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A KINETIC MODEL AND COMPUTER SIMULATION FOR A PULSED DF-CO2 CHEMICAL TRANSFER LASER

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Laboratory Operations
THE AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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FOREWORD

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13. ABSTRACT

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I. INTRODUCTION

Evaluation of the performance of gas and chemical lasers requires an understanding of the kinetic and chemical mechanisms that pump and deactivate the energy levels associated with lasing. Normally, a simple model may be constructed that explains why lasing occurs for a particular species. However, a more detailed representation of the mechanisms is needed for an accurate prediction of laser performance. Recently, comprehensive theoretical models for computer simulation of laser performance have been developed [1-4] that utilize a detailed formulation of the kinetics of the lasing system. A review of the kinetics for the CO_2-N_2 laser system is given by Taylor and Bitterman [5]; Cohen [6] gives a similar review for the H_2+F_2 chemical laser. With the discovery and development [7-16] of the DF-CO_2 chemical transfer laser, it is desirable to assemble a kinetic model that will facilitate future studies of this laser.

This report presents the results of our efforts to gather and compile a complete set of the required rate coefficients based on data available in the literature, comparisons with similar reactions with known rate coefficients, or various theoretical approaches. We have drawn heavily on Refs. [5] and [6]; we include data prior to those studies only when necessary.

A schematic of the DF-CO_2 transfer and the CO_2 kinetics is shown on an energy level diagram in Fig. 1. The vibration-translation (VT) energy transfer reactions are denoted by dotted lines; intramolecular vibration-vibration (VV) reactions are shown as solid lines; and the intermolecular VV

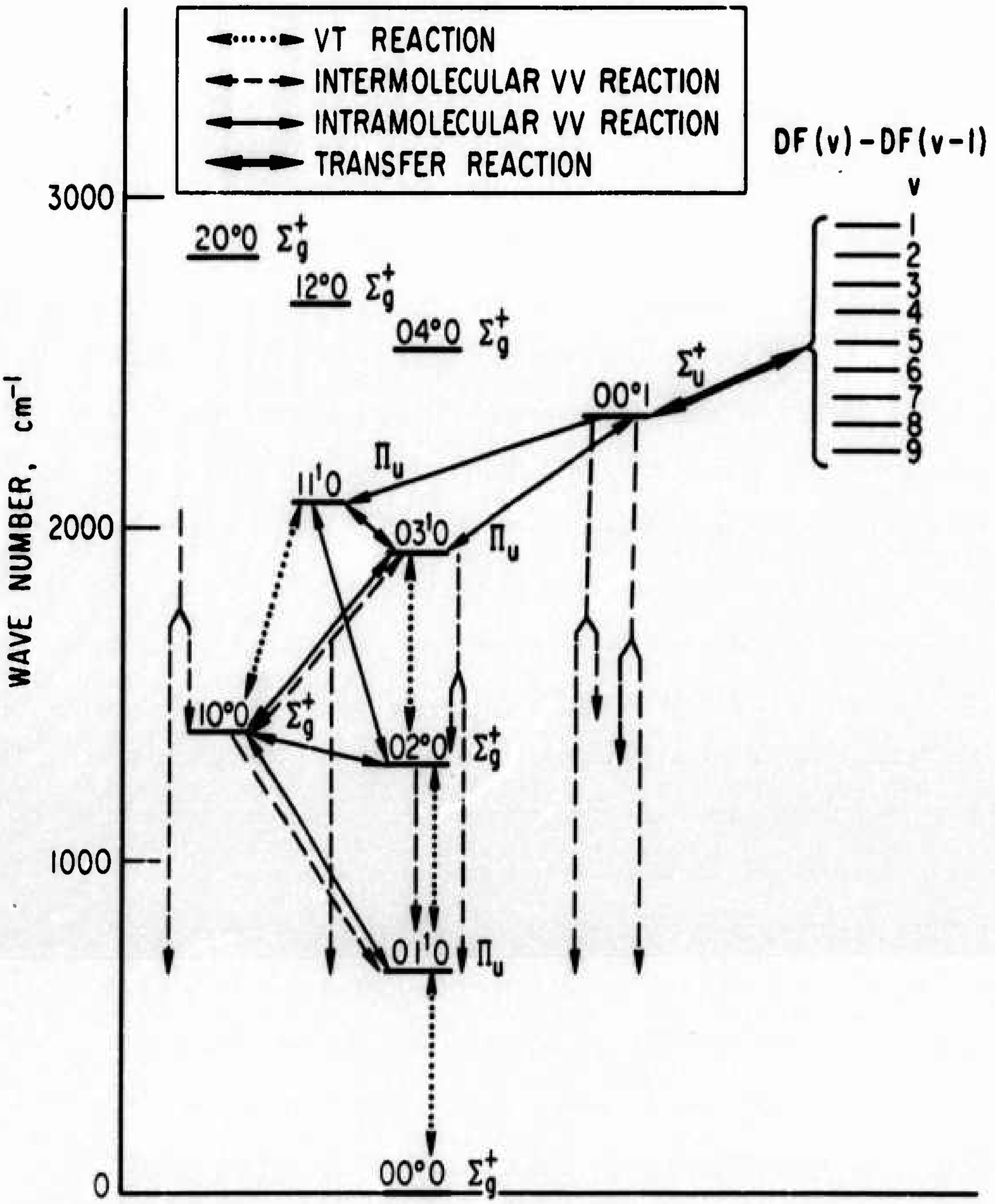

Fig. 1. Vibrational energy level diagram for CO_2 kinetics including the DF transfer energy. The states (03^30) and (02^20) are deleted for clarity. These states are included in the model.

transfer reactions are denoted by dashed lines with arrows to the final states. Initial states of these intermolecular VV reactions are $CO_2(00^0C)$ and the CO_2 state at the tail of the dashed arrow. The states (03^10) and (03^30) are assumed to be in equilibrium and are statistically combined as (030). Reactions involving the state (02^20) are similar to those for (02^00) but have been omitted from the figure to preserve clarity.

We limit our model to energy levels in CO_2 below $CO_2(00^01)$; for comparison, Fig. 1 shows three higher states. This limitation is artificial; however, we expect levels above (00^01) to play a minor role in transfer laser performance. We assume DF to transfer only to CO_2 (00^01). The net effect on laser performance of transfer to levels higher than $CO_2(00^01)$ and their ultimate deactivation to (00^01) should be small.

The laser simulation program used in this study utilizes rate coefficients of the form [2]

$$k = AT^D e^{-E/RT}$$

where A and D are constants, E is the activation energy, R is the gas constant, and T is the temperature. All rate coefficients are presented in this form. The proposed kinetic model is used with this program to determine the relative importance of kinetic mechanisms during a pulse for two different initial F atom concentrations. This model has proven successful in the prediction of characteristics of the HF pulsed laser [17]. A number of rate coefficients are roughly approximated; therefore, they are varied to determine the sensitivity of laser performance to their values under typical laboratory conditions. This sensitivity study shows that the peak pulse power and pulse energy are sensitive to the $F_2 + D_2$ pumping reactions and to the temperature dependence of the DF(v)-CO_2 transfer rate coefficient and its variation with v. The temperature variation of the rate of VT deactivation of $CO_2(00^01)$ by DF and the DF-F and DF-D VT processes are also important in predicting laser performance. For the reactant mixtures studied, the rate of equilibration of the lower levels in CO_2 is so fast that they are near equilibrium, and thus modeling is insensitive to the value of rate coefficients for these levels.

In Section II, we review the kinetics for the $D_2 + F_2$ system, which may be used for modeling the DF chemical laser. Sections III and IV review the kinetics of DF - CO_2 vibrational energy transfer and the kinetics of CO_2 relaxation, respectively. Section V describes the computer experiments, and Section VI gives a brief summary of the work.

II. THE $D_2 + F_2$ KINETICS

Theoretical and experimental studies of the kinetics of $H_2 + Cl_2$ and of $H_2 + F_2$ mixtures have been made to test proposed theories and increase our understanding of the underlying processes. We draw heavily on these and analogous mixtures for modeling of $D_2 + F_2$ kinetics when direct experimental measurements are not available.

A. RECOMBINATION - DISSOCIATION REACTIONS

The initiating step in the exothermic chemical reaction is usually dissociation of F_2 or D_2. Conversely, the recombination of D and F with themselves or each other represents a potential energy loss mechanism for laser systems. Under typical operating conditions, these reactions have little or no effect on laser performance; however, we include them for completeness. For the dissociation rate of F_2, we use the rate coefficient given by Ref. [6],

(1) $$F_2 + M \rightleftharpoons F + F + M$$

$$k_1 = 5 \times 10^{13} e^{35.30}$$

where M is all collision partners. All rate coefficients are given in units of cc/mole-sec and $\theta = -10^3/RT$. The recombination rate data of Jacobs, Giedt, and Cohen [18] for React. (2) are used:

(2) $$D_2(0) + M \rightleftharpoons D + D + M$$

where

$$k_{-2} = 10^{18} T^{-1}$$

for M equals all species except D_2 and D. For D_2 and D, this rate is increased by a factor of 1.75 and 20, respectively. The minus subscript indicates a backward rate. The populations in the higher levels of $D_2(v)$ are small and are not included in React. (2).

The rate of dissociation of HF has been measured by Jacobs, Giedt, and Cohen [19]. We take their rate coefficient for DF dissociation by all species

$$(3) \qquad DF(v) + M \rightleftharpoons D + F + M \qquad v = 0,\ldots,9$$

with

$$k_3 = \frac{1.2 \times 10^{19}}{n} T^{-1.0} e^{-(D^* - E_v)/RT}$$

where D* (137.13 kcal) is the dissociation energy of DF(0), E_v is the vibrational energy above ground state, and n is the number of vibrational levels considered, here taken as 10. The factor 1/n is used so that the total recombination rate is in agreement with experiment; thus, all rates of recombination have equal probability. The vibrational energy for level v is computed from data given by Herzberg [20]. The enthalpies of formation are listed in Table I for all species included in our model.

Table I. Enthalpy of Formation of Included Species

Species	ΔH_f^0 (kcal/mole)	Species	ΔH_f^0 (kcal/mole)
DF(0)	-64.98	$CO_2(00^01)$	-87.331
DF(1)	-56.67	$CO_2(11^10)$	-88.111
DF(2)	-48.62	$CO_2(030)$	-88.531
DF(3)	-40.83	$CO_2(10^00)$	-90.081
DF(4)	-33.29	$CO_2(02^20)$	-90.236
DF(5)	-26.00	$CO_2(02^00)$	-90.381
DF(6)	-18.95	$CO_2(01^10)$	-92.141
DF(7)	-12.13	$CO_2(00^00)$	-94.051
DF(8)	- 5.56	$D_2(0)$	0.00
DF(9)	0.786	$D_2(1)$	8.544
F	18.9	$D_2(2)$	16.764

B. CHEMICAL PUMPING REACTIONS

The overall rate coefficients of the chemical pumping reactions

(4) $$F + D_2 \overset{k_4(v)}{\rightleftharpoons} DF(v) + D$$

and

(5) $$D + F_2 \overset{k_5(v)}{\rightleftharpoons} DF(v) + F$$

have been calculated to be $10^{13.79}e^{1.46\theta}$ and $10^{14.24}e^{2.4\theta}$ by Wilkins [21] using absolute reaction rate theory. An overall rate of $10^{13.8}e^{2.16\theta}$ for k_4 has been obtained by Jaffe and Anderson [22] from a limited number of classical trajectory calculations. In addition, Monte Carlo calculations by Muckerman [23] indicate that the overall rate for React. (4) is about 0.6 times that of $F + H_2$, in agreement with Ref. [22] and the calculations of Wilkins [24].

