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Numerical Model Simulation of DF-CO_2 Transfer Chemical Laser

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Theoretical analysis of DF-CO_2 transfer chemical laser is performed through simple kinetic model consisting of 30 chemical reactions. In this model, we calculate the power theoretically by solving the rate equations, which are related to the $D_2 + F_2$ chain reaction and the DF-CO_2 resonance energy transfer, combined with both the gain processes and the stimulated emission processes. The calculated powers are verified with previously reported results in good agreements. The output energy rises linearly with the increase in pressure, and the duration time of output pulse show the inverse dependence on pressure. Through the detailed calculation of temperature and concentrations of reactants as a function of time, it is found that the deactivation processes of DF(v) can be neglected in low pressure, but they have to be considered in high pressure. From the parametric study for the variation on $[D_2]/[F_2]$ and $[CO_2]/[D_2 + F_2]$ at several constant total pressure, the optimum lasing conditions are found to be in a range of 1/3 to 1 and 2 to 4, respectively.

Introduction

A chemical laser which operates on a population inversion produced in the course of an exothermic chemical reaction has many advantages[1]. It provides a direct conversion of chemical energy into electromagnetic energy. And it generates high output power due to available large energy released from chemical reaction. On the other hand, the molecule which is excited by chemical reaction can induce the population inversion in other molecule through the vibrational energy transfer. It is called transfer chemical laser(TCL). The first observations of this type of laer operation were made by Gross[2] and Chen *et al.*[3], for the DF-CO_2 system. With their efforts to increase power of CO_2 laser, they found efficient pulse CO_2 laser operation at 10.6 μm when CO_2 was added to pulsed DF chemical laser. It gives a strong laser output by excited CO_2 whose energy is transferred from excited DF formed by chain chemical reactions[1]. Because population inversion of CO_2 is obtained from the chemical reaction, it is classified into chemical laser and it does not have to maintain the flash photolysis or electric discharges continuously.

The phenomena occurring in the chemical laser system are very complicated, and have not been well understood. In

Table 1. Kinetic Model for DF-CO_2 Transfer Laser

Reaction No.	Reaction	Rate constant
R-1	$F \rightarrow 2F$	
R-2	$F + D_2 \rightleftharpoons DF(1) + D$	$k_c(1) = 6.54 \times 10^{12} \exp(-1460/RT)$
	$F + D_2 \rightleftharpoons DF(2) + D$	$k_c(2) = 1.52 \times 10^{13} \exp(-1460/RT)$
	$F + D_2 \rightleftharpoons DF(3) + D$	$k_c(3) = 2.34 \times 10^{13} \exp(-1460/RT)$
	$F + D_2 \rightleftharpoons DF(4) + D$	$k_c(4) = 1.66 \times 10^{13} \exp(-1460/RT)$
	$F + D_2 \rightleftharpoons DF(5) + D$	$k_c(5) = 4.0 \times 10^{12} 1^{0.15} \exp(-300/RT)$
	$F + D_2 \rightleftharpoons DF(v) + D$	$k_c(v) = 1.2 \times 10^{13} T^{0.15} v = 6,....,9$
R-3	$D + F_2 \rightleftharpoons DF(1) + F$	$k_h(1) = 2.61 \times 10^{12} \exp(-2400/RT)$
	$D + F_2 \rightleftharpoons DF(2) + F$	$k_h(2) = 3.26 \times 10^{12} \exp(-2400/RT)$
	$D + F_2 \rightleftharpoons DF(3) + F$	$k_h(3) = 3.82 \times 10^{12} \exp(-2400/RT)$
	$D + F_2 \rightleftharpoons DF(4) + F$	$k_h(4) = 4.0 \times 10^{12} \exp(-2400/RT)$
	$D + F_2 \rightleftharpoons DF(5) + F$	$k_h(5) = 1.04 \times 10^{13} \exp(-2400/RT)$
	$D + F_2 \rightleftharpoons DF(6) + F$	$k_h(6) = 2.48 \times 10^{13} \exp(-2400/RT)$
	$D + F_2 \rightleftharpoons DF(7) + F$	$k_h(7) = 3.98 \times 10^{13} \exp(-2400/RT)$
	$D + F_2 \rightleftharpoons DF(8) + F$	$k_h(8) = 5.02 \times 10^{13} \exp(-2400/RT)$
	$D + F_2 \rightleftharpoons DF(9) + F$	$k_h(9) = 3.52 \times 10^{13} \exp(-2400/RT)$
R-4	$DF(v) + M_1 \rightleftharpoons DF(v-1) + M1$	$k_{df} = 4.0 \times 10^{3} vT^{2.2}$ $v = 1,...,9$
	$DF(v) + M2 \rightleftharpoons DF(v-1) + M2$	$k_{df} = 3.7 \times 10^{-6} vT^{4.66}$ $v = 1,...,9$
	$DF(v) + M3 \rightleftharpoons DF(v-1) + M3$	$k_{df} = 2.44 \times 10^{-11} vT^{6.71} \exp(-8884/RT) v = 1,...,9$
	$DF(v) + M4 \rightleftharpoons DF(v-1) + M4$	$k_{df} = 0.14 vT^{3.66}$ $v = 1,...9$
R-5	$DF(v) + CO_2(00^{\circ}0) \rightleftharpoons DF(v-1) + CO_2(00^{\circ}1)$	$k_{tr} = 9.2 \times 10^{14} vT^{-1.0} v = 1,...,9$
R-6	$CO_2(00^{\circ}1) + M1 \rightleftharpoons CO_2(11^{1}0) + M1$	$k_{dc} 8.85 \times 10^{-4} T^{4.75} \exp(-1484/RT)$
	$CO_2(00^{\circ}1) + M7 \rightleftharpoons CO^{1}0) + M7$	$k_{dc} = 1.13 \times 10^{-7} T^{5.8} \exp(-2436/RT)$
	$CO_2(00^{\circ}1) + M8 \rightleftharpoons CO_2(11^{1}0) + M8$	$k_{dc} = 6.4 \times 10^{7} T^{1.5}$
	$CO_2(00^{\circ}1) + M3 \rightleftharpoons CO_2(11^{1}0) + M3$	$k_{dc} = 1.45 \times 10^{14} T^{-1.0}$
	$CO_2(00^{\circ}1) + M1 \rightleftharpoons CO_2(0.3\ 0) + M1$	$k_{dc} = 6.8 \times 10^{-7} T^{5.55} \exp(-1484/RT)$
	$CO_2(00^{\circ}1) + M7 \rightleftharpoons CO_2(03\ 0) + M7$	$k_{dc} = 8.7 \times 10^{-11} T^{6.6} \exp(-2436/RT)$
	$CO_2(00^{\circ}1) + M8 \rightleftharpoons CO_2(03\ 0) + M8$	$k_{dc} = 4.9 \times 10^{4} T^{2.3}$
	$CO_2(00^{\circ}1) + M3 \rightleftharpoons CO_2(03\ 0) + M3$	$k_{dc} = 1.1 \times 10^{11} T^{-0.2}$
R-7	$CO_2(00^{\circ}1) + M \rightarrow CO_2(10^{\circ}0) + h\nu$	

