Theoretical Analysis for the HF Chemical Laser System with a Selected Fluoride Molecule

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The possibility for the high intensity and energy possessing a short pulse in the HF chemical laser system which contained fluoride molecules (RF) was demonstrated theoretically through the numerical model simulation. The calculation was accomplished by assuming that the thermal branched chain mechanism of RF was occurred in the initiation step of $H_2 + F_2$ chain reaction. Variations of the major chemicals and the temperature in the system were calculated as a function of time. An analysis was also performed to evaluate output pulse profile through parametric studies.

Introduction

During last two decades a great interest has been made to the utilization of a hydrogen-fluorine chain reaction in the chemical laser systems.[1-3] The enhancement of the specific output energy and the lasing efficiency has been a major subject in the field of a pulsed HF laser.[4-8] In the case of pulsed laser, many researches[9-11] have been carried out to obtain high intensity and energy in the duration of short time. The continuous investigation has been tried to explore the higher intensity, energy, and efficiency of the laser system by controlling the concentration of F atom and the initiation materials of H_2/F_2 chain reaction in the HF laser. Since the initiation of chemical laser requires an expenditure of energy, it has become an important aspect to develop a chemical laser that needs a small external energy.

In 1984, in order to satisfy this requirements, A. N. Oraevskii[12] proposed branched chain reaction mechanism, which is the basis of a chemical laser, and calculated the influence of the energy branching on the characteristics of these kinds of pulsed laser. He showed that this process may improve the efficiency of the laser by controling the initiation step of $H_2 + F_2$ chain reactions. In 1987, E.U. Baikov, A.S. Bashkin and A.N. Oraevskii[13] reported a new possibility for using the thermal branching mechanism. This involves thermal dissociation of specially selected fluoride molecules (RF) which undergo the dissociation as a result of heating released directly from the $H_2 + F_2$ chain reaction. However, this research is still at the beginning stages. It is therefore undoubtedly of interest to look into this purely chemical laser system in details.

In the present work, HF chemical laser utilizing a mixture consisted with a specially selected fluoride molecule, RF, will be analyzed theoretically by the numerical model simulation. Variations of the major chemicals, temperature, and lasing power in the system will be calculated as a function of time by the detailed kinetic analysis. From parametric studies, the effect of the level of initiation and inert gas to determine the characteristic of the laser light also will be evaluated.
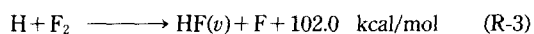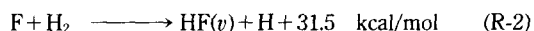
Kinetic Model

The major reactions for the laser system with a in

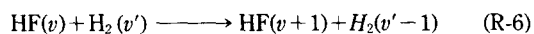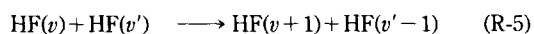selected fluoride compound, RF, can be represented by the followings;

a) Initiation

$$F_2 \longrightarrow 2F \qquad \text{(R-1)}$$

b) $H_2 + F_2$ chain reaction (pumping reaction)

$$F + H_2 \longrightarrow HF(v) + H + 31.5 \quad \text{kcal/mol} \qquad \text{(R-2)}$$

$$H + F_2 \longrightarrow HF(v) + F + 102.0 \quad \text{kcal/mol} \qquad \text{(R-3)}$$

c) Vibrational-Translational (V-T) deactivation

$$HF(v) + M \longrightarrow HF(v-1) + M \qquad \text{(R-4)}$$

d) Vibrational-Vibrational (V-V) exchange

$$HF(v) + HF(v') \longrightarrow HF(v+1) + HF(v'-1) \qquad \text{(R-5)}$$

$$HF(v) + H_2(v') \longrightarrow HF(v+1) + H_2(v'-1) \qquad \text{(R-6)}$$

e) Inhibition by O_2

$$H + O_2 + M \longrightarrow HO_2 + M \qquad \text{(R-7)}$$

$$F + O_2 + M \longrightarrow FO_2 + M \qquad \text{(R-8)}$$
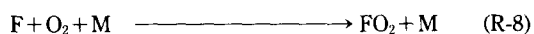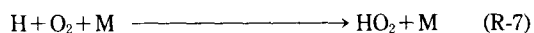
f) Stimulated emission