On the basis of heats of formation in Table I, these reactions release 30.63 and 99.33 kcal/mole, respectively, for v = 0. The distribution of this energy among the vibrational levels of DF(v) for React. (4) has been measured by Parker and Pimentel [25] at 390°K, using an equal gain chemical laser experiment, and by Schafer, et al. [26] and Anlauf, et al. [27], using a crossed molecular beam and a discharge flow technique, respectively. These data are compared in Table II. The data of Schafer, et al., are for back scattering only and are inconsistent with trends found for the more widely studied $F + H_2$ reaction. Their distribution also disagrees

Table II. F + D_2 Pumping Distribution

Vibrational Level	E_v (kcal/mole)[a]	k_v [27]	k_v [26]	k_v [25]
0	0	----	0.012	----
1	8.31	0.1	0.019	----
2	16.36	0.5	0.051	0.63
3	24.15	1.0	0.285	1.0
4	31.69	0.72	1.0	<1.19

[a] Vibrational energy above ground state

with the laser experiments of Basov, et al. [14]. The pumping distribution data for F + H_2 includes the equal gain measurement at 539°K of Parker and Pimentel [25]; crossed molecular beam studies of Schafer, et al. [26]; discharge flow system measurements of Anlauf, et al. [27], Polanyi and Tardy [28], and Jonathan, et al. [29-31]; and the trajectory calculations of Wilkins [32]. These data are compared to those of React. (4) in Fig. 2. The abscissa in the figure $[(E_v - E_o)/|\Delta H|]$ is the ratio of the vibrational energy of a given level to the heat released for the particular reaction. From the figure, we see that the data of Anlauf, et al., are the most consistent with the expected trends; we use this distribution and the total rate computed by Wilkins.

Reaction (4) is not sufficiently exothermic to produce DF(v) above v = 4; however, there is some evidence in the H_2 + F_2 system [6] that this reaction, running in reverse at the higher v levels, is a sink for excited species produced by reactions like (5). Hence, we use rate coefficients analogous to those of Cohen for H_2 + F_2:

$$k_{-4}(v = 5) = 4 \times 10^{12} T^{0.15} e^{30}$$

and

$$k_{-4}(v \geq 6) = 1.2 \times 10^{13} T^{0.15}$$

These values are roughly twice as large as predicted by the recent Monte Carlo calculations of Wilkins [33].

No studies have been made to determine the distribution of pumping by React. (5). Evidence that this reaction pumps to v = 9 is given by the

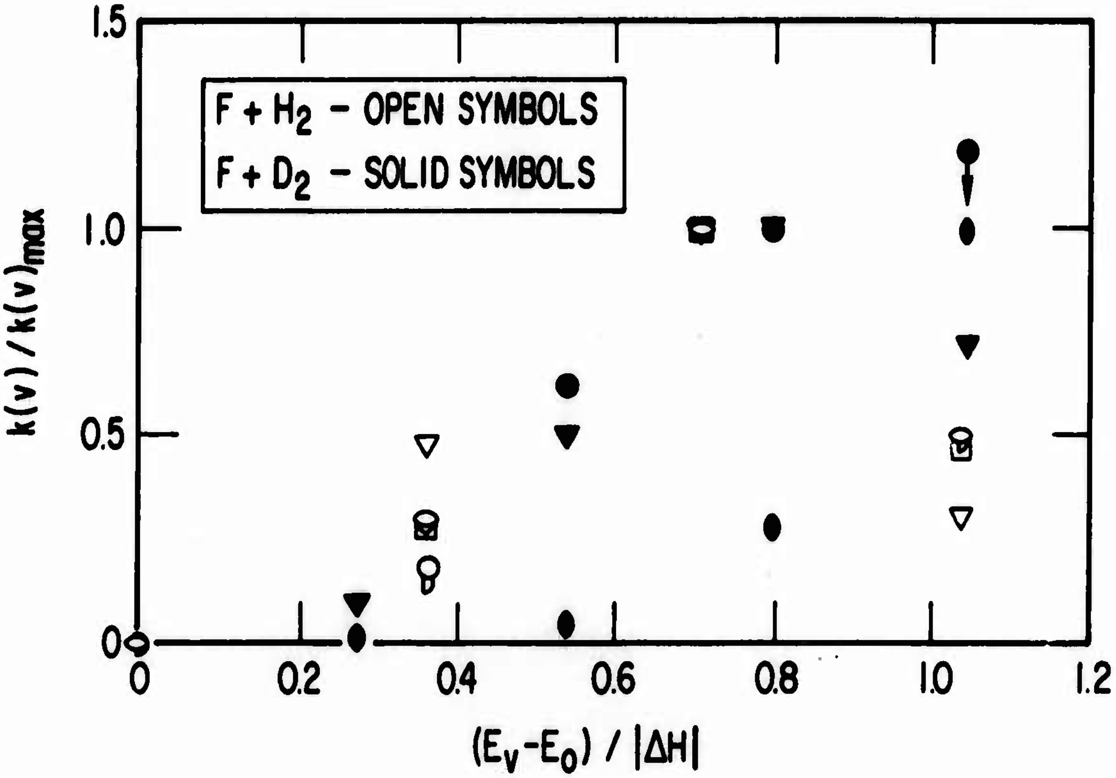

Fig. 2. Pumping distributions for F + H_2 and F + D_2: equal gain technique, ○ Ref. [25]; crossed molecular beam study, ⬯ Ref. [26]; discharge flow system, ▽ Ref. [27]; □ Ref. [28], ◇ Refs. [29] and [30], ⬭ Ref. [31]; Monte Carlo calculations, D Ref. [32].

spectral output of the DF laser measurements of Basov, et al. [14]. Jonathan, et al. [29, 30] have reported the distribution of pumping by $H + F_2$. We expect that the similarity shown in Fig. 2 between $F + H_2$ and $F + D_2$ will hold between $H + F_2$ and $D + F_2$. In Fig. 3, we plot the distributions reported by Jonathan, et al. [29, 30]. By connecting the data points with a smooth curve and denoting the vibrational energy levels of DF(v), we estimate the pumping distribution to be

$$k_5(0):k_5(1):k_5(2):k_5(3):k_5(4):k_5(5):k_5(6):k_5(7):k_5(8):k_5(9)$$

$$= 0:0.16:0.27:0.40:0.57:0.72:0.86:1:0.97:0.61$$

With these estimates of the distribution of pumping into DF(v), Reacts. (4) and (5) convert 79% and 46%, respectively, of the available chemical energy into vibrational energy.

C. VIBRATIONAL-TRANSLATIONAL ENERGY TRANSFER IN DF

Vibrational deactivation of an excited species through collisions is a significant energy loss mechanism in chemical lasers,

$$(6) \qquad DF(v) + M \rightleftharpoons DF(v-1) + M$$

This rate coefficient has been measured in a shock tube for v = 1 by Bott and Cohen [34] over a wide temperature range for M = H_2, N_2, Ar, and DF. These measurements of the Napier time $p\tau$ are converted to rate coefficients by assuming an harmonic oscillator model and using the relation

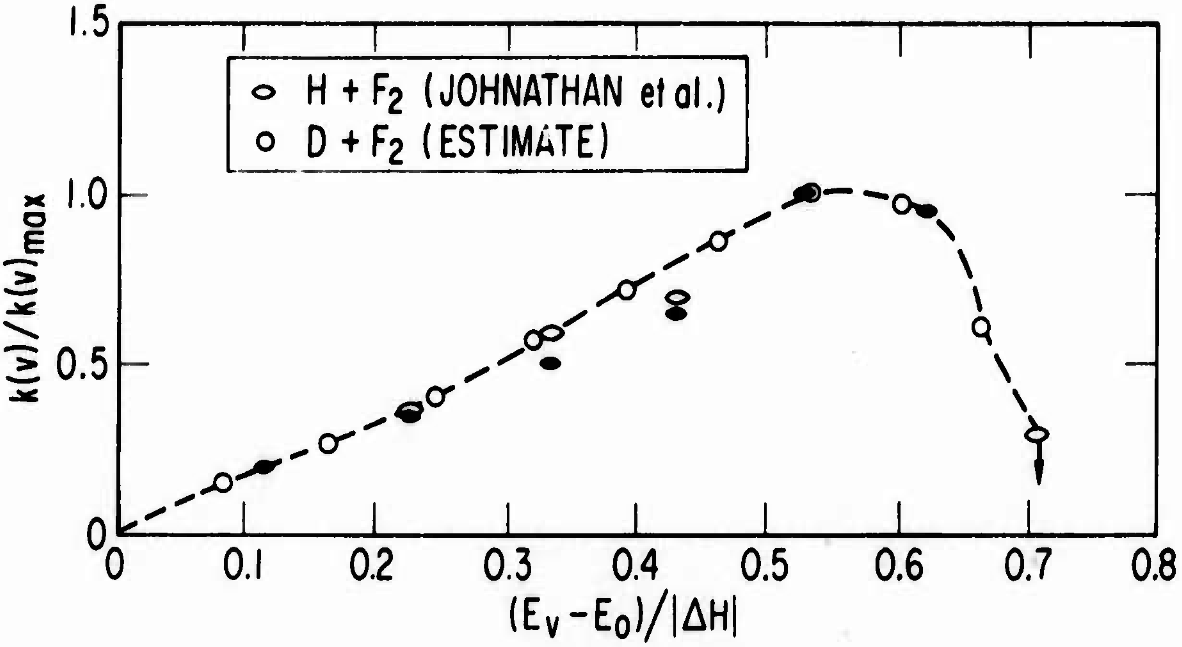

Fig. 3. Estimate of D + F_2 pumping distribution from H + F_2 data: ● Ref. [29], ○ Ref. [30].

$$k = \frac{RT}{p\tau(1 - e^{-E_1/RT})} \tag{1}$$

Stephens and Cool [35] also measured the DF-DF VT rate using a chopped DF laser at 350°K. These experimental rates are shown in Fig. 4 on a Landau-Teller plot with approximate analytic rate coefficients matched to the data for the temperature range 300° to 2000°K. The character of the DF-DF rate as a function of temperature is similar to that of the HF-HF rate [6, 36]. The rate coefficients matched to the data in Fig. 4 are:

$$k_6 = 3.4 \times 10^4 T^{2.2} \qquad M = H_2$$

$$k_{6a} = 4.0 \times 10^3 T^{2.2} \qquad M = N_2$$

$$k_{6b} = 3.7 \times 10^{-6} T^{4.66} \qquad M = Ar$$

$$k_{6c} = 4.5 \times 10^4 T^{2.2} + 5.3 \times 10^{16} T^{-2.0} \qquad M = DF$$

Except for high-temperature measurements of DF-F, deactivation of DF(v) by other collision partners has not been measured. The efficiency of H_2 in deactivating DF is close to the efficiency of H_2 in deactivating HF [34]. Hence, we use the measurement of HF relaxation by D_2 of Bott and Cohen [36] for relaxation of DF by D_2

$$k_{6d} = 0.14\ T^{3.66} \qquad M = D_2$$

We estimate the efficiency of F_2 in deactivating DF to be approximately the same as Ar, and the rate for DF-He is taken as twice the DF-Ar rate

