to convolute the spectral line shapes, and the rotational distribution was assumed to be Boltzmann distribution. The derived rotational constants of $^{63}$CuF and $^{65}$CuF radicals are summarized in Tables 1 and 2. The simulated spectra of 506 and 478.3nm bands are shown in Figs.1 and 2. The simulated spectra of all the bands are in reasonable match with the observed spectra at the rotational temperature $T_{\rm rot}$=80K.

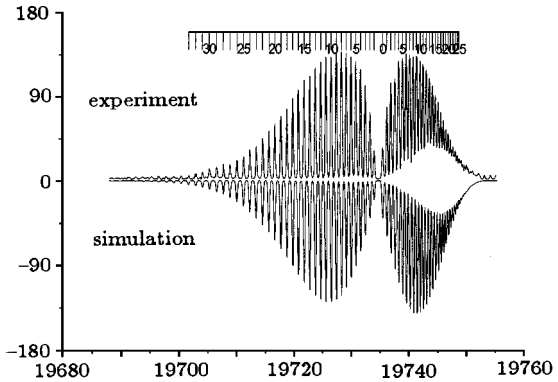



**Fig.1.** LIF spectrum of a [19.7] $^1\Sigma^+$–$X^1\Sigma^+(0-0)$ band of transition (506 nm,19734cm$^{-1}$) of CuF. The upper trace is the experiment spectrum; the lower trace is the simulated spectrum for $^{63}$CuF.

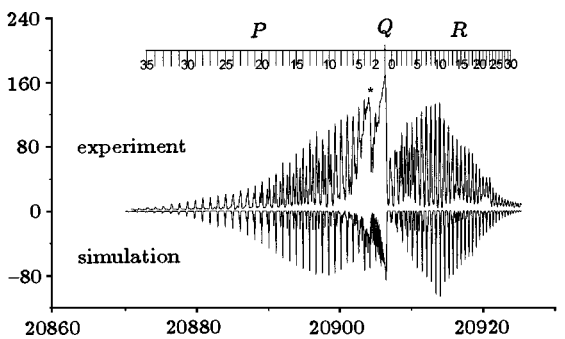



**Fig.2.** LIF spectrum of a [20.9] $^1\Pi$–$X^1\Sigma^+$ transition (478.3nm, 20906cm$^{-1}$) of CuF. The upper trace is the experimental spectrum; * is the $Q$ head belonging to isotopic $^{65}$CuF. The lower trace is the simulated spectrum of $^{63}$CuF and $^{65}$CuF.

**Table 1.** Band constants(cm$^{-1}$)for the $B$–$X$ system of CuF.

| | $v_0$ | $B'$ | $10^7D'$ | Lifetime/$\mu$s |
|---|---|---|---|---|
| $^{63}$CuF 0–0 | 19734.78 | 0.36985 | 4.71 | 1.50 |
| $^{63}$CuF 0–0 | 19734.7[a] | 0.36974[a] | 4.70[a] | |
| $^{63}$CuF 1–0 | 20383.79 | 0.36691 | 4.35 | 1.53 |
| $^{63}$CuF 1–0 | 20383.49[a] | 0.36745[a] | 4.73[a] | 1.2[b] |
| $^{65}$CuF 1–0 | 20381.41 | 0.36430 | 4.31 | |
| $^{63}$CuF 2–0 | 21025.2 | 0.36395 | 4.01 | 1.32 |
| $^{65}$CuF 2–0 | 21020.55 | 0.36136 | 3.98 | |
| $^{63}$CuF 3–0 | 21659.52 | 0.36108 | 4.72 | 1.37 |
| $^{65}$CuF 3–0 | 21652.70 | 0.35851 | 4.68 | |

a: Ref.[11], b: Ref.[7].

### 3.2.The $B^1\Sigma^+$–$X^1\Sigma^+$ and $C^1\Pi$–$X^1\Sigma^+$ transition

The group one shows only $R$ and $P$ branches, and it is of the $\Sigma$–$\Sigma$ transition. In Ref.[7], Steele *et al* assigned it as the $B^1\Sigma^+$–$X^1\Sigma^+$ transition and analysed the rotational structures of (0,0) and (1,0) bands. In this paper, we have observed four bands located at 19735, 20384, 21025 and 21659cm$^{-1}$. The 19735cm$^{-1}$band is a typical $\Sigma$–$\Sigma$ transition, other bands look more complicated and there are extra branches appearing in the spectra, as shown in Fig.1. For the natural copper, it has two stable isotopes, $^{63}$Cu and $^{65}$Cu, with a natural abundance ratio of about 2:1. The spectra of $^{63}$CuF and $^{65}$CuF are expected to be observed. The isotopic shift for (0,0) band cannot be resolved but other bands ($v$', 0) are observed in the present resolution. Based on the assignment in Ref.[7] with the help of the isotopic shift, we have assigned these four vibronic bands as the $B^1\Sigma^+$–$X^1\Sigma^+$ transitions from the $v''$=0 to $v'$=0,1,2,3, respectively. The complexities of $v'$=1–3 bands are caused by the combination of the two transitions of $^{63}$CuF and $^{65}$CuF. We simulated the observed spectra of $^{63}$CuF and $^{65}$CuF. The spectroscopic constants of $B$–$X$ for $^{63}$CuF and $^{65}$CuF radicals are listed in Table 1. The results of the (0,0) and (1,0) bands for $^{63}$CuF are in good agreement with Ahmed's results.[11] The spectroscopic constants of $^{65}$CuF and the (2,0) and (3,0) bands of $^{63}$CuF are obtained for the first time, so far as we know.