$$HF(v+1) \longrightarrow HF(v) + h\nu \qquad \text{(R-9)}$$

g) Thermal dissociation

$$RF \longrightarrow R + F \qquad \text{(R-10)}$$
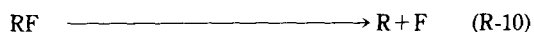
The reactions from (R-1) to (R-9) represent the general mechanism of $H_2/F_2/O_2$ laser system without RF molecules where RF indicates any fluoride compound such as KrF_2, XeF_2, CH_3F, F_2SO_3, etc. The reaction

of (R-10) is a thermal dissociation process of RF. The selected fluoride molecule can be dissociated with a fairly high rate when the system temperature reaches a certain level. The F atoms from the RF take part in the chain reaction (R-2) and (R-3) and accelerate this step. Thus the mechanism from (R-1) to (R-10) represent the thermal branched chain reaction.

Generally, the computer model simulations for the thermal branched chain reactions are carried out by simply adding one more equation to the multi-coupled differential equations which are used in RF free system.[3,14] However, the calcualtions of the RF system should be done very carefully since the numerical solution of RF system has a very stiff change after a long induction period in which reactions go on at very slow rate. This appearance causes a problem such that the conditions of calculation applied to the induction period become unsuitable for the abrupt changing stage. Therefore when we come into calculations, the level of initiation, the mole ratio of reactants, and the dissociation rate constant of RF should be taken into account.

Result and Discussion

To calculate the changes in concentration of reactants, temperature and output pulse power, etc., we update our simulation model[14] by adding one differential equation. Over-all rate coefficients for chemical reactions used for the calculations are listed in Table 1 & Table 2. The composition of reactants mixture consists $F/F_2/H_2/O_2/RF/He$ in the initial ratios of 0.03/100/

Table 1. Kinetic model for H_2/F_2 system

No.	Reaction	Rate coefficient	Distribution constants			
			$v=1$	$v=2$	$v=3$	$v=4$
1	$F + H_2 \rightarrow HF(v) + H$	$1.62E14 \ \exp(-1600/RT)$	0.056	0.111	0.555	0.278
2	$H + F_2 \rightarrow HF(v) + F$	$1.2E14 \ \exp(-2400/RF)$	0.050	0.050	0.075	0.133
3	$H + F_2 \rightarrow HF(v) + F$	$1.2E14 \ \exp(-2400/RT)$	0.167	0.257	0.250	$v=4-6$
4	$HF(v) + H \rightarrow F + H_2$	$1.0E12 \ T^{0.78}$	$v=4-6$			
5	$HF(v) + HF \rightarrow HF(v-1) + HF$	$6.0E16 \ T^{-1.43}$	0	0.167	0.333	0.500
6	$HF(v) + H_2 \rightarrow HF(v+1) + HF(v+1)$	$8.3E5 \ T^{2.2} \ \exp(-562/RT)$	0	0.965	0.035	0
7	$2HF(v) \rightarrow HF(v-1) + HF(v+1)$	$4.0E5 \ T^{2.2}$	0	0.333	0.333	0.333
8	$HF(v) + F \rightarrow HF(v-1) + F$	$5.4E9 \ T^{1.3}$	0	0.167	0.333	0.500

$R = 1.987$ cal/mole · K
All rate coefficients are in $(cm^3/mole)^{N-1}/sec$ where N is the reaction order.

Table 2. Kinetic model for $H_2/F_2/O_2$ system.