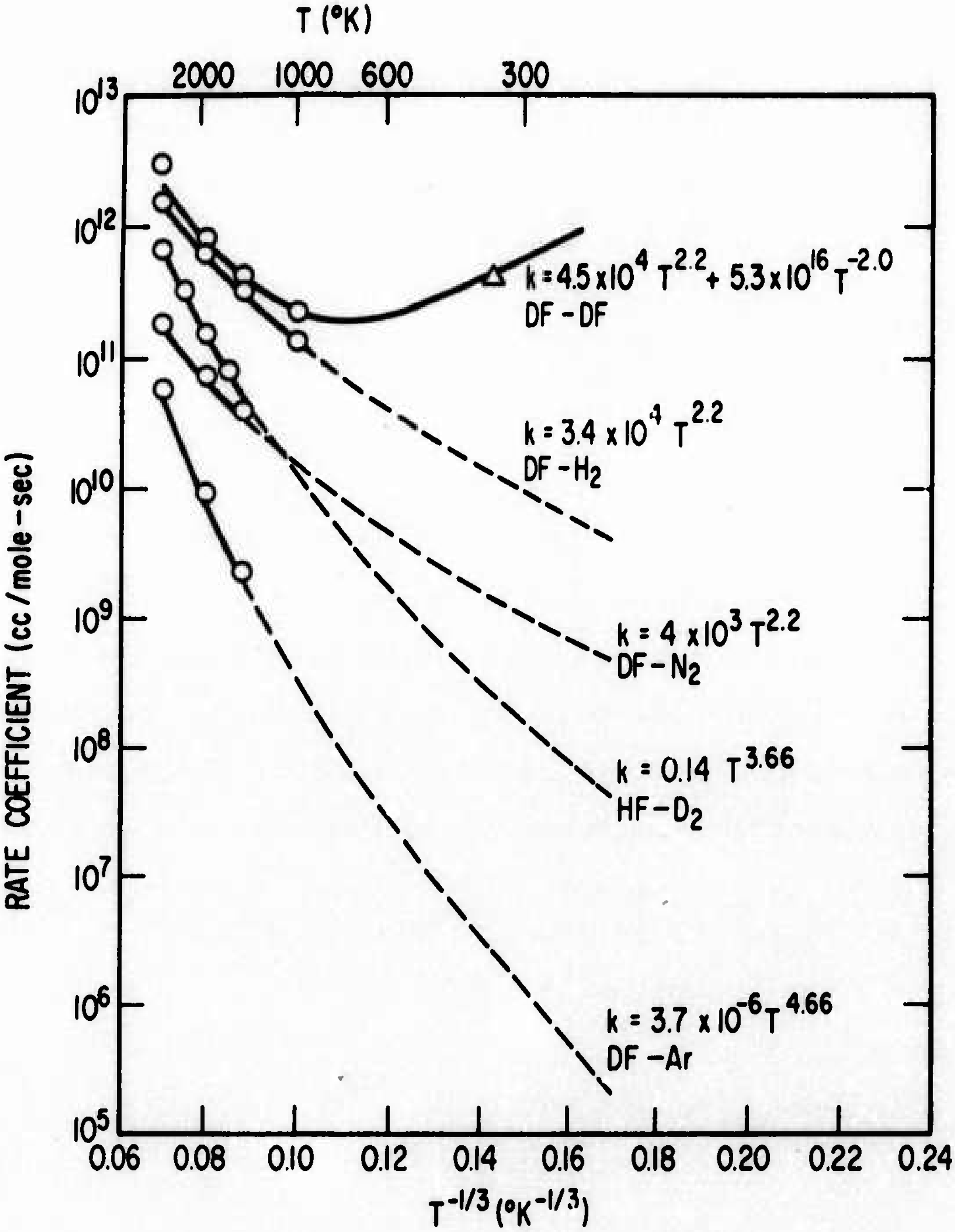

Fig. 4. Measured rate coefficients for VT deactivation of DF(1): ○ Ref. [34], △ Ref. [35].

analogous to their efficiency in deactiviating HF [36]. The deactivation rate for DF - CO_2 is assumed to be similar to that of N_2. For all these reactions, we assume the deactivation rate is linear with v; i.e., we assume an harmonic model. There has been speculation regarding the variation of these rates with v; however, this question can only be answered by careful experiment.

We expect the deactivation rate with F and D to be quite fast. Shock tube measurements of the HF - F VT rate near 2000°K by Bott and Cohen [37] show relaxation by F to be 26.5 times more efficient than HF self-relaxation at 2000°K. Also at 2000°K, shock tube measurements of Blauer, et al. [38] show that HF-F/DF-F ~ 2.4 and DF - F is approximately 1.5×10^{13} cc/mole-sec, which is in agreement with the shock tube measurements of Bott and Cohen [34]. Ridley and Smith [39] have measured the rate coefficients for deactivation of HCl(v) by Cl for v = 3, 2, and 1 to be 4.8×10^{12}, 1.9×10^{12}, and 5.8×10^{11} cc/mole-sec at room temperature. We have used these rates to approximate the efficiency of F and D in deactivating DF(v). Thus, for M = D and F, we take

$$k_{6e}(1) = 5.0 \times 10^{12} e^{1.25\theta}$$

$$k_{6e}(2) = 5.0 \times 10^{12} e^{0.55\theta}$$

$$k_{6e}(v \geq 3) = 5.0 \times 10^{12}$$

The activation energies for v = 1 and 2 are chosen to approximate the measurements of Ref. [39].

These values are consistent with extrapolation of Ref. [38] and with recent trajectory calculations of the HF -H VT rate by Wilkins [33] where multiple quantum deexcitation was predicted. We have deviated from the $k_{v,v-1} = vk_{1,0}$ form for these reactions, since they are apparently chemical in nature.

D. VIBRATIONAL-VIBRATIONAL ENERGY TRANSFER IN DF

Since the efficiency of quantum exchange for $\Delta v > 1$ is expected to be orders of magnitude less than for $\Delta v = 1$, we follow Ref. [6] and consider only

$$DF(v) + DF(v') \rightleftharpoons DF(v+1) + DF(v'-1) \tag{7}$$

where v - v' = 0, 1, 2. Cohen includes up to v - v' = 3; however, with the increased complexity of this system, we must limit the number of reactions. At present, no experimental data on VV transfer in DF are available. For reactions of this type, the rate varies with degree of resonance and, hence, would be expected to vary with the rotational levels of the colliding molecules. We make no attempt to correct for this effect and choose a rate suggested by Cohen [6] that is based on the theory of Rapp and Englander-Golden [40] and the data of Chen and Moore [41] for HCl

$$k_{0,1;1,0} = Z \times 4 \times 10^{-5} T \times 10^{-\Delta\nu/433}$$

where Z is the gas kinetic bimolecular collision rate and $\Delta\nu$ is the translational energy released in wave numbers. The gas kinetic bimolecular collision rate is given by

$$Z = \left|8\pi RT\left(\frac{1}{m_A} + \frac{1}{m_B}\right)\right|^{1/2}\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 N_A \qquad (2)$$

and N_A is Avogadro's number. Table III contains a list of the collision diameters σ_j and the masses m_j used in our gas kinetic calculations. We assume that the rate coefficients behave as though the vibrational levels of the molecule are harmonic and

$$k_{v,\, v+1;v',\, v'-1} = (v+1)v'Z \times 4 \times 10^{-5}T \times 10^{-\Delta\nu/433}$$

where $\Delta\nu$ is the translational energy released for each reaction.

Recent measurements [42] for HCl VV reactions indicate that this theory may not be appropriate for hydrogen halides with v and v' > 1. Although these VV rates are in question, they probably do not play a major role in predicting laser performance, as suggested by computer calculations of Kerber, Emanuel, and Whittier [43] and the analytic study by Emanuel and Whittier [44] for the HF pulsed laser.

E. VIBRATIONAL-VIBRATIONAL ENERGY TRANSFER BETWEEN DF AND D_2

Since vibrational energy transfer between DF and D_2 may represent a significant loss of laser energy, we include the reaction

$$(8) \qquad DF(v) + D_2(v') \rightleftharpoons DF(v-1) + D_2(v'+1)$$

in our kinetic model. We use the same probability for the backward rate of this reaction as for DF-DF VV reactions,

Table III. Molecular Parameters Used in Data Analysis

Species	Molecular Weight	σ(Å)
CO_2	44.01	3.95
Ar	39.94	3.405
DF	21.01	3.0
F_2	38.00	3.41
F	19.00	2.9
D	2.02	2.68
D_2	4.03	2.92
N_2	28.01	3.85
He	4.00	2.57

$$k_{-8} = (v' + 1)vZ \times 4 \times 10^{-5}T \times 10^{-\Delta\nu/433} \qquad (3)$$

Recent measurements by Airey and Fried [45] of the rate of the HF-H_2 VV reaction are of the same order as predicted by Eq. (3).

F. VIBRATIONAL-TRANSLATIONAL ENERGY TRANSFER IN D_2

These reactions are included to prevent unrealistic inversions in the D_2 populations. Hence, we include

$$(9) \qquad D_2(v) + M \rightleftharpoons D_2(v-1) + M$$

This rate is determined from the compilation of Napier times given by Stretton in Ref. [46]. For M = Ar, this gives

$$k = 1.51 \times 10^{-5}T^{4.6}$$

We use this rate for all species except D_2, D, and He. For M = D_2, we increase the rate by a factor of 4.8 to be consistent with Ref. [46], and we estimate that D and He are at least twice as effective as Ar.

The proposed kinetic model for the F_2 + D_2 chemical system is summarized by Reacts. (1) - (9) of Table IV.

Table IV. Recommended Rate Coefficients for the D_2 - F_2 - CO_2 Chemical Laser

React.	Reaction[a]	Rate Coefficient[b]
1[c]	$F_2 + M_1 \rightleftharpoons F + F + M_1$	$k_1 = 5.0 \times 10^{13} e^{35.3\theta}$
2	$D_2(0) + M_2 \rightleftharpoons D + D + M_2$	$k_{-2} = 10^{18} T^{-1.0}$
3_v	$DF(v) + M_1 \rightleftharpoons D + F + M_1$	$k_{3_v} = 1.2 \times 10^{18} T^{-1.0} e^{(137.13-E_v)\theta}$ v=0,...,9
4a	$F + D_2(0) \rightleftharpoons DF(1) + D$	$k_{4a} = 2.66 \times 10^{12} e^{1.46\theta}$
4b	$F + D_2(0) \rightleftharpoons DF(2) + D$	$k_{4b} = 1.33 \times 10^{13} e^{1.46\theta}$
4c	$F + D_2(0) \rightleftharpoons DF(3) + D$	$k_{4c} = 2.66 \times 10^{13} e^{1.46\theta}$
4d	$F + D_2(0) \rightleftharpoons DF(4) + D$	$k_{4d} = 1.91 \times 10^{13} e^{1.46\theta}$
4e	$F + D_2(0) \rightleftharpoons DF(5) + D$	$k_{-4e} = 4.0 \times 10^{12} T^{0.15} e^{3\theta}$
$4f_v$	$F + D_2(0) \rightleftharpoons DF(v) + D$	$k_{-4f_v} = 1.2 \times 10^{13} T^{0.15}$ v=6,...,9
5a	$D + F_2 \rightleftharpoons DF(1) + F$	$k_{5a} = 5.0 \times 10^{12} e^{2.4\theta}$
5b	$D + F_2 \rightleftharpoons DF(2) + F$	$k_{5b} = 8.45 \times 10^{12} e^{2.4\theta}$
5c	$D + F_2 \rightleftharpoons DF(3) + F$	$k_{5c} = 1.25 \times 10^{13} e^{2.4\theta}$
5d	$D + F_2 \rightleftharpoons DF(4) + F$	$k_{5d} = 1.78 \times 10^{13} e^{2.4\theta}$
5e	$D + F_2 \rightleftharpoons DF(5) + F$	$k_{5e} = 2.25 \times 10^{13} e^{2.4\theta}$

Table IV. Recommended Rate Coefficients for the D_2 - F_2 - CO_2 Chemical Laser (Continued)