**Table 2.** Band constants(cm$^{-1}$)for the $C$–$X$ system of $^{63}$CuF.

| Transition | $v_0$ | $B'$ | $10^7D'$ | Lifetime/$\mu$s |
|---|---|---|---|---|
| $^{63}$CuF 0–0 | 20270.30 | 0.37485 | 5.71 | 0.52 |
| $^{63}$CuF 0–0 | 20269.76[a] | 0.37475[a] | 5.33[a] | |
| $^{63}$CuF 1–0 | 20906.52 | 0.37145 | 4.35 | 0.51 |
| $^{63}$CuF 1–0 | 20906.17[a] | 0.37189[a] | 5.20[a] | 0.6[b] |
| $^{65}$CuF 1–0 | 20904.23 | 0.36880 | 4.269 | |
| $^{63}$CuF 2–0 | 21535.59 | 0.36842 | 4.52 | 0.51 |
| $^{65}$CuF 2–0 | 21531.02 | 0.3658 | 4.48 | |

a: Ref.[11], b: Ref.[7].

The group two exhibits $P$, $Q$ and $R$ branches. It belongs to the $\Pi$–$\Sigma$ transition. Ahmed *et al*[11] analysed the rotational structure of (0,0),(1,1) and (2,2) bands. In our present work, the three bands were observed and assigned to the transition from $v''$=0 to $v'$=0,1,2, respectively. The (0,0) band is a typical $\Pi$–$\Sigma$ transition including $P$, $Q$ and $R$ branches. The rotational constants were derived only by simulating the $P$ and $R$ branches of the $C$–$X$ transitions because the $Q$ branch is blended without a very clear structure. The observed and simulated spectra of the (1,0) band of the transition $C$–$X$ are illustrated in Fig.2. The results of (0,0) and (1,0) bands for $^{63}$CuF are in agreement with Ahmed's results.[11] The spectroscopic constants of $^{63}$CuF and $^{65}$CuF are listed in Table 2 according to the simulations of the observed bands.

The rotational constants and vibrational interval in Tables 1 and 2 may be fitted using the customary expressions from Herzberg[16] to obtain the equilibrium molecular constants of $B(^1\Sigma^+)$ and $C(^1\Pi)$ states and are summarized in Table 3. The values of $\omega_e$ and $\omega_e X_e$ may be used to test the isotopic relation based on values of reduced mass $\rho = [\mu(^{63}\mathrm{CuF}) / \mu(^{65}\mathrm{CuF})]^{1/2} = \omega_e^i/\omega_e$. Using the atomic masses for $^{63}$CuF and $^{65}$CuF, we obtain $\rho$=0.9964. Calculations of these values using the data in Table 3 give results in favourable agreement with the theoretical values.

**Table 3.** Equilibrium constant for the $B(^1\Sigma^+)$ and $C(^1\Pi)$ states ($\mathrm{cm}^{-1}$).

| State | $T_e$ | $\omega_e$ | $\chi_e\omega_e$ | $B_e$ | $10^3\alpha_e$ | $10^7 D_e$ | $r_e$/nm |
|---|---|---|---|---|---|---|---|
| $C^1\Pi$ | 20259.39 | 643.37 | 3.57 | 0.37634 | 3.15 | 5.71 | 0.17522 |
| $B^1\Sigma^+$ | 19717.44 | 656.25 | 3.67 | 0.37130 | 2.93 | 4.70 | 0.17633 |

### 3.3.New band

A new band at 508.7nm was observed which shows $P$, $R$ and $Q$ branches with an isotopic shift of 2.1$\mathrm{cm}^{-1}$. It is assigned as a $\Pi$–$\Sigma$ transition. The observed and simulated spectra are shown in Fig.4. The rotational constant of the lower state is $B''$=0.37773, which is equal to the constant of the ground state. We can conclude that the new band originates from the ground state. The rotational constant of the upper state $B'$=0.3781$\mathrm{cm}^{-1}$ is obtained, which is different from the other states we observed. The isotope shift of $^{63}$CuF and $^{65}$CuF is 2.1$\mathrm{cm}^{-1}$, which means that this band belongs to vibronic transition from $v''$=0 to $v'$=1. Based on the above analysis, it may be concluded that the new band is the $(^1\Pi, v = 1) - X(^1\Sigma^+ v = 0)$ transition. We have searched in the range of 510–530nm to find (0,0) band, but no similar rotational structure was observed.