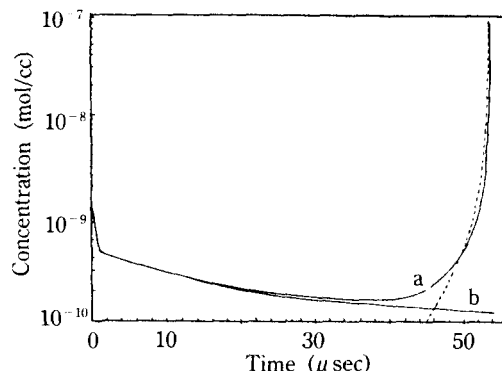| No.	Reaction	Rate Coefficient
9	$H+O_2 \rightarrow HO_2+H_2$	50.7E14 exp(994/RT)
10	$H+O_2 \rightarrow HO_2+H_2O$	315.0E14 exp(994/RT)
11	$H+O_2 \rightarrow HO_2+M$	149.0E13 exp(994/RT)
12	$H+HO_2 \rightarrow OH+OH$	25.3 E13 exp($-$1888/RT)
13	$H_2+OH \rightarrow H_2O+H$	21.7E12 exp($-$5146/RT)
14	$H+OH+H_2O \rightarrow$	141.3E21 T^{-2}
	H_2O+H_2O	
15	$H+H_2O \rightarrow H_2+O_2$	25.3E12 exp($-$695/RT)
16	$H+OH+M \rightarrow H_2O+M$	217.4E T^{-2}
17	$H+O_2 \rightarrow OH+O$	22.3E13 exp($-$16790/RT)
18	$O+HO_2 \rightarrow OH+O_2$	48.2E12 exp($-$994/RT)
19	$H+H+H_2O \rightarrow$	72.5E17 T^{-1}
	H_2+H_2O	
20	$H+H+M \rightarrow H_2M$	65.2E16 T^{-1}
21	$H+O+M \rightarrow OH+M$	61.6E15
22	$O_2+O+O \rightarrow O_2+O_2$	79.2E26 $T^{-1.5}$
23	$F+O_2+M \rightarrow FO_2+M$	181.0E13
24	$F+F+M \rightarrow F_2+M$	108.7E14 T^{-1}
25	$O+O+O \rightarrow O_2+O$	224.7E18 $T^{-1.5}$
26	$O+H_2 \rightarrow OH+H$	18.1E9 exp($-$8902/RT)
27	$H+H+H_2 \rightarrow H_2+H_2$	195.7E16 T^{-1}
28	$H+H+H \rightarrow H_2+H$	108.7E17 T^{-1}
29	$OH+O+MHO_2+M$	36.2E13
30	$H_2O+O \rightarrow OH+OH$	66.2E12 exp($-$18360/RT)
31	$H+F+M \rightarrow HF+M$	26.1E17 T^{-1}
32	$O+O+M \rightarrow O_2+M$	61.6E14 $T^{-0.5}$

Fig. 1. Temporal profile of the concentration of F; (a) RF system, (b) RF free system. The dashed line indicates the concentration of F purely from RF. The composition ratio of reactants was F/H_2/F_2/O_2/RF/He=0.03/50/100/10/10/400 in torr.
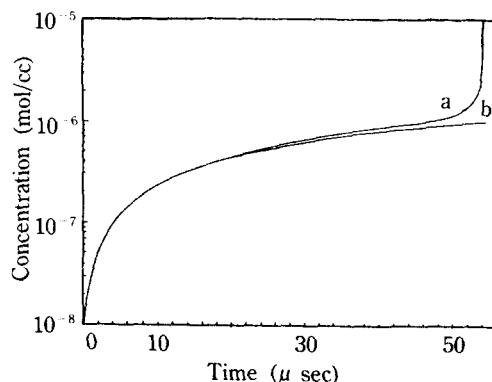

Fig. 2. Temporal profile of the concentration of HF for the RF system (a) and RF free system (b). The composition ratio of reactants was F/H_2/F_2 /O_2/RF/He=0.03/50/100/10/10/400 in torr.