React.	Reaction[a]	Rate Coefficient[b]
5f	$D + F_2 \rightleftharpoons DF(6) + F$	$k_{5f} = 2.69 \times 10^{13}\ e^{2.4\theta}$
5g	$D + F_2 \rightleftharpoons DF(7) + F$	$k_{5g} = 3.13 \times 10^{13}\ e^{2.4\theta}$
5h	$D + F_2 \rightleftharpoons DF(8) + F$	$k_{5h} = 3.04 \times 10^{13}\ e^{2.4\theta}$
5i	$D + F_2 \rightleftharpoons DF(9) + F$	$k_{5i} = 1.91 \times 10^{13}\ e^{2.4\theta}$
$6a_v$	$DF(v) + M_3 \rightleftharpoons DF(v-1) + M_3$	$k_{6a_v} = 4.0 \times 10^{3}\ v\ T^{2.2}$ $v=1,\ldots,9$
$6b_v$	$DF(v) + M_4 \rightleftharpoons DF(v-1) + M_4$	$k_{6b_v} = 3.7 \times 10^{-6}\ v\ T^{4.66}$ $v=1,\ldots,9$
$6c_v$	$DF(v) + M_5 \rightleftharpoons DF(v-1) + M_5$	$k_{6c_v} = 4.5 \times 10^{4}\ v\ T^{2.2} + 5.3 \times 10^{16}\ v\ T^{-2.0}$ $v=1,\ldots,9$
$6d_v$	$DF(v) + M_6 \rightleftharpoons DF(v-1) + M_6$	$k_{6d_v} = 0.14\ v\ T^{3.66}$ $v=1,\ldots,9$
$6e_1$	$DF(1) + M_7 \rightleftharpoons DF(0) + M_7$	$k_{6e_1} = 5.0 \times 10^{12}\ e^{1.25\theta}$
$6e_2$	$DF(2) + M_7 \rightleftharpoons DF(1) + M_7$	$k_{6e_2} = 5.0 \times 10^{12}\ e^{0.55\theta}$
$6e_v$	$DF(v) + M_7 \rightleftharpoons DF(v-1) + M_7$	$k_{6e_v} = 5.0 \times 10^{12}$ $v=3,\ldots,9$
$7a_v$	$DF(v) + DF(v) \rightleftharpoons DF(v-1) + DF(v+1)$	$k_{7a_v} = v(v+1)\ 3.06 \times 10^{8}\ T^{1.5}\ 10^{-\Delta\nu/433}$ $v=1,\ldots,8$
$7b_v$	$DF(v) + DF(v+1) \rightleftharpoons DF(v-1) + DF(v+2)$	$k_{7b_v} = v(v+2)\ 3.06 \times 10^{8}\ T^{1.5}\ 10^{-\Delta\nu/433}$ $v=1,\ldots,7$

Table IV. Recommended Rate Coefficients for the D_2 - F_2 - CO_2 Chemical Laser (Continued)

React.	Reaction[a]	Rate Coefficient[b]	
$7c_v$	$DF(v) + DF(v+2) \rightleftharpoons DF(v-1) + DF(v+3)$	$k_{7c_v} = v(v+3)\ 3.06 \times 10^8\ T^{1.5}\ 10^{-\Delta E/433}$	$v=1,\ldots,6$
8a	$DF(1) + D_2(0) \rightleftharpoons DF(0) + D_2(1)$	$k_{-8a} = 3.3 \times 10^8\ T^{1.5}$	
8b	$DF(2) + D_2(0) \rightleftharpoons DF(1) + D_2(1)$	$k_{-8b} = 4.05 \times 10^8\ T^{1.5}$	
8c	$DF(3) + D_2(0) \rightleftharpoons DF(2) + D_2(1)$	$k_{-8c} = 3.78 \times 10^8\ T^{1.5}$	
8d	$DF(1) + D_2(1) \rightleftharpoons DF(0) + D_2(2)$	$k_{-8d} = 1.23 \times 10^9\ T^{1.5}$	
8e	$DF(2) + D_2(1) \rightleftharpoons DF(1) + D_2(2)$	$k_{-8e} = 1.51 \times 10^9\ T^{1.5}$	
9_v	$D_2(v) + M_8 \rightleftharpoons D_2(v-1) + M_8$	$k_{9_v} = 1.51 \times 10^{-5}\ v\ T^{4.6}$	
10_v^{d}	$DF(v) + CO_2(00^00) \rightleftharpoons DF(v-1) + CO_2\ (00^01)$	$k_{10_v} = 4.7 \times 10^{17}\ T^{-2}$	$v=1,\ldots,9$
11	$CO_2(00^01) + CO_2(00^00) \rightleftharpoons CO_2(10^00) + CO_2(01^10)$	$k_{11} = 3.4 \times 10^1\ T^{2.5}\ e^{0.39\theta}$	
12^0	$CO_2(00^01) + CO_2(00^00) \rightleftharpoons CO_2(02^00) + CO_2(01^10)$	$k_{12}^0 = 1.2 \times 10^1\ T^{2.5}\ e^{\theta}$	
13	$CO_2(11^10) + CO_2(00^00) \rightleftharpoons CO_2(10^00) + CO_2(01^10)$	$k_{13} = 7.5 \times 10^{10}\ T^{0.5}$	
14	$CO_2(030) + CO_2(00^00) \rightleftharpoons CO_2(10^00) + CO_2(01^10)$	$k_{14} = 1.1 \times 10^9\ T^{0.5}$	
15^0	$CO_2(030) + CO_2(00^00) \rightleftharpoons CO_2(02^00) + CO_2(01^10)$	$k_{15}^0 = 1.1 \times 10^{11}\ T^{0.5}$	
15^2	$CO_2(030) + CO_2(00^00) \rightleftharpoons CO_2(02^20) + CO_2(01^10)$	$k_{15}^2 = 2.25 \times 10^{11}\ T^{0.5}$	

Table IV. Recommended Rate Coefficients for the D_2 - F_2 - CO_2 Chemical Laser (Continued)

React.	Reaction[a]	Rate Coefficient[b]
16	$CO_2(10^00) + CO_2(00^00) \rightleftharpoons CO_2(01^10) + CO_2(01^10)$	$k_{16} = 1.5 \times 10^{11} T^{0.5}$
17^0	$CO_2(02^00) + CO_2(00^00) \rightleftharpoons CO_2(01^10) + CO_2(01^10)$	$k^0_{17} = 1.5 \times 10^{11} T^{0.5}$
17^2	$CO_2(02^20) + CO_2(00^00) \rightleftharpoons CO_2(01^10) + CO_2(01^10)$	$k^2_{17} = 1.2 \times 10^{12} T^{0.5}$
18a	$CO_2(00^01) + M_3 \rightleftharpoons CO_2(11^10) + M_3$	$k_{18a} = 8.85 \times 10^{-4} T^{4.75} e^{-1.484\theta}$
18b	$CO_2(00^01) + M_9 \rightleftharpoons CO_2(11^10) + M_9$	$k_{18b} = 1.13 \times 10^{-7} T^{5.8} e^{-2.436\theta}$
18c	$CO_2(00^01) + M_{10} \rightleftharpoons CO_2(11^10) + M_{10}$	$k_{18c} = 1.2 \times 10^{6} T^{1.5}$
19a	$CO_2(00^01) + M_3 \rightleftharpoons CO_2(030) + M_3$	$k_{19a} = 6.8 \times 10^{-7} T^{5.55} e^{-1.484\theta}$
19b	$CO_2(00^01) + M_9 \rightleftharpoons CO_2(030) + M_9$	$k_{19b} = 8.7 \times 10^{-11} T^{6.6} e^{-2.436\theta}$
19c	$CO_2(00^01) + M_{10} \rightleftharpoons CO_2(030) + M_{10}$	$k_{19c} = 9.2 \times 10^{2} T^{2.3}$
20	$CO_2(11^10) + M_{11} \rightleftharpoons CO_2(030) + M_{11}$	$k_{20} = 2.6 \times 10^{7} T^{1.5}$
21^0	$CO_2(11^10) + M_{11} \rightleftharpoons CO_2(02^00) + M_{11}$	$k^0_{21} = 8.6 \times 10^{-3} T^{4.19} e^{0.903\theta}$
21^2	$CO_2(11^10) + M_{11} \rightleftharpoons CO_2(02^20) + M_{11}$	$k^2_{21} = 7.9 \times 10^{4} T^{2.5} e^{4.41\theta}$
22	$CO_2(11^10) + M_{11} \rightleftharpoons CO_2(10^00) + M_{11}$	$k_{22} = 5.9 T^{3.78} e^{0.549\theta}$
23^0	$CO_2(030) + M_{11} \rightleftharpoons CO_2(02^00) + M_{11}$	$k^0_{23} = 3.87 \times 10^{2} T^{3.3} e^{1.24\theta}$

Table IV. Recommended Rate Coefficients for the $D_2 - F_2 - CO_2$ Chemical Laser (Continued)

React.	Reaction[a]	Rate Coefficient[b]
23^2	$CO_2(030) + M_{11} \rightleftharpoons CO_2(02^20) + M_{11}$	$k_{23}^2 = 5.7 \times 10^2\ T^{3.32}\ e^{1.22\theta}$
24	$CO_2(030) + M_{11} \rightleftharpoons CO_2(10^00) + M_{11}$	$k_{24} = 4.9 \times 10^2\ T^{3.04}\ e^{1.06\theta}$
25^0	$CO_2(10^00) + M_{11} \rightleftharpoons CO_2(02^00) + M_{11}$	$k_{25}^0 = 2.6 \times 10^8\ T^{1.5}$
25^2	$CO_2(10^00) + M_{11} \rightleftharpoons CO_2(02^20) + M_{11}$	$k_{25}^2 = 5.8 \times 10^8\ T^{1.5}$
26a	$CO_2(10^00) + M_{12} \rightleftharpoons CO_2(01^10) + M_{12}$	$k_{26a} = 4.4 \times 10^2\ T^{3.26}\ e^{1.48\theta}$
26b	$CO_2(10^00) + M_{13} \rightleftharpoons CO_2(01^10) + M_{13}$	$k_{26b} = 1.5 \times 10^3\ T^{2.95}\ e^{-0.8433\theta}$
26c	$CO_2(10^00) + M_{14} \rightleftharpoons CO_2(01^10) + M_{14}$	$k_{26c} = 1.65 \times 10^{14}\ T^{-1.0}$
27	$CO_2(02^20) + M_{11} \rightleftharpoons CO_2(02^00) + M_{11}$	$k_{-27} = 5.9 \times 10^8\ T^{1.5}$
$28a^0$	$CO_2(02^00) + M_{12} \rightleftharpoons CO_2(01^10) + M_{12}$	$k_{28a}^0 = 2.4 \times 10^3\ T^{3.1}\ e^{1.4\theta}$
$28b^0$	$CO_2(02^00) + M_{13} \rightleftharpoons CO_2(01^10) + M_{13}$	$k_{28b}^0 = 2.8 \times 10^{13}\ T^{2.95}\ e^{-0.8433\theta}$
$28c^0$	$CO_2(02^00) + M_{14} \rightleftharpoons CO_2(01^10) + M_{14}$	$k_{28c}^0 = 3.13 \times 10^{14}\ T^{-1.0}$
$28a^2$	$CO_2(02^20) + M_{12} \rightleftharpoons CO_2(01^10) + M_{12}$	$k_{28a}^2 = 6.0 \times 10^2\ T^{3.31}\ e^{1.3\theta}$
$28b^2$	$CO_2(02^20) + M_{13} \rightleftharpoons CO_2(01^10) + M_{13}$	$k_{28b}^2 = 3.3 \times 10^3\ T^{2.95}\ e^{-0.8433\theta}$
$28c^2$	$CO_2(02^20) + M_{14} \rightleftharpoons CO_2(01^10) + M_{14}$	$k_{28c}^2 = 3.68 \times 10^{14}\ T^{-1.0}$

Table IV. Recommended Rate Coefficients for the D_2 - F_2 - CO_2 Chemical Laser (Continued)

React.	Reaction[a]	Rate Coefficient[b]
29a	$CO_2(01^10) + M_{12} \rightleftharpoons CO_2(00^00) + M_{12}$	$k_{29a} = 2.17 \times 10^{-2}\ T^{4.19}\ e^{-1.132\theta}$
29b	$CO_2(01^10) + M_{13} \rightleftharpoons CO_2(00^00) + M_{13}$	$k_{29b} = 8.27 \times 10^{2}\ T^{2.95}\ e^{-0.8433\theta}$
29c	$CO_2(01^10) + M_{14} \rightleftharpoons CO_2(00^00) + M_{14}$	$k_{29c} = 9.2 \times 10^{13}\ T^{-1.0}$

[a] Catalytic species:

M_1 = all species

M_2 = $1.75D_2$, 20D, F, Ar, He, DF, F_2, CO_2

M_3 = CO_2

M_4 = Ar, 2He, F_2

M_5 = DF

M_6 = D_2

M_7 = F, D

M_8 = $4.8D_2$, 2D, F, Ar, 2He, DF, F_2, CO_2

M_9 = He, Ar, 4D, $2F_2$

M_{10} = D_2, 53DF, 53F

M_{11} = CO_2, F, DF, $2D_2$, Ar, 1.5He, 2D, F_2

M_{12} = CO_2, F_2, F, DF, 0.06Ar

M_{13} = He

M_{14} = D_2, D

[b] The rate coefficients k_+ and k_- designate forward and backward rates, respectively, with units in terms of moles, cm^3, and sec. For each reaction, the missing rate coefficient is determined from the equilibrium constant.