Catalytic species: $M_1 = CO_2$ $M_2 = $Ar, 2He, F_2 $M_3 = $DF $M_4 = D_2$ $M_7 = $He, Ar, 4D, $2F_2$ $M_8 = $F, $0.02D_2$. The rate constants k_3 and k_- designate forward and backward rates respectively, with units in terms of moles, cm^3, and sec. The temperature T is in K and R is 1.987 cal/mole-K These constants are selected from ref. 9.

order to explain the lasing phenomena, to predict experimental data, and to update the system, the theoretical investigations of the chemical laser have been progressed significantly. Since the success of computer model simulation of chemical laser by Cohen[4] and Airey *et al.*[5] in 1969 firstly, the computer simulations have been developed by many researchers[6] including one[7] of us. And we are able to perform the present study with the informations which is obtained from it.

The first simulation for the DF-CO_2 system was reported by Kerber *et al.*[8] They calculated the power with the kinetic model which consists of 72 chemical reactions. They also reported the simple kinetic model, which considered the dominant reactions of this system and agreed well with experimental data at low pressure condition[9]. Almost simultaneously, Poehler *et al.*[10] gave a similar simulation model in which 41 chemical reactions were considered and that was consistent with experiment at high pressure condition. These investigations have been continued by Igonishin[11], Baskin[12], Bryl[13] and others.[14-16]

In the present paper we suggest a simple kinetic model which consists of only 30 chemical reactions, and agrees with both low and high pressure operating conditions. In order to calculate the change of the concentrations and temperature of the reactants as a function of time, the detailed kinetics is analyzed. And to obtain the optimum lasing condition, the parametric study is also performed.

Model Formulation

The major reactions of DF-CO_2 TCL system can be classified by initiation, chain reaction, V-T deactivation of DF, V-V transfer, collisional deactivation of CO_2 and stimulated emission reactions.