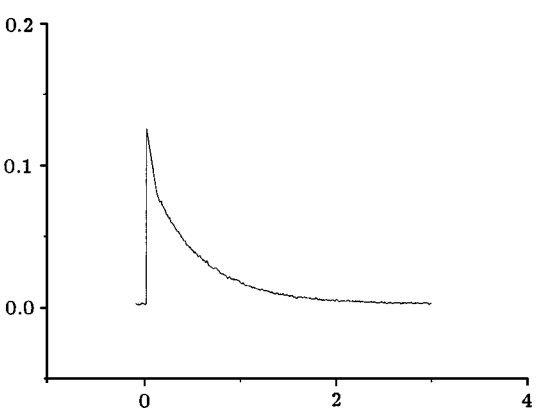



**Fig.3.** A typical time-resolved fluorescence spectrum of the 493.3nm band.

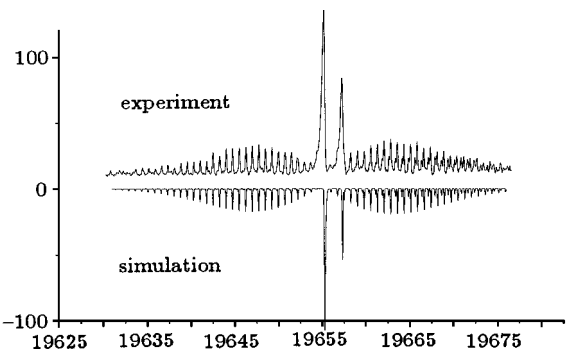



**Fig.4.** The observed new band. The upper trace is the experimental spectrum. The lower trace is the simulated spectrum.

### 3.4.Lifetime measurement

The lifetime of the upper states was measured by monitoring the time-resolved LIF signal when the pulsed dye laser was tuned to excite the radical to a selected rotational level of the upper state. The fluorescence decay following the short excitation pulse (5ns) was monitored by a photomultiplier and averaged on a transient digitizer. Since the CuF radical is present with a low concentration under supersonic-jet conditions, the lifetime of the excited state can be measured directly by observing the decay of the fluorescence signal. The typical time-resolved fluorescence signal corresponding to the (0–0) band of $C$–$X$ transition is illustrated in Fig.3. The time-resolved signal can be fitted to an exponential decay without deconvolution of the system response function. The lifetime measured in our experiment is listed in Table 5, which is quite long for an allowed transition.

## 4. Discussion

It can be easily identified that the ground state $X^1\Sigma^+$ is associated with $Cu^+(3d^{10})$ $F^-(2p^6)$, Dufour[17] calculated the excited state of CuF using ab initio calculation. Five electronic states, namely $^3\Sigma$ $^3\Pi$ $^1\Sigma$ $^1\Pi$ and $^3\Delta$ states, where the $^3\Pi_0$(f) interacts with the upper-lying $^1\Sigma$ state, are predicted. All the excited states are associated with the open shell $Cu^+(3d^9 4s)$ $F^-(2p^6)$. The rotational constant of the lower state for the new band is equal to that of the ground state. So we can assign the new band to the transition between the excited $Cu^+(3d^9 4s)$ $F^-(2p^6)$ structure and the closed-shell $Cu^+(3d^{10})$ $F^-(2p^6)X^1\Sigma^+$. The corresponding 3d–4s transition in $Cu^+$ is forbidden in the atomic limit. This can explain the fairly long lifetime of the unknown band. We suggest that the new band is involved in a transition between a new state above a state with $\Pi$ component and the ground state. According to Dufour's[16] calculation, the new band could be the transition between the ground state and the $^3\Pi_0$(f) state by borrowing some transition intensity from the upper $^1\Sigma^+$ state which interacts with it. It seems that further theoretical work and more experimental investigation with high resolution will be helpful for understanding the electronic structure of CuF.

## 5. Conclusion

The jet-cooled CuF spectrum in the visible region have been studied by laser-induced fluorescence. Eight vibronic transition bands observed belong to the transitions from the ground state $X(^1\Sigma^+)$ to $B(^1\Sigma^+)$, $C(^1\Pi)$, and an unreported upper state have been observed and analysed. The molecular constant and isotopic shifts for the $B(^1\Sigma^+)$ and $C(^1\Pi)$ states have been determined. In addition, the lifetimes of the $B$ and $C$ states were measured for the first time, so far as we know.

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