50/10/10/400 in torr. The thermal dissociation rate constant of RF in the simulation is selected to be k=5× 10^{12} exp(-25000/RT) from the report of E.U. Baikov et al.[12]

1. Concentration and Temperature

The time dependence of concentrations of F and HF in the RF system is compared with those in the RF free system as shown in Fig. 1 and Fig. 2. They demonstrate a general feature of the kinetic simulation in two different cases. The concentration of F in the RF free system monotonously decreases in time due to very low level of initiation, while the concentration of F in the RF system has an abrupt increase after the slowly decreasing stage which is called as a induction period. Fig. 3 shows that the RF molecules are dissociated strikingly at the end of the induction period. In these figures, it is notable that the concentration of HF in the RF free system increases continuously. However, note that HF concentration in RF system

increases considerably after the slowly increasing stage. The changing tendency of F concentration due to the dissociation of RF molecule (dashed line in Fig. 1) is similar to the concentration profile of HF and F. This suggests that the generation of F from RF plays an important role in this chain reaction mechanism. Consequently the selection of RF would be a critical factor to control the rate in the production of HF and F.

In Fig. 4, the sudden increase of temperature can be also observed to occur at the end of the induction period. This is due to the rapid consumption of H_2
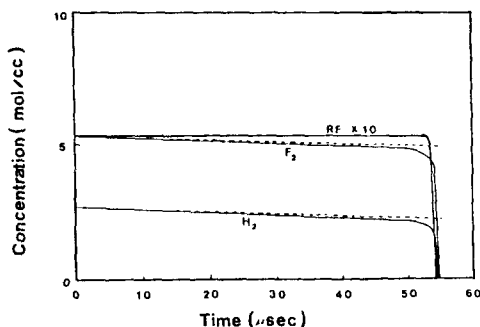
Fig. 3. The variation of the concentration in H_2, F_2, and RF for the RF system ($-$) and for RF free system ($--$). The composition ratio of reactants was $F/H_2/F_2/O_2/RF/He = 0.03/50/100/10/10/400$ in torr.
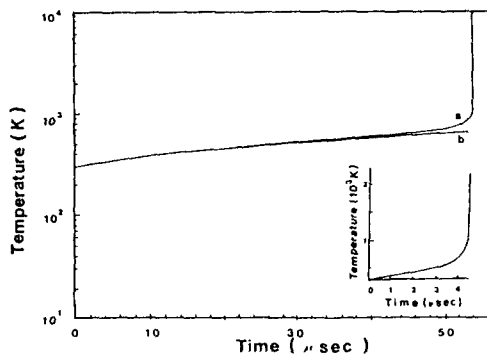

Fig. 4. Temperature changes in the RF system (a) and RF free system (b). The inserted figure is adapted from Ref. 11.

and F_2 during the propagation steps through the reactions of (R-2) and (R-3). During the initial stage after a very weak initiation of the reaction, the mixture undergoes quite slow self-heating through the HF chain reactions from (R-1) to (R-3). At these processes, the dissociation of RF from the reaction (R-10) is so slow that the amount of F atoms from RF is negligible. However, if the mixtures reach the temperature at which rapid thermal dissociation of the RF molecules is initiated, the effect of RF on the system becomes noticeable. It produces in an abrupt increase in the number of active centers to accelerate the reaction rate. This mechanism is called "thermal branched chain reaction". According to the results shown in Fig. 4, the temperature for onset of thermal branching is about
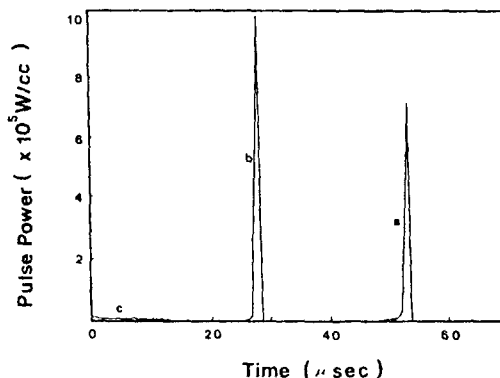

Fig. 5. Power characteristics for the case of He = 400 torr (a), He = 300 torr (b), and for the RF free system (c). The composition ratio of reactants were $F/H_2/F_2/O_2/RF = 0.03/50/100/10/10$ in torr (a,b) ; $F/H_2/F_2/O_2/He = 0.03/50/100/10/400$ in torr (c).