(a) Initiation

$$F_2 \xrightarrow{h\nu} 2F \qquad \text{(R-1)}$$

(b) D_2+F_2 chain reaction

$$F + D_2 \xrightarrow{k_c} DF(v) + D + 30.63\ \text{kcal/mole} \qquad \text{(R-2)}$$

$$D + F_2 \xrightarrow{k_h} DF(v) + F + 99.33\ \text{kcal/mole} \qquad \text{(R-3)}$$

(c) Vibration-Translation (V-T) deactivation

$$DF(v) + M \xrightarrow{k_{DF}} DF(v-1) + M \qquad \text{(R-4)}$$

(d) Vibration-Vibration transfer from DF to CO_2

$$DF(v) + CO_2(00^\circ 0) \xrightarrow{k_{tr}} DF(v-1) + CO_2(00^\circ 1) \qquad \text{(R-5)}$$

(e) Collisional deactivation of $CO_2(00^\circ 1)$

$$CO_2(00^\circ 1) + M \xrightarrow{k_{dc}} CO_2(v_1, v_2\ , 0) + M \qquad \text{(R-6)}$$

(f) Stimulated emission

$$CO_2(00^\circ 1) \longrightarrow CO_2(10^\circ 0) + h\nu \qquad \text{(R-7)}$$

Over-all rate coefficients for chemical reactions are listed in Table 1[9]. The initiation step is the generation of F radical by flash photolysis or electric discharge, and the ratio of F radical by F_2 molecule, *i.e.* $[F]/[F_2]$, is defined as level of initiation. Chain reaction step is the chemical pumping reactions that produce excited DF molecules by $D + F_2$ and $F + D_2$ reactions. The excited DF(v) molecules can be deactivated either by to collision with other species as (R-4), or by energy transfer to CO_2 molecules as (R-5). The $CO_2(00^\circ 1)$ molecules formed by the former reaction also can lose their energy through collisional deactivation, or radiate the 10.6 μm wave by stimulated processes.

Calculation

Power Output. By noting the conservation of the amounts of the vibrational molecules which is produced in DF(v) by the chain and transfer reaction, we may deduce the relation

$$\Sigma_v \frac{d[DF(v)]}{dt} = \Sigma v P_v - \Sigma T_v - \Sigma D_{DF} \qquad (1)$$

where

$$\Sigma P_v = \sum_{v=1}^{4} k_c(v)[F][D_2] + \sum_{v=1}^{9} kh(v)[D][F_2] - \sum_{v=5}^{9} k_{-c}(v)[DF(v)][D]$$

$$\Sigma v P_v = k_{c(1)}[F][D_2]\sum_{v=1}^{4} v g_c(v) + kh_{(1)}[D][F_2]\sum_{v=1}^{9} v gh(v) - \sum_{v=5}^{9}[DF(v)][D]_v k_{-c}(v)$$

$$\Sigma T_v = [CO_2(00^\circ 0)]\,\Sigma k_{tr}(v)[DF(v)]$$

$$D_{DF} = [DF(v)]\,\Sigma k_{DF}(M, v)[M]$$

$$g_c(v) = k_c(v)/k_{c(1)},\ gh(v) = kh(v)/kh_{(1)}$$

$d[DF(v)]/dt$ is the rate of increase of the DF(v) population. The sum ΣPv is the sum of the rate of DF(v) generation by the pumping reactions, (R-2) and (R-3), ΣTv is the sum of the rate of transfer into $CO_2(00^\circ 1)$ and ΣD_{DF} is sum of the rate of deactivation by collision. If all of the excited DF(v) molecules are deactivated or transfered their vibrational energies to CO_2 molecules, the steady state for DF(v) can be assumed, and $d[DF]/dt$ term can be neglected.

$$\Sigma v P_v = \Sigma T_v + \Sigma D_{DF} \qquad (2)$$

If the rate of change of $[CO_2(00^\circ 1)]$ by the chemical reaction is defined as $\frac{d}{dt}[CO_2(00^\circ 1)]_{ch}$, it can be expressed by the relation

$$\frac{d}{dt}[CO_2(00^\circ 1)]_{ch} = \Sigma T_v - \Sigma D_{dc} \qquad (3)$$

where

$$\Sigma D_{dc} = [CO_2(00^\circ 1)]\,\Sigma k_{dc}(M)(M)$$

In this equation, ΣT_v term is the rate of transfer and ΣD_{dc} term is the rate of deactivation. Because lower state of laser system, $CO_2(10^\circ 0)$, is close to the ground state, the population of this level is assumed to be Boltzmann distribution during lasing. Therefore $[CO_2(10^\circ 0)]$ can be written

$$[CO_2(10^\circ 0) = [CO_2]\exp(3.97\theta)/\{1+2\exp(1.91\theta) + \exp(3.67\theta) + 2\exp(3.185\theta) + \exp(3.97\theta)\} \qquad (4)$$

$$\theta = -1000/RT$$

and the concentration of $[CO_2(10^\circ 0)]$ at rotational level J is represented by

$$[CO_2(10^\circ 0, J)] = [CO_2(10^\circ 0)]\frac{2\theta_r}{T}(2J+1)\exp[-hcAJ(J+1)/kT] \qquad (5)$$

where

θ_r: rotational characteristic temperature
A : rotational constant
c : velocity of light