[c] The quantity $\theta = -(10^3/RT)$, where the temperature T is in °K and R is 1.987 cal/mole - °K.

[d] This temperature dependence may be too pronounced (see Section III).

III. DF - CO_2 VIBRATIONAL ENERGY TRANSFER

The most important reaction in the DF-CO_2 laser system is the transfer of vibrational energy from DF(v) to $CO_2(00^01)$

$$DF(v) + CO_2(00^00) \rightleftharpoons DF(v-1) + CO_2(00^01) \tag{10}$$

The rate coefficient of this reaction has been determined to be 3.82×10^{12} cc/mole-sec for v = 1 by Stephens and Cool [35] using a laser-induced fluorescence technique at 350°K. Preliminary measurements of Cool [47] at 300°K suggest that this rate coefficient may vary as strongly as T^{-2}. Basov, et al. [14] estimate this rate to be 9×10^{11} cc/mole-sec at 300°K from a DF-CO_2 pulsed laser experiment. The rate of vibrational energy transfer from other hydrogen halides to CO_2 has also been measured by the laser fluorescence technique. Stephens and Cool [35] found $k_{HF\text{-}CO_2} = 8.1 \times 10^{11}$ cc/mole-sec at 350°K, and Chen, et al. [48] report $k_{HCl\text{-}CO_2} = 1.8 \times 10^{12}$ cc/mole-sec and $k_{HI\text{-}CO_2} = 2.4 \times 10^{12}$ cc/mole-sec. Although the degree of resonance for v = 1 is 1612 cm^{-1}, 537 cm^{-1}, and -116 cm^{-1}, respectively, for these reactions compared to 558 cm^{-1} for DF, their efficiencies of transfer are all the same order of magnitude as the DF - CO_2 value.

An analysis of the energy spacing of the $\Delta v = 1$ transitions in DF (Fig. 1) shows that the closest resonance for J = 0 is at v = 8. We have also calculated the relative probabilities of transfer as a function of v, by assuming rotational equilibrium in DF(v) and $CO_2(00^00)$ at the translation temperature. We assume that the transfer probability decreases about one order of magnitude for every 150 cm^{-1} of energy separation as Callear [49] found for certain diatomics. In the final states, all values of J are assumed possible; however, because of the resonance argument, those values that release the smallest quantity of energy to translation are most likely. At 300°K, the higher levels, v = 6, 7, and 8, are still most likely to transfer. A calculation made on the assumption of a decrease of one order of magnitude for every 450 cm^{-1} of energy separation gave a similar result. At this time, a rate of transfer based on these resonance and equilibrium population arguements seems unwarranted, especially in light of the apparent insensitivity to resonance exhibited by the transfer efficiencies of other hydrogen halides. Hence, until more data are available, we estimate the rate to be the same for all v.

We use the values of Refs. [35] and [47] to obtain

$$k_{10_v} = 4.7 \times 10^{17} T^{-2}$$

Since the temperatures used to determine this function are very close together, this rate coefficient should be used with prudence outside the 300° to 350°K temperature range. In fact, for large temperature variations the 3.82×10^{12} cc/mole-sec rate of Ref. [35] may be more appropriate.

IV. CO_2 KINETICS

An extensive theoretical study of the rates of VV and VT reactions of CO_2-CO_2 and CO_2-N_2 has been made by Herzfeld [50, 51]. We use his work as the basis for selecting the reactions shown in Fig. 1, and we use Ref. [51] as a guide for estimating rates when experimental measurements are not available. In addition, many of the reactions in our model are common to those reviewed by Taylor and Bitterman [5]. The states (03^10) and (03^30) are assumed in equilibrium and statistically combined. We denote this combined state as (030) and adjust the kinetics accordingly. The small energy difference, 73 cm^{-1}, between these states is neglected, and both states are assigned the energy of (03^10).

A. VIBRATIONAL - VIBRATIONAL TRANSFER IN CO_2

Intermoleculaar VV transfer processes represent important and fast mechanisms for energy transfer within CO_2. These reactions have a significant effect on the relative populations of the CO_2 levels, including those that participate in lasing.

$$(11) \qquad CO_2(00^01) + CO_2(00^00) \rightleftharpoons CO_2(10^00) + CO_2(01^10) + 294\ cm^{-1}$$

$$(12^{\ell}) \qquad CO_2(00^01) + CO_2(00^00) \rightleftharpoons CO_2(02^{\ell}0) + CO_2(01^10) + \begin{cases} 397\ cm^{-1} & \ell = 0 \\ 347\ cm^{-1} & \ell = 2 \end{cases}$$

$$(13) \qquad CO_2(11^10) + CO_2(00^00) \rightleftharpoons CO_2(10^00) + CO_2(01^10) + 21\ cm^{-1}$$

(14) $CO_2(030) + CO_2(00^00) \rightleftharpoons CO_2(10^00) + CO_2(01^10) - 123\ cm^{-1}$

(15^ℓ) $CO_2(030) + CO_2(00^00) \rightleftharpoons CO_2(02^\ell0) + CO_2(01^10) - \begin{cases} 20\ cm^{-1} & \ell = 0 \\ 70\ cm^{-1} & \ell = 2 \end{cases}$

(16) $CO_2(10^00) + CO_2(00^00) \rightleftharpoons CO_2(01^10) + CO_2(01^10) + 54\ cm^{-1}$

(17^ℓ) $CO_2(02^\ell0) + CO_2(00^00) \rightleftharpoons CO_2(01^10) + CO_2(01^10) + \begin{cases} -49\ cm^{-1} & \ell = 0 \\ 1\ cm^{-1} & \ell = 2 \end{cases}$

Rate coefficients for Reacts. (11) and (12) have been calculated by Herzfeld [51] between 300° and 3000°K. We have approximated these rates as a function of T to be

$$k_{11} = 34.0\ T^{2.5} e^{0.39\theta}$$

$$k_{12}^{\ell} = \begin{cases} 12.0\ T^{2.5} e^{\theta} & \ell = 0 \\ \text{neglected} & \ell = 2 \end{cases}$$

The value of k_{12}^2 is nearly two orders of magnitude less than k_{12}^0 [51].

Theoretical or experimental estimates of rates of Reacts. (13) - (15) are not available. There is, however, a laser fluorescence measurement by Rhodes, Kelly, and Javan [52] that has been interpreted as either the rate of React. (16) or (17). At 296°K, they found this rate coefficient to be 7.5×10^{12} cc/mole-sec. Sharma [53], using the theory of Sharma and Brau [54, 55], and Seeber [56], using a modified SSH theory, have calculated the rate coefficient of React. (16) at 300°K and find 3.2×10^{12} and 2.5×10^{12} cc/mole-sec, respectively.

Sharma [53] suggests that the experiment of Rhodes, et al. [52] is controlled by React. (17^2), which he finds is 21 times faster than React. (16). Seeber [56] rejects this interpretation and suggests that the measurement reflects a stimulated Raman effect, multiple photon process, and a subsequent rotational relaxation. Even if this interpretation is correct, this effect is enhanced by the simultaneous application of 10.6 and 9.6-μm radiation in the experiment of Ref. [52] and would not arise during normal lasing conditions. Nevertheless, interpretation of the experiment remains in question. Seeber [56] calculates $k_{17}^2 \approx 8k_{16}$, and Seeber and Sharma both find k_{17}^2 to be larger than k_{17}^0 by the factors of 8 and 35, respectively.

Other measurements of the relaxation of the (10^00) state [57 - 62] give rate coefficients ranging from 0.4 to 2.8 × 10^{11} cc/mole-sec. Interpretation of these measurements is very difficult, and the uncertainty in the reported rate coefficients is large.

In view of these uncertainties, we estimate the rates of Reacts. (16) and (17^{ℓ}) from the SSH calculations of Seeber [56] and assume that the probability is independent of T; hence, we set

$$k_{16} = 1.5 \times 10^{11} T^{0.5}$$

$$k_{17}^0 = 1.5 \times 10^{11} T^{0.5}$$

$$k_{17}^2 = 1.2 \times 10^{12} T^{0.5}$$

Reaction (13) is similar to React. (17^{ℓ}), in that both involve the transfer of one quantum of ν_2 to a ground state molecule; hence, we set[1]

$$k_{13} = 0.5\, k_{17}^{0}$$

Approximation of the bending mode of CO_2 by an harmonic oscillator model suggests that[1]

$$k_{15}^{0} = 0.75\, k_{17}^{0}$$

$$k_{15}^{2} = 1.5\, k_{17}^{0}$$

Reaction (14) involves the transfer of one ν_2 quantum and the excitation of ν_1 at the expense of $2\nu_2$. We estimate that this process is 10^{-2} times as efficient as React. (15), i.e., one order of magnitude slower for each quantum changing modes; hence, we set

$$k_{14} = 10^{-2} k_{15}^{0}$$

B. VIBRATIONAL - TRANSLATIONAL TRANSFER

We discuss two types of reactions in this section. The first type is the VT process by which exactly one quantum of an excited mode is

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[1] The value of k_{17}^{0} is used as a reference, since the degree of resonance is much less than that of (17^{2}) for these reactions.

exchanged for translational energy during a collision. An example of such a reaction is

$$CO_2(01^10) + M \rightleftharpoons CO_2(00^00) + M + 667\ cm^{-1}$$

The second reaction type is an intramolecular VV process that leaves the excited molecule in a different mode from the original state. These processes differ from the intermolecular VV reactions where the state of both molecules is changed during the collision. Again, the excess energy is exchanged for translational energy. An example of such a reaction is

$$CO_2(00^01) + M \rightleftharpoons CO_2(11^10) + M + 273\ cm^{-1}$$

Both processes represent transfer of vibrational energy to translational energy of the colliding pair.

Deactivation of the upper laser level by collisions represents a loss of laser energy, whereas deactivation of the lower laser level enhances the inversion. In addition, mechanisms that couple levels adjacent to and below the lasing levels are important for realistic computer modeling. In Table IV, Reacts.(18) - (29) include processes of this type considered important in the modeling of CO_2 relaxation for transfer laser simulation. We first discuss those reactions where experimental measurements are available, and then we complete the discussion by making theoretical estimates of the rates of the remaining reactions.