700 K-800 K. The value shows good agreement with the inserted figure, which is adapted from the result of E.U. Baikov et al.[13]

2. Power and Parametric study

In Fig. 5, the laser power from our calculation is provided to display the temporal characteristic of the output pulse of RF system possessing a high-power, short pulse with a long induction period. It is obvious that, under same initial condition, the RF free system shows no significant lasing property (Fig. 5c), while the RF system demonstrates a high-power short pulse even without an additional energy (Fig. 5a and Fig. 5b). In addition to this significance of RF system, note that no tailing end can be also attainable. It is explained by the fact due to the rapid consumption of fuel supply (F_2 & H_2) instead of V-T deactivation process in RF free system.

The effects of level of initiation, the ratio of [F]/[F $_2$], and lasing power were studied by fixing the initial mole ratio of reactants and the dissociation rate constant of RF. The Fig. 6 shows that maximum peak of power depends weakly on the level of initiation, α, where it is higher than 3×10^{-4}. In addition, the induction period decreases as the level of initiation increases.

It is well known that the He gas does not participate in the H_2/F_2 chain reaction and it only changes the heat
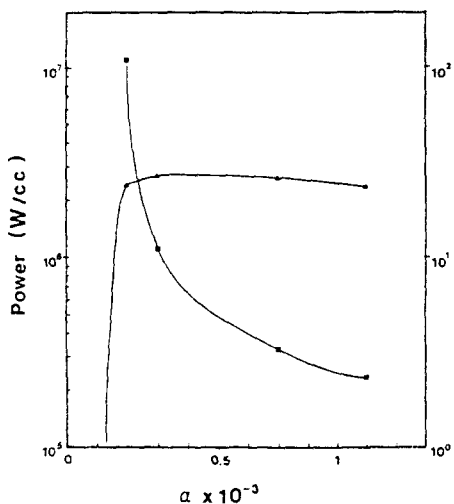
Fig. 6. Behavior of the induction period (■) and of the maximum power (▲) as a function of the level of initiation, α.
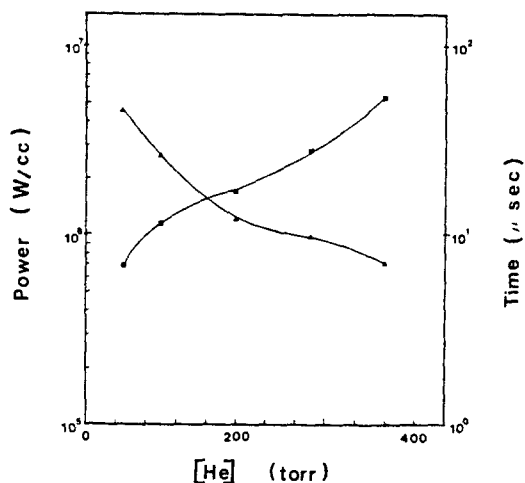

Fig. 7. Behavior of the induction period (■) and the maximum power (▲) as a function of the Helium concentration. The composition ratio of reactants was $F/H_2/O_2/RF = 0.03/100/10/10$ in torr.

capacity of reaction mixture. Therefore we consider the effects of added He gas on the characteristics of laser power. In the condition of a fixed level of initiation at 3×10^{-4}, the height of maximum peak of power and the induction period are also found to depend on the He concentration in the initial reaction mixture. By adding He to the reaction mixture, the induction period is increased, while the maximum power is decreased as depicted in Fig. 7. This result suggests that in RF system, helium can be used as a diluent for the temperature control.

In conclusion, the calculations of the kinetic model in this work show the possibility of HF laser possessing the high intensity and short pulse by adding a certain RF molecule to the mixture conventionally used in the HF laser system. Additional gas, RF, improves the laser performance by the thermal branched chain mechanism. If the dissociation rate constant of RF and the composition of mixture are constant, the extremely large contribution of thermal branching can be affected by the level of initiation. When the level of initiation is suitably fixed, the maximum peak during the fast stage is mostly governed by the concentration of He. Additionally, the induction period is influenced by the level of initiation and the concentration of He. It ap-

pears that this theoretical analysis might provide a possible improvement for a new design of the HF chemical laser system.

Acknowledgements

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