With assumption of gain-equals-loss condition, the concentration of the upper lasing level $CO_2(00^\circ 1)$ is given by[9]

$$[CO_2(00^\circ 1)] = \frac{2\pi\alpha_{th} T\exp[hcAJ(J-1)/kT]}{hN_A\omega_c B\phi\theta_r(2J+1)} + [CO_2(10^\circ 0)]\exp(-hcAJ/kT) \qquad (6)$$

where

α_{th} : threshold gain;
value depends on the optical geometry of cavity condition

$\alpha_{th} = -(1/2L)\ln(r_o \cdot r_L)$

L: the length between the mirror
r_o, r_L: reflectivity of mirror

h : Planck constant
N_A: Avogadro number
wc : line position (10.6 μm)
B : Einstein coefficient[17-20]
ϕ : line profile[21-23]

If we define the rate of real change of $[CO_2(00^\circ 1)]$ in the upper level as $\frac{d}{dt}[CO_2(00^\circ 1)]_{Re}$, it is obtained from the differentiation of Eq. 6.

$$\frac{d}{dt}[CO_2(00^\circ 1)]_{Re} = d[CO_2(00^\circ 1)]/dt \qquad (7)$$

Table 2. Initial condition for identifying the model

	Mol ratio of the reactants				Initial temperature	Pressure		Cavity condition		Level of initiation	
	D_2	F_2	CO_2	He	K	(torr)	R_o	R_1	L(cm)		
Case I	1	1	50	0	300	50	0.9	1	100	0.1-0.001	low pressure ref. 20
Case II	1	1	8	40	300	50	0.9	1	100	0.1-0.0001	low pressure ref. 20
Case III	1	1	6	19	300	45-760	0.8	1	61	0.0149	high pressure ref. 21

The subtraction of $\frac{d}{dt}[CO_2(00°1)]_{Re}$ from $\frac{d}{dt}[CO_2(00°1)]_{ch}$, which is obtained from Eq.3 and 7, is the laser photon emission rate (x) of $CO_2(00°1)$. The pulse power and energy can be calculated from following relations.

$$P(t) = hcN_A \omega_c x \qquad (8)$$

$$E(t) = \int_0^{T_c} P(t)\, dt \qquad (9)$$

T_c: duration time

Concentration of Reactants and Temperature of the System. For the calculation of lasing power, we need detailed informations on the concentrations and the temperature of reactants as a function of time. If we define that [DF1] and [DF2] are the concentration of DF(v) which is produced by the reaction (R-2) and (R-3) respectively, and [DF3] is that of DF(v)-whose vibrational level is higher than 5-decomposed by the reverse reaction of (R-2), these relation can be expressed as follows

$$d[\mathrm{DF1}]/dt = \sum_{v=1}^{4} g_c(v)\, k_c(i)\, [\mathrm{F}]\, [\mathrm{D_2}] \qquad (10)$$

$$d[\mathrm{DF2}]/dt = \sum_{v=1}^{9} g_h(v)\, k_h(i)\, [\mathrm{D}]\, [\mathrm{F_2}]$$

$$d[\mathrm{DF3}]/dt = -[\mathrm{D}]\, [\mathrm{DF2}] \sum_{v=5}^{9} k_{-c}(v) g_h(v) / \Sigma g_h(v)$$

where

$$[D_2] = [D_2]_o - [DF1] - [DF3]$$
$$[F_2] = [F_2]_o - [DF2]$$
$$[D] = [DF1] - [DF2] + [DF3]$$
$$[F] = [F]_o - [DF1] + [DF2] - [DF3]$$
$$[DF] = [DF1] + [DF2] + [DF3]$$

Since a CO_2 transfer chemical laser usually extracts for lasing by 10% or less the energy released by the chemical reactions (R-2) and (R-3)[9], the rate of increase of temperature may be obtained from the energy equation.

$$\frac{dT}{dt} = \frac{\frac{d[\mathrm{DF1}]}{dt}\Delta H_c + \frac{d[\mathrm{DF2}]}{dt}\Delta H_h}{\Sigma N_i C_v} \qquad (11)$$

where $\Sigma N_i C_v$ is the total heat capacity of reactants at the initial condition.