1. DEACTIVATION OF THE UPPER LASER LEVEL

Reactions (18) and (19) represent a loss of laser power through collisional deexcitation of $CO_2(00^01)$

(18) $$CO_2(00^01) + M \rightleftharpoons CO_2(11^10) + M + 273\ cm^{-1}$$

(19) $$CO_2(00^01) + M \rightleftharpoons CO_2(030) + M + 417\ cm^{-1}$$

Experimental data for the relaxation rate of $CO_2(00^01)$ are generally presented without specifying the final state of CO_2. The most probable final states are those of Reacts. (18) and (19). One might also expect $CO_2(04^{\ell}0)$ to be a product of this VT reaction of $CO_2(00^01)$; however, we have limited our consideration to levels below (00^01). Herzfeld's calculations show that the final state (03^30) may be neglected, while the ratio for pure CO_2 of k_{19} (with final state (03^10)) to k_{18} may be approximated by $7.7 \times 10^{-4} T^{0.8}$. This ratio is 0.074 at 300°K and 0.19 at 1000°K; hence, React. (18) is expected to be the dominant mechanism over this temperature range.

Experimental measurements of the relaxation of mode ν_3 in CO_2 have been made by several techniques. Laser fluorescence measurements have been made by several investigators. Hocker, et al. [63] found this rate to be 385 $torr^{-1}$-sec^{-1} for pure CO_2 at room temperature. Similar measurements were made at 293°K for the relaxation of ν_3 by collisions with He, H_2, D_2, H_2O, N_2, and pure CO_2 by Moore, et al.[64] and by Yardley and Moore [65] for collisions with He, Ne, Ar, Kr, Xe, and pure CO_2. Alexander, et al. [66] measured the relaxation rate in pure CO_2 at 233° and 293°K. A comprehensive study of the temperature variation of this relaxation rate in pure CO_2 and N_2 has been made by Rosser, Wood, and Gerry [67]. Rosser and Gerry [68, 69] have also measured this rate over a wide temperature range for deactivation by He, O_2, H_2O, H_2, NO, and Cl_2. The temperature dependence of ν_3 relaxation for deactivation by H_2, He, Ne, Ar, Kr, Xe, HD, and D_2 over the range 298° to 800°K is given by Stephenson, Wood, and Moore [70]. Deactivation of ν_3 by DF and HF has been measured by Chang, McFarlane, and Wolga [71] at 348° and 373°K and by Stephens and Cool [35] at 350°K. With the use of a standard modulated light source, instead of a laser, Houghton [72] measured the relaxation of ν_3 in pure CO_2 and in Ar. Cheo [61, 62] measured this relaxation rate at 300°K for pure CO_2, H_2, He, N_2, and other species with the pulse-gain method. The shock tube has also been used to study this relaxation rate by Simpson and Chandler [73] for mixtures of pure CO_2 and CO_2 with Ar, N_2, Ne, He, D_2, and H_2 over a wide temperature range. In general, their results are in poor agreement with laser fluorescence measurements. We expect that the process involved in relaxation of ν_3 in the shock tube is much more complex than that in the laser fluorescence measurements, since with laser excitation only one state (00^01) is produced in abundance and interpretation of the intramolecular VV data is more straightforward. The relaxation times observed with laser fluorescence are essentially a direct measure of (00^01) deactivation, to (11^10) based on the calculation of Herzfeld [51], whereas, in the shock tube, many adjacent levels are contributing to the activation and deactivation of ν_3 and the interpretation of $p\tau$ is much more complicated. We expect that detailed modeling of the CO_2 kinetics may be helpful in explaining these shock tube results. Similar problems have been found for measurements made with the spectrophone technique [74 - 79]. Levinson, et al. [80] have measured the relaxation rate of $CO_2(00^01)$ by exciting a gas mixture with a current pulse and monitoring the 4.3-μm spontaneous decay. Finally, Biryukov, Serikov, and Trekhov [81] measured the rate of relaxation of ν_3 induced by collisions with N_2, He, and H_2O and in pure CO_2 with the phase method.

Reduction of the experimental relaxation times to rate coefficients is not always a straightforward process. Taylor and Bitterman [5] have used the 5-reaction model of Taylor, et al. [82] to reduce the $p\tau$ data for (00^01). We believe that it is just as appropriate to interpret the laser fluorescence measurements when intermolecular VV processes are not involved as direct measurements of k_{18}. Hence, we use

$$k_{18} = \frac{RT}{p\tau_{CO_2\text{-}M}} \tag{4}$$

to reduce this data. The ratio of k_{19} to k_{18} calculated by Herzfeld is then used to determine k_{19}.

Reduction of the shock tube data of Ref. [73] represents an even more difficult problem. We have not used these data, since they are in poor agreement with other measurements. In Fig. 5, we show the rate coefficients for the various species of interest in our model. For modeling simplicity, rates for all species have been approximated by one of three different functions.

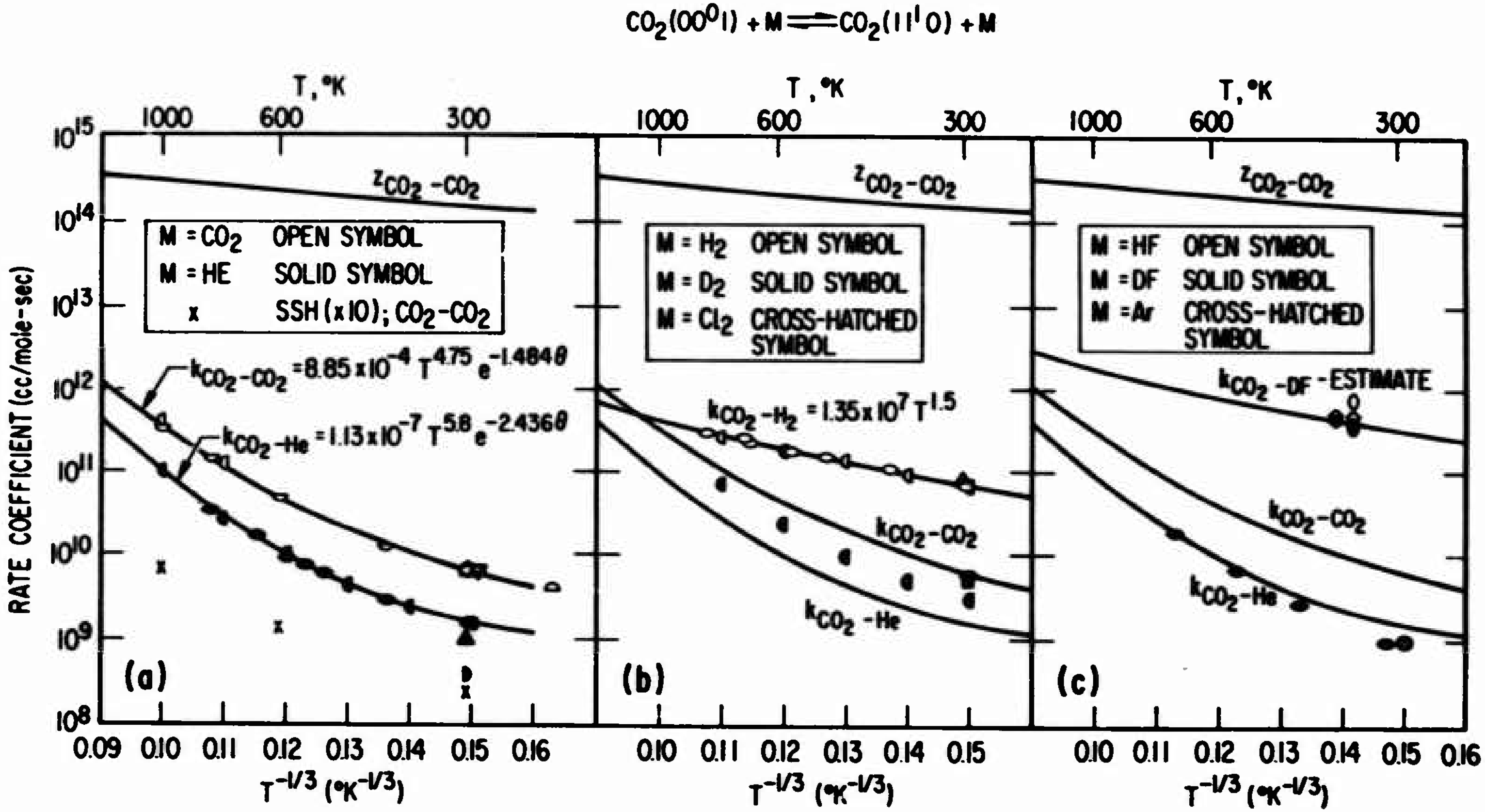

Fig. 5. Experimentally derived rate coefficients for deactivation of CO_2 (00^01) by M: X SSH calculations, Ref. [51]; laser fluorescence, ◑ Ref. [35], ◁ Ref. [63], □ Ref. [64], ○ Ref. [65], ◠ Ref. [66], ◡ Ref. [67], ◖ Ref. [68], and [69], ⬭ Ref. [70], ◇ Ref. [71]; pulse gain, △ Refs. [61] and [62]; other fluorescence, ▽ Ref. [72], ◗ Ref. [80]; phase method, ▷ Ref. [81]. (a) Deactivation by CO_2 and He. (b) Deactivation by H_2, D_2, and Cl_2. (c) Deactivation by Ar, HF, and DF.

For CO_2-CO_2, we have approximated the data of Rosser, et al. [67] and Rosser and Gerry [69] to be

$$k_{18a} = 8.85 \times 10^{-4} T^{4.75} e^{-1.484\theta}$$

and for CO_2-He, we find that

$$k_{18b} = 1.13 \times 10^{-7} T^{5.8} e^{-2.436\theta}$$

approximates the data of Rosser and Gerry [68] and Stephenson, et al. [70]. For M = H_2 (Fig. 5b), we find that a $T^{1.5}$ temperature dependence matches the data of Refs. [69] and [70]. Hence, from Refs. [64] and [70], we estimate the rate coefficient for deactivation by D_2 to be

$$k_{18c} = 1.2 \times 10^{6} T^{1.5}$$

In addition, we estimate from Refs. [35] and [71] that DF is 4.5 times as effective as H_2 at 350° K in deactivating ν_3. We feel that the large CO_2-DF deactivation rate at 350° K indicates a weak temperature dependence such as $T^{1.5}$. Relaxation of ν_3 by Ar is approximately as fast as He [70]. We also use four times the CO_2-He rate for D by assuming CO_2-D_2 and CO_2-D are about the same at room temperature, and we estimate the rate of deactivation by F to be similar to DF. We assume that the rate coefficient for F_2 is similar to Cl_2; hence, we take CO_2-F_2 rate to be twice that for CO_2-He. In Fig. 5a, the SSH rate for CO_2-CO_2 calculated by Herzfeld has been increased by a factor of 10 for graphic comparison with experimental data.

2. TRANSFER BETWEEN FERMI RESONANCE STATES

Theoretical SSH calculations by Herzfeld [51] and Seeber [56] for pure CO_2 indicate that the rate of energy transfer between the strongly coupled levels in Fermi resonance

$$CO_2(10^00) + M \rightleftharpoons CO_2(02^{\ell}0) + M + 102.8\ \mathrm{cm}^{-1} \qquad \ell = 0 \tag{25^{ℓ}}$$

is fast. However, these calculations also show that the reaction coupling the levels not in Fermi resonance, (25^2), is faster than (25^0). The laser fluorescence measurement of Rhodes, Kelly, and Javan [52] at 300°K in pure CO_2 indicates that k_{25}^0 or k_{25}^2 is possibly 10 times faster than the calculated rate coefficients of Ref. [51], which vary as $T^{1.5}$. Since interpretation of this experiment remains in question, we use the results of Seeber at 300°K, and the rate coefficients are assumed proportional to $T^{1.5}$,

$$k_{25}^0 = 2.6 \times 10^8 T^{1.5}$$

$$k_{25}^2 = 5.8 \times 10^8 T^{1.5}$$

Herzfeld's calculations also show that N_2 is nearly as efficient as CO_2 for these reactions. We adjust the rate coefficient for each species such that all have nearly the same probability per collision as CO_2. Note the rate of

Reacts. (25^{ℓ}) during lasing will always be less than the transfer rate of DF to CO_2.