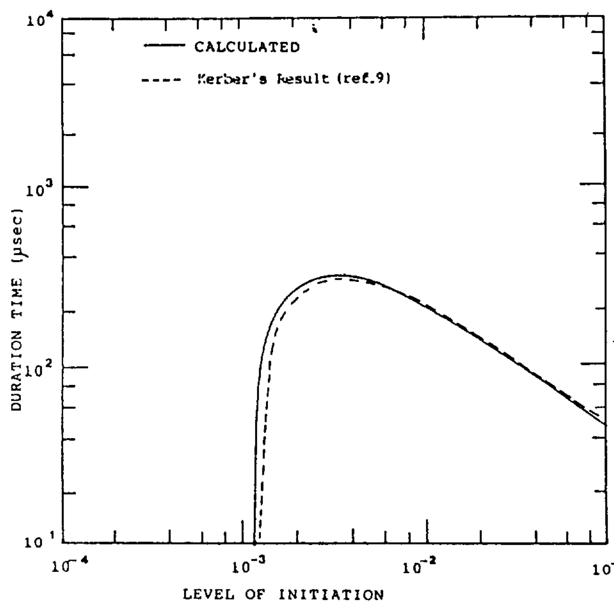

Figure 1. Effect of level of initiation on pulse duration. F_2:D_2:CO_2:He = 1:1:50:0.

Since Eq.10 and 11 are coupled differential equations, one can solve these equations by modified Runge-Kutta-Gill method. The solutions of these equations present the time history of concentrations and temperature of reactants. On the basis of this, we can obtain the rate of photon emission(x) from the Eq.3 and 7. Laser pulse power is calculated from Eq.8 and the pulse energy is obtained from the integration of the power as a function of time as in Eq. 9.

Result and Discussion

Verification of the Present Model. The initial conditions of the reactants presented in Table 2 is selected for comparison with previously reported results[8-10]. Case 1 is selected for the comparison in low pressure condition, case 2 also for low pressure in the presence of inert gas such as He, and case 3 for high pressure condition. For the case 1, effects of level of initiation on lasing duration, peak power and pulse power are shown in Figure 1 to 3. The higher the level of initiation, the faster is the rate of the chain reaction. So the increment of level of initiation makes the peak power increase.

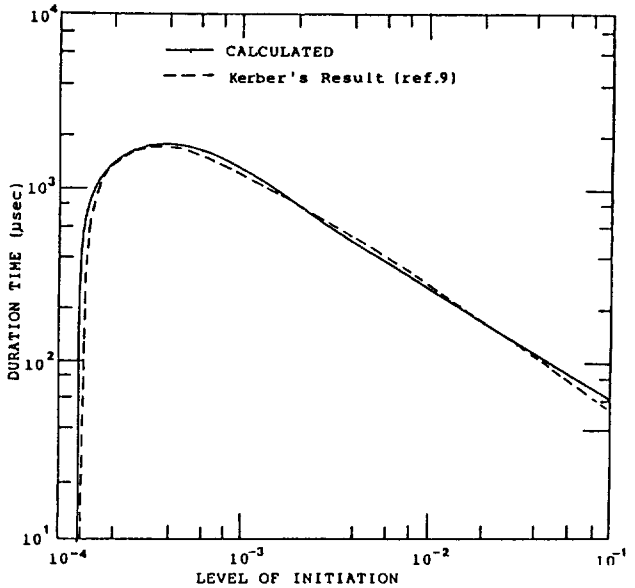

Figure 2. Effect of level of initiation on pulse duration. F_2:D_2CO_2:He = 1:1:8:40.

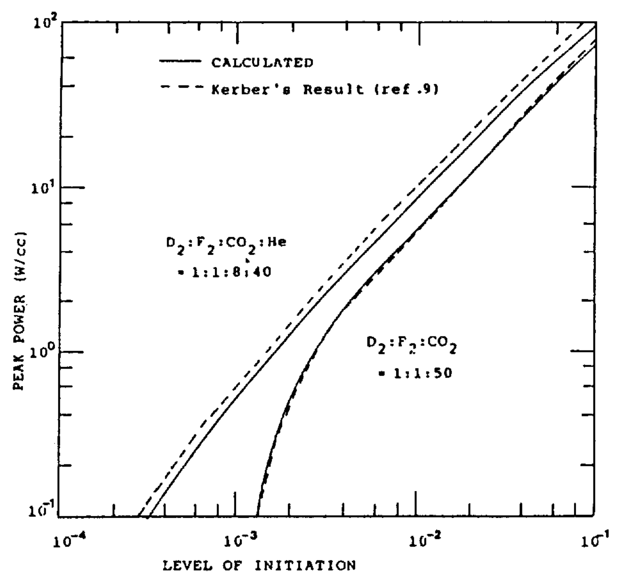

Figure 3. Effect of level of initiation on peak poer.

These figures show this tendency very well and are consistent with the Kerber's work[9]. For a gas mixture with a fixed composition, the effect of varying the total pressure on the lasing energy is found to be a linearly increasing function of pressure. However the duration time of the laser pulse shows the inverse dependence. Figure 4 and 5 indicate this tendency very well. Line A in Figure 4 corresponds to the case which does not consider the deactivation of DF(v), while line B is the case which considers the deactivation process. Line B approaches that of Poehler's result[10] as we consider the deactivation of DF(v). In Figure 5 the tendency shows good agreement, but the absolute value has some difference. It is anticipated that this discrepancy occurs due to the difference in rate coefficients between our study and Poeher's[10]

Temperature and Concentration of Reactants. To understand detailed chemical reactions, we perform the calculation of the concentrations and temperature of reaction

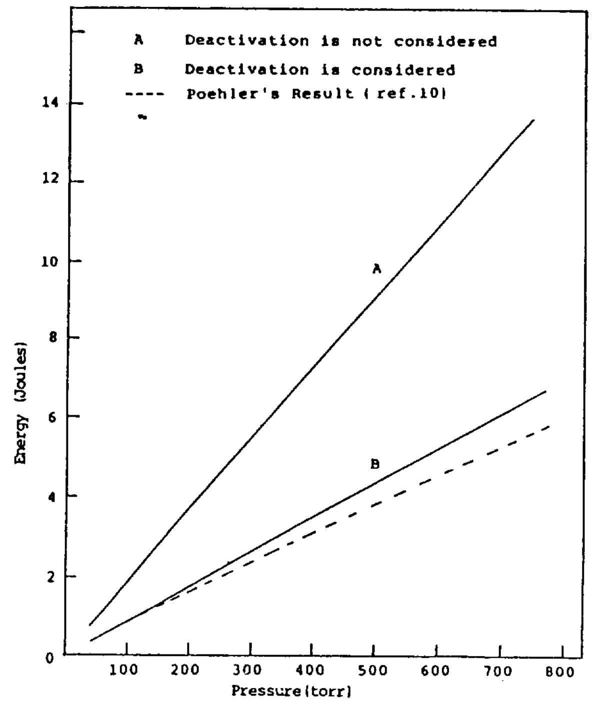

Figure 4. Laser energy versus pressure. D_2:F_2:CO_2:H = 1:1:6:19 level of ini. = 0.0149.

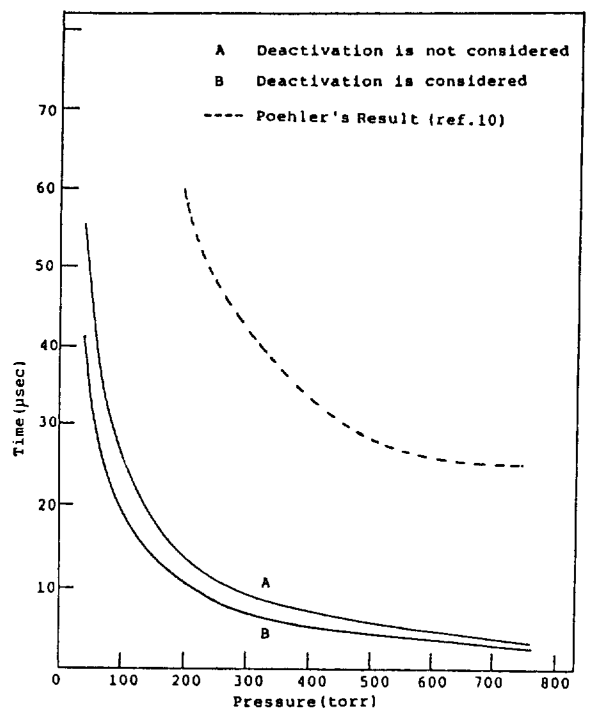

Figure 5. Pulse duration versus pressure. D_2:F_2:CO_2:He = 1:1:6:19 level of ini. = 0.0149.

mixture in the cavity. In Figure 6, both of case 1 and 2 show the similar tendency of increase of temperature as a function of time. Time dependence of concentrations of reactants are presented in Figure 7. Concentration of F radical drops drastically within one micro second, and then slowly increase as time passes. But the concentration of D radical shows the inversion of this tendency. So the sum of concen-