The transfer between the other states in Fermi resonance, $(11^10,\ 03^10)$, is given in React. (20):

$$(20) \qquad CO_2(11^10) + M \rightleftharpoons CO_2(03^10) + M + 144\ \mathrm{cm}^{-1}$$

Although Herzfeld does not compute this rate, he does compute the total rate of deactivation of the combined $(11^10,\ 03^10)$ state to be 20 times slower than React. (25^0) at 300° K. This is probably a lower limit on k_{20}; we estimate

$$k_{20} \simeq k_{25}^{0}/10$$

In our model, React. (20) includes the relaxation between the levels (11^10) and (03^30) that are not in Fermi resonance. In any case, React. (20) is of very little importance during lasing.

3. DEACTIVATION OF THE BENDING MODE OF CO_2

Relaxation of mode ν_2 of CO_2 has been widely studied [83 - 86]. Taylor and Bitterman [5] have compiled relaxation rates for this reaction

$$(29) \qquad CO_2(01^10) + M \rightleftharpoons CO_2(00^00) + M + 667\ \mathrm{cm}^{-1}$$

and they indicate a "best fit" over the temperature range of interest for $M = CO_2$, He, H_2 and for other species not of interest in our model.

Conversion of the recommendations of Ref. [5] to forward rate coefficients with Eq. (1) yields for M = CO_2

$$k_{29a} = 2.17 \times 10^{-2} T^{4.19} e^{-1.132\theta}$$

For He, we use

$$k_{29b} = 8.27 \times 10^{2} T^{2.95} e^{-0.8433\theta}$$

The recommended value for M = H_2 decreases with T. Sharma [85], using the theory of Sharma and Brau [54, 55], has found the efficiency of H_2 in deactivating ν_2 to vary approximately as T^{-1}, and the agreement of theory and experiment is good. Thus, for M = D_2, we assume the rate is proportional to T^{-1} and adjust it to the value reported by Cottrell and Day [86] at 303°K, since their values for M = CO_2 and He are close to the "best fit" curves of Ref. [5]. In addition, Simpson and Chandler [73] have determined this rate from their shock tube measurements. Although these values are in closer agreement with other measurements than their observed relaxation curves for (00^01), we have not used their values in the present model. The temperature variation of these rate coefficients is shown in Fig. 6, along with values calculated by Herzfeld [51] for pure CO_2. The overall agreement of the theoretical and experimental rates is much better than that found for relaxation of ν_3.

Relaxation times for CO_2-Ar have been reported by Huety and Chevalier [84] and Simpson and Chandler [73]. The impact tube measurements

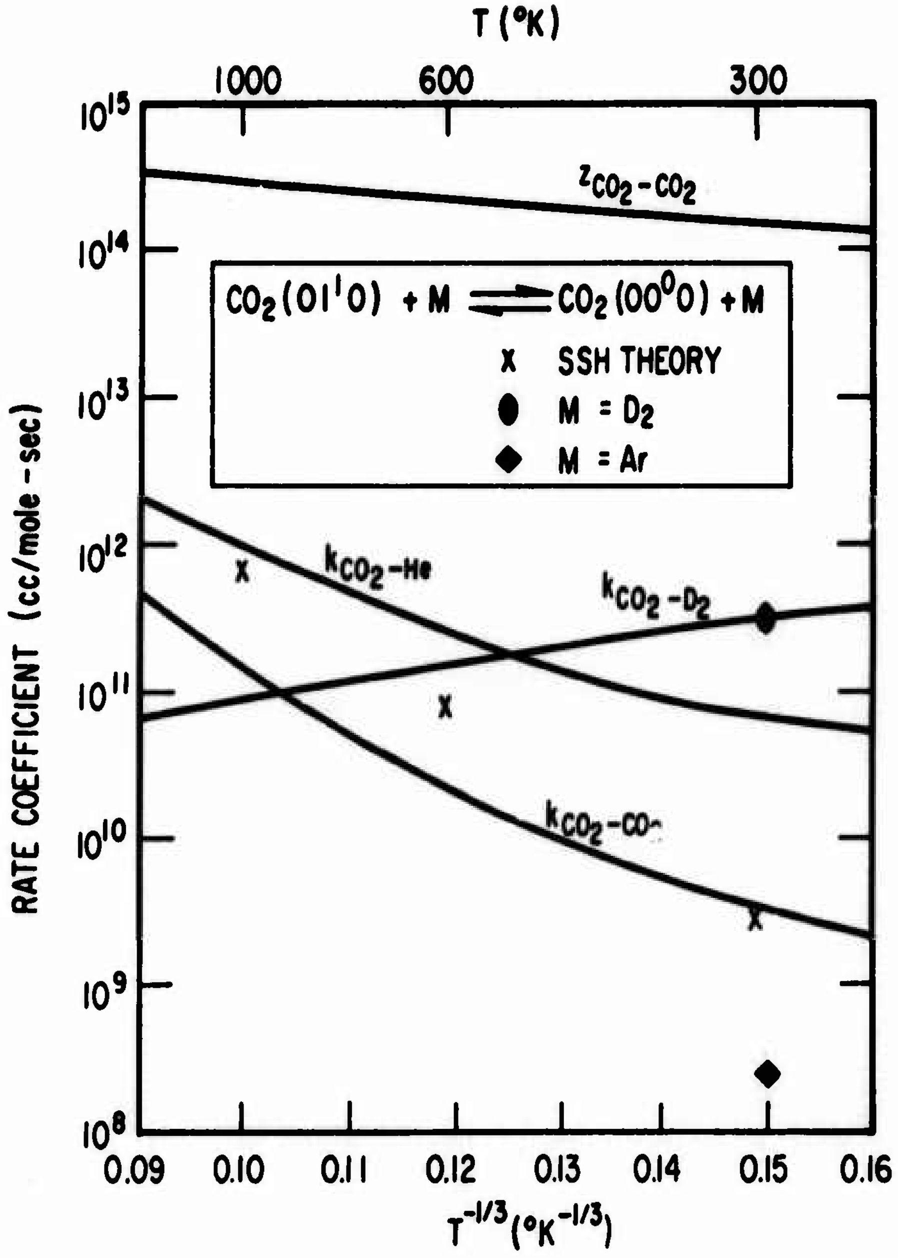

Fig. 6. Experimentally derived rate coefficients for deactivation of $CO_2(01^10)$ by M: M = CO_2 and He, Ref. [5]; ◇ Ref. [84], ○ Ref. [86]; X SSH calculations, Ref. [51].

of Ref. [84] are more consistent with data of other investigators; thus, we take their results and assume Ar to be 6% as efficient as CO_2 in deactivating ν_2. Relaxation of ν_2 by F, F_2, DF, and D has not been measured. The efficiencies of these species are estimated to be similar to CO_2 with the exception of D, which is assumed similar to D_2. These are gross approximations, and additional measurements for these species are needed.

4. OTHER REACTIONS

The rates of the remaining reactions have not been measured. These reactions include

$$CO_2(11^10) + M \rightleftharpoons CO_2(02^\ell 0) + M + \left\{\begin{matrix} 791\ cm^{-1} \\ 741\ cm^{-1} \end{matrix}\right. \qquad \begin{matrix} \ell = 0 \\ \ell = 2 \end{matrix} \tag{21$^\ell$}$$

$$CO_2(11^10) + M \rightleftharpoons CO_2(10^00) + M + 688\ cm^{-1} \tag{22}$$

$$CO_2(030) + M \rightleftharpoons CO_2(02^\ell 0) + M + \left\{\begin{matrix} 647\ cm^{-1} \\ 597\ cm^{-1} \end{matrix}\right. \qquad \begin{matrix} \ell = 0 \\ \ell = 2 \end{matrix} \tag{23$^\ell$}$$

$$CO_2(030) + M \rightleftharpoons CO_2(10^00) + M + 544\ cm^{-1} \tag{24}$$

$$CO_2(10^00) + M \rightleftharpoons CO_2(01^10) + M + 721\ cm^{-1} \tag{26}$$

$$CO_2(02^20) + M \rightleftharpoons CO_2(02^00) + M + 50\ cm^{-1} \tag{27}$$

$$CO_2(02^\ell 0) + M \rightleftharpoons CO_2(01^10) + M + \left\{\begin{matrix} 618\ cm^{-1} \\ 668\ cm^{-1} \end{matrix}\right. \qquad \begin{matrix} \ell = 0 \\ \ell = 2 \end{matrix} \tag{28$^\ell$}$$

Theoretical estimates of the rates of these reactions have been made by Herzfeld [51] for M = CO_2. Our analytical approximations of his rates are

$$k_{21}^{0} = 8.6 \times 10^{-3} T^{4.19} e^{0.903\theta}$$

$$k_{21}^{2} = 7.9 \times 10^{4} T^{2.5} e^{4.41\theta}$$

$$k_{22} = 5.9 T^{3.78} e^{0.549\theta}$$

$$k_{23}^{0} = 3.87 \times 10^{2} T^{3.3} e^{1.24\theta}$$

$$k_{23}^{2} = 5.7 \times 10^{2} T^{3.32} e^{1.22\theta}$$

$$k_{24} = 4.9 \times 10^{2} T^{3.04} e^{1.06\theta}$$

$$k_{26a} = 4.4 \times 10^{2} T^{3.26} e^{1.48\theta}$$

$$k_{-27} = 5.9 \times 10^{8} T^{1.5}$$

$$k_{28a}^{0} = 2.4 \times 10^{3} T^{3.1} e^{1.4\theta}$$

$$k_{28a}^{2} = 6.0 \times 10^{2} T^{3.31} e^{1.3\theta}$$

We assume both levels of vibrational angular momentum in (030) are deactivated at the same rate in determining k_{23}^{ℓ} and k_{24}.

Seeber [56] has also calculated k_{-27} at 300°K, and his value is 35% larger than that of Herzfeld and has been used with the temperature variation calculated by Ref. [51] to determine k_{-27}.

Reactions (21) through (24) represent collisional mechanisms that may contribute to the population of the lower laser level from products of deexcitation of the upper laser level. Since experimental estimates of the rate of these reactions are not available, we use Herzfeld's rate coefficients and assume the probability for reaction is the same for each species. In addition, we assume that all species are equally efficient in equilibration of the vibrational momentum of $(02^{\ell}0)$, React. (27).

For Reacts. (26) and (28), we use the theoretical rate coefficients of Herzfeld for species M_{12} (Table IV). Since the temperature variation of React. (29) for M_{13} and M_{14} is considerably different from the calculation of Herzfeld, we use the temperature dependence of the rates of React. (29) for these species and adjust the relative rates of the reaction to be in the same ratio as that calculated by Herzfeld for CO_2-CO_2 at 1000°K, where the relative magnitude of the calculated rates may be expected to be fairly accurate. At 1000°K for CO_2-CO_2, Herzfeld finds

$$k_{26}:k_{28}^{0}:k_{28}^{2}:k_{29} = 1.8:3.4:4.0:1.0$$

Hence, we take

$$k_{26b} = 1.8k_{29b}$$

$$k_{26c} = 1.8k_{29c}$$

$$k_{28b}^{0} = 3.4k_{29b}$$

and continue.

The complete kinetic model for the $DF\text{-}CO_2$ chemical transfer laser is given in Table IV.