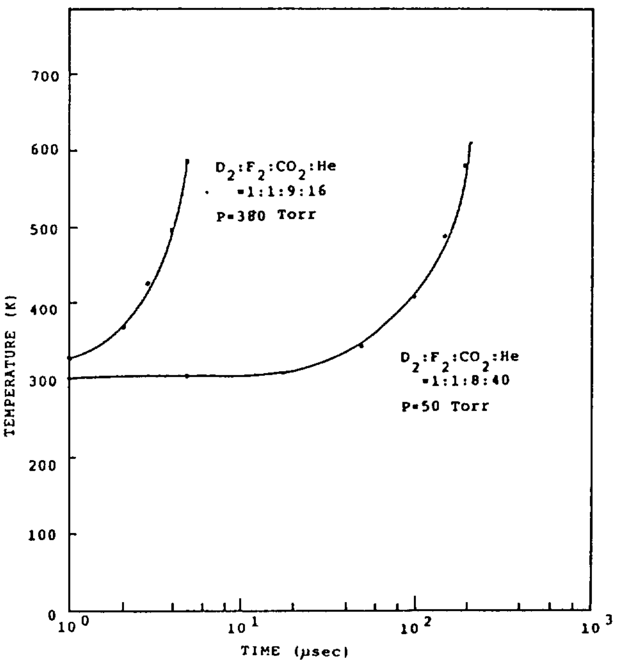

Figure 6. The temperature profiles as a function of time.

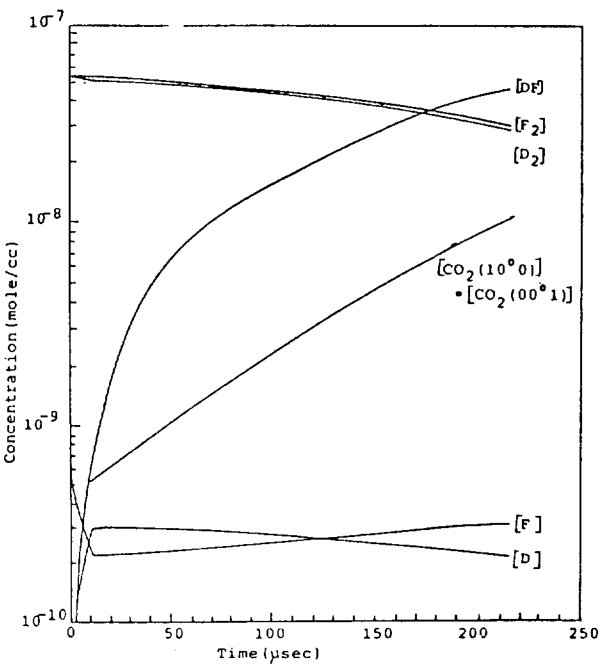

Figure 7. The concentration profiles as a function of time. F_2:D_2:CO_2:He = 1:1:8:40.

trations of these two radicals keep constant during the reaction. It is also shown that concentrations of reaction mixture, $[F_2]$ and $[D_2]$, decrease gradually and that of product, [DF] increases as time passes. The CO_2 concentrations of both $[CO_2(00°1)]$ and $[CO_2(10°0)]$ of lasing species, are also shown in Figure 8. Because $[CO_2(00°1)]$ is the rest of the concentration consumed by stimulated emission, it is lower than $[CO_2(10°0)]$ more or less. But the CO_2 concentrations of both level increase as the temperature increases. Condition of this figure is for the case 2 (level of initiation = 0.01). Those of the case 1 and the case 3 show also the similar tendency.

Optimum Condition. The chemical efficiency of the

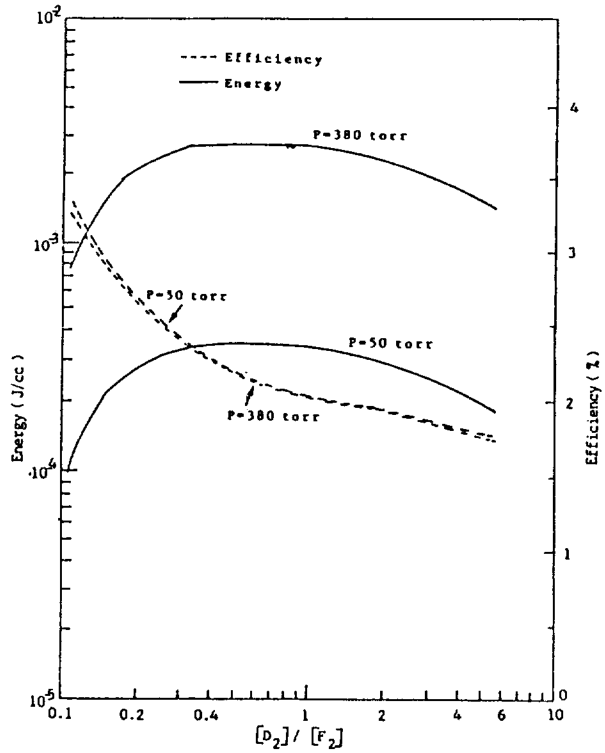

Figure 8. Effect of ratio of $[D_2]/[F_2]$ on laser energy. $D_2 + F_2$:CO_2:He = 2:8:40 level of ini. = 0.0149.