V. COMPUTER EXPERIMENTS

A. LASER SIMULATION

The chemical laser computer simulation used in this study is described in Ref. [2]. A resume of its features is presented here. Rate equations are used to represent the chemical kinetic and stimulated emission processes occurring in a representative unit volume within a Fabry-Perot cavity. All processes are assumed to be uniform throughout the cavity. Only the (00^01) - (10^00) band is permitted to lase, and a Boltzmann distribution of the rotational levels at the translational temperature T is assumed. Only the transition with maximum gain is assumed to lase, and this is always in the P-branch. During lasing, the gain at line center is held constant at its threshold value α_{thr}.

The chemical reactions may be written as

$$\sum_i \alpha_{ri} [N_i] \underset{k_{-r}}{\overset{k_r}{\rightleftharpoons}} \sum_i \beta_{ri} [N_i] \tag{5}$$

where $[N_i]$ is the molar concentration of species i, α_{ri} and β_{ri} are stoichiometric coefficients, and $k_{\pm r}$ are the forward and backward rate coefficients. The rate of change of concentration of $CO_2(00^01)$ is given by

$$\frac{d\left[CO_2(00^01)\right]}{dt} = -\chi_{rad}(J) + \chi_{ch}(00^01) \tag{6a}$$

For $CO_2(10^00)$, we have

$$\frac{d[CO_2(10^00)]}{dt} = \chi_{rad}(J) + \chi_{ch}(10^00) \tag{6b}$$

and for all other species

$$\frac{d[N_i]}{dt} = \chi_{ch}(i) \tag{6c}$$

The photon emission rate $\chi_{rad}(J)$ is the rate of change of concentration resulting from lasing, and J is the rotational quantum number for the lower level of the maximum gain transition within the 10.6-μm band. The rate of change of species concentration resulting from chemical reactions is

$$\chi_{ch}(i) = \sum_r (\beta_{ri} - \alpha_{ri}) L_r \tag{7}$$

where

$$L_r = k_r \prod_j [N_j]^{\alpha_{rj}} - k_{-r} \prod_j [N_j]^{\beta_{rj}}$$

The laser cavity is assumed to have a uniform photon flux with active medium length L and mirror reflectivities R_0 and R_L. Lasing initiates when the highest gain transition of the band is equal to the threshold gain α_{thr} where

$$\alpha_{thr} = -\frac{1}{2L} \ln(R_0 R_L) \tag{8}$$

Only P-branch transitions need be considered; thus, the gain of a transition with lower level J is

$$\alpha(J) = \frac{hN_A}{4\pi}\omega(J)B(J)\phi(J)\left\{\frac{2J+1}{2J-1}[CO_2(00^01,J-1)] - [CO_2(10^00,J)]\right\} \qquad (9)$$

where the wave number of the transition is $\omega(J)$ and $B(J)$ is the Einstein isotropic absorption coefficient based on the intensity. Line-broadening constants and resonance constants used in the Voigt profile $\phi(J)$ at line center are those of Ref. [2].

The Boltzmann distribution of the rotational populations is given by

$$[CO_2(\nu_1,\nu_2^{\ell},\nu_3;J)] = [CO_2(\nu_1,\nu_2^{\ell},\nu_3)]\,\frac{(2J+1)}{T/2\theta_r}\,e^{-hcE_J/kT} \qquad (10)$$

where $T/2\theta_r$ is the rotational partition function, the additional factor of 2 is a statistical symmetry factor, θ_r is the characteristic rotational temperature [2], and rotational energy E_J is from Herzberg [20]. We note that only odd J values are present in the upper states and even values in the lower states. Planck's constant, the speed of light, and Boltzmann's constant are denoted as h, c, and k, respectively. The energy equation for a constant density gas is written in the form

$$\sum_i [N_i] C_{pi}\frac{dT}{dt} - \frac{dp}{dt} = -P_L - \sum_i \frac{d[N_i]}{dt} H_i \qquad (11)$$

where C_{pi} is the specific heat at constant pressure, H_i is the molar enthalpy of species i, p is the pressure, and P_L is the output lasing power per unit volume given by

$$P_L(t) = hcN_A \omega(J) \chi_{rad}(J) \tag{12}$$

The average intensity inside the cavity may be calculated from the relation

$$I = P_L(t)L/(1 - \sqrt{R_0 R_L})$$

A fourth-order Runge-Kutta routine is used to solve Eqs. (6), (11), and the equation of state to determine pressure, temperature, and species concentrations until, at some time t_0 and for some value $J = J_0$, the gain on a given vibration-rotation transition reaches α_{thr}. At this time, the laser pulse begins. Then Eqs. (6), (8), (11), (12), and the equation of state are solved for the transient temperature, pressure, concentrations, output power, and active J. During lasing, this value of J shifts as a result of the temperature rise and concentration changes. Lasing terminates when all gains drop below α_{thr}.

The pulse energy per unit volume is given by

$$E = \int_{t_0}^{t_0+t_c} P_L \, dt \tag{13}$$

where t_c is the pulse duration. For simplicity, initiation is modeled by the introduction of a finite concentration of F atoms into the initial gas mixture.

B. CHEMICAL, COLLISIONAL, AND CAVITY MECHANISMS

The relative importances of the various kinetic processes are examined by simulating laser performance at typical laboratory conditions. Two initial gas mixtures of $XF{:}1F_2{:}1D_2{:}40He{:}8CO_2$ at 300°K and 50 torr with $X = 0.1$ and 0.01 are used, where the F atoms represent varying degrees of dissociation of F_2 by some initiation method. Mirror reflectivities are 0.9 and 1.0, and the active medium length is 53.3 cm. The following paragraphs give an interpretation of the principal kinetic mechanisms of these cases.

By noting the conservation of vibrational quanta in DF(v) and properly accounting for the vibrational levels, one may deduce the relation

$$\sum_{v=1}^{9} vP_v = \sum_{v=1}^{9} T_v + \sum_{v=1}^{9} v \frac{dDF(v)}{dt} + \sum_{v=1}^{9} D_{v,v-1} \qquad (14)$$

where P_v is the rate of pumping into level v by Reacts. (4) and (5), T_v is the rate of transfer from DF(v) to $CO_2(00^01)$ by React. (10), dDF(v)/dt is the rate of change of the DF(v) concentration, and $D_{v,v-1}$ is the total rate of deactivation of DF(v) to DF(v-1) by Reacts. (6) and (8).[2] The terms in Eq. (14) may be interpreted as

$$\begin{bmatrix}\text{Chemical}\\ \text{pumping}\\ \text{rate}\end{bmatrix} = \begin{bmatrix}\text{Collisional}\\ \text{transfer}\\ \text{rate}\end{bmatrix} + \begin{bmatrix}\text{Level filling}\\ \text{rate in DF}\end{bmatrix} + \begin{bmatrix}\text{Collisional}\\ \text{deactivation}\\ \text{rate of DF}\end{bmatrix}$$

The rate of excitation of $CO_2(00^01)$ by DF(v) is equal to the transfer rate; therefore, conservation of number density of $CO_2(00^01)$ may be expressed as

$$\sum_{v=1}^{9} T_v = \frac{d\left|CO_2(00^01)\right|}{dt} + D_C + X_{rad}(J) \tag{15}$$

where D_C is the rate of collisional deactivation of (00^01).

The relative importance of these mechanisms throughout the pulse is graphically illustrated in Fig. 7. An abbreviated notation for the terms in Eqs. (14) and (15) is used where the contribution from the pumping React. (4) for v = 1, · · · , 4 is referred to as P_C. For $v \geq 5$, React. (4) normally transfers matter in the reverse direction and is denoted as P_R. The contribution from React. (5) is labelled P_H. The total rate of collisional deactivation of DF(v) is denoted by D_D. The total collisional transfer rate is T, and the rates of level filling for DF(v) and $CO_2(00^01)$ are denoted as L_D and L_C, respectively.

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[2] The rate of React. (3) is normally too small to contribute to this term, and the number of quanta is not changed by the VV processes, React. (7).

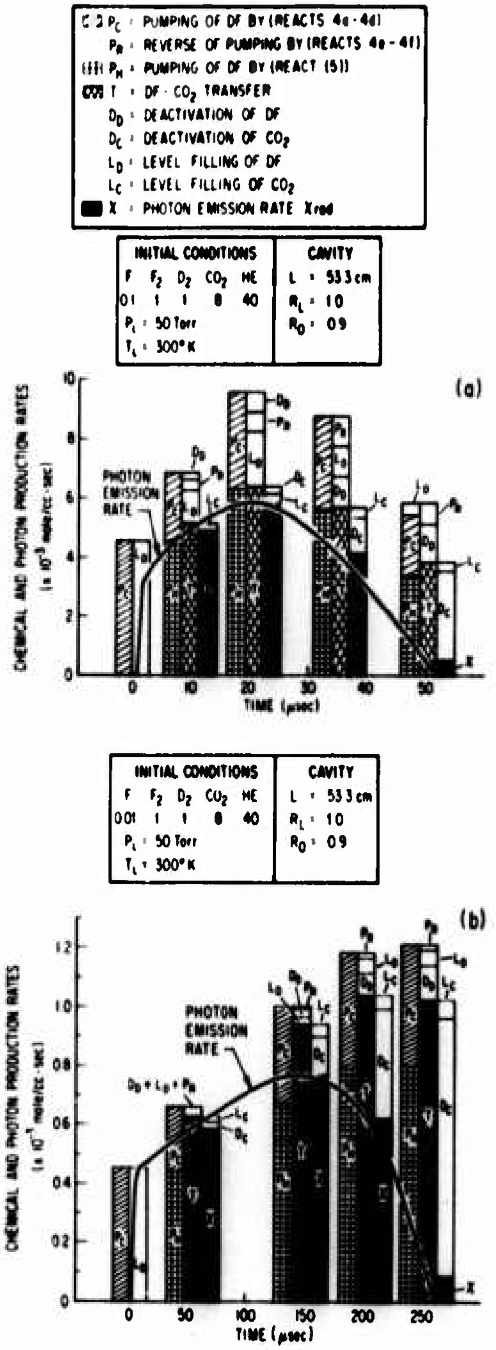

Fig. 7. Relationship of dominant kinetic mechanisms in the DF-CO_2 model. (a) Initial F = 0.1. (b) Initial F = 0.01.

We examine the mechanisms for $F = 0.1$, Fig. 7a, in detail and point out only those features that are different for $F = 0.01$ (Fig. 7b). Approximately 60% of the initial F atom concentration is consumed in the first few microseconds by React. (4), P_C. During this period, D atoms are produced, and the vibrational levels of DF(v) begin filling. During this transient, the rate of React. (5) increases with onset of operation of the chain, and transfer to $CO_2(00^01)$ is followed by emission of lasing photons when cavity threshold is reached. After the large initial consumption of F atoms, the concentration of F atoms increases slowly and monotonically, and we have quasisteady chain operation such that

$$[F]_{t=0} = [F]_{t\geq 0} + [D]_{t\geq 0}$$

Time histories of species concentrations for initial $F = 0.1$ are shown in Fig. 8.

The rate of level filling in DF, L_D, represents a rate of energy storage. Some of this stored energy is lost to collisional deactivation at a later time. From Fig. 7a, we see that only a small quantity of the stored energy in DF is available at pulse termination. A small rate of level filling in $CO_2(00^01)$, L_C, is required to maintain the necessary gain, Eq. (8). This rate is coupled to the rate of deactivation of the lower level, $\chi_{rad}(J)$, D_C, and the transfer rate.

Lasing continues until the rate of transfer into (00^01) is not sufficient to offset the loss mechanisms, and all $\alpha(J)$ drop below α_{thr}. Pulse termination is caused in part by three processes. First, depletion of the fuel