TCL system is defined by the ratio of radiated energy to heats of formation of the combined chain reaction. For obtaining the optimum condition of the composition of the initial mixture of the laser in a typical condition, we calculated the output energy and efficiency as a function of the ratio of the concentrations of D_2, F_2, and CO_2 for both low and high pressures. These results are shown in Figure 8 and 9. In Figure 8, the energy and efficiency of this laser system against the ratio of $[D_2]/[F_2]$ are presented. When the ratio of $[D_2]/[F_2]$ is low, the output is small. The output increases with the increment of this ratio. Especially, when the ratio of $[D_2]/[F_2]$ is in a range between 1/3 and 1, it gives a maximum power output. However, when the ratio is higher than this range, *i.e.* D_2:F_2 = 1:3-1:1, the output energy decreases again. On the other hand the efficiency decreases slowly as the ratio of $[D_2]/[F_2]$ increases. Because the output energy is practically more important than the efficiency, the optimum ratio of $[D_2]/[F_2]$ can be regarded as 1/3-1 in Figure 8. This tendency is independant of the total pressure of the system. The variations of energy and efficiency show same tendency in both pressures, 380 torr and 50 torr. If the ratio of $[D_2]/[F_2]$ is too small or large, *i.e.* out of this range, the chain propagation does not occur properly, so the energy and efficiency decrease. The optimum ratio of $[CO_2]/[D_2 + F_2]$ is shown in Figure 9. The maximum range of the output energy and efficiency can be considered as 1 to 4 and 2 to 4, respectively. Unlike the case of the $[D_2]/[F_2]$ variation, the maximum ranges of both the output energy and efficiency are located within same range. Therefore one can definitely consider the optimum ratio of $[CO_2]/[D_2 + F_2]$ to be in a range between 2 and 4. It means that this ratio has strong relation with the energy of transfer from excited DF to CO_2. If the amount of $[D_2 + F_2]$ is small, it generates small amount of the

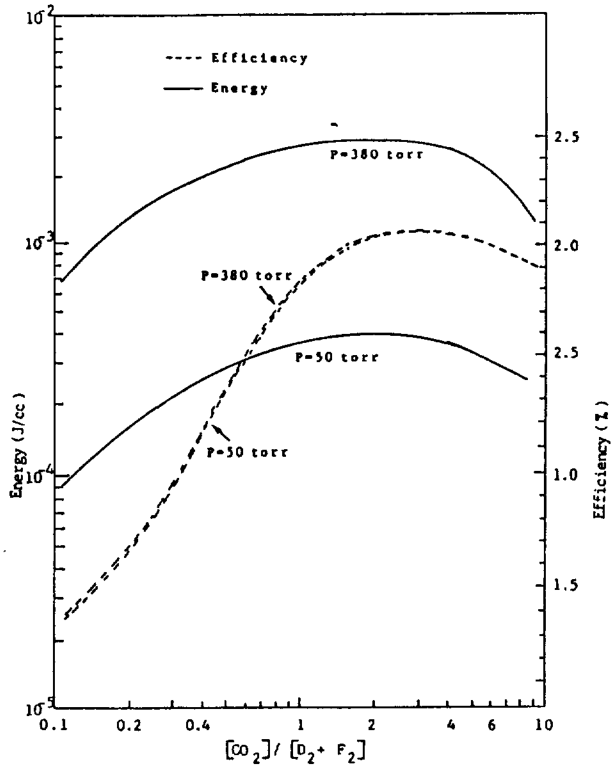

Figure 9. Effect of ratio of $[CO_2]/[D_2+F_2]$ on laser energy. $D_2+F_2+CO_2$:He = 10:40 level of ini. = 0.0149.

excited DF, so it can not pump the CO_2 enough. And if this amount is too high, the excited state of DF can be thought as not to transfer the energy to CO_2 effectively but to be wasted to ground state of DF by deactivation processes. In summary, the optimum ratio of $[D_2]/[F_2]$ is about 1/3-1 and that of $[CO_2]/[D_2+F_2]$ is about 2-4. The present work and most experimental work (including addition of O_2 for high pressure system) have been performed within the above optimal range[11-16].

Conclusion

The power calculation of $DF\text{-}CO_2$ TCL system can be performed well for both low and high pressure range with the simple kinetic model which is considered only 30 reactions. The power rises linearly with increase of total pressure of reactants, and the duration of lasing pulse shows the inverse dependence on pressure. Effect of deactivation of DF(v) on power can be neglected at low pressure and low level of initiation conditions, but this becomes important as pressure increase. The increase of pressure and level of initiation make duration short. However, the changes of concentrations and temperature of reaction show similar tendency in this condition. For a given condition (P = 50 torr and 380 torr, level of initiation = 0.0149). The optimum range of $[D_2]/[F_2]$ is 1/3-1 and that of $[CO_2]/[D_2+F_2]$ is 2-4.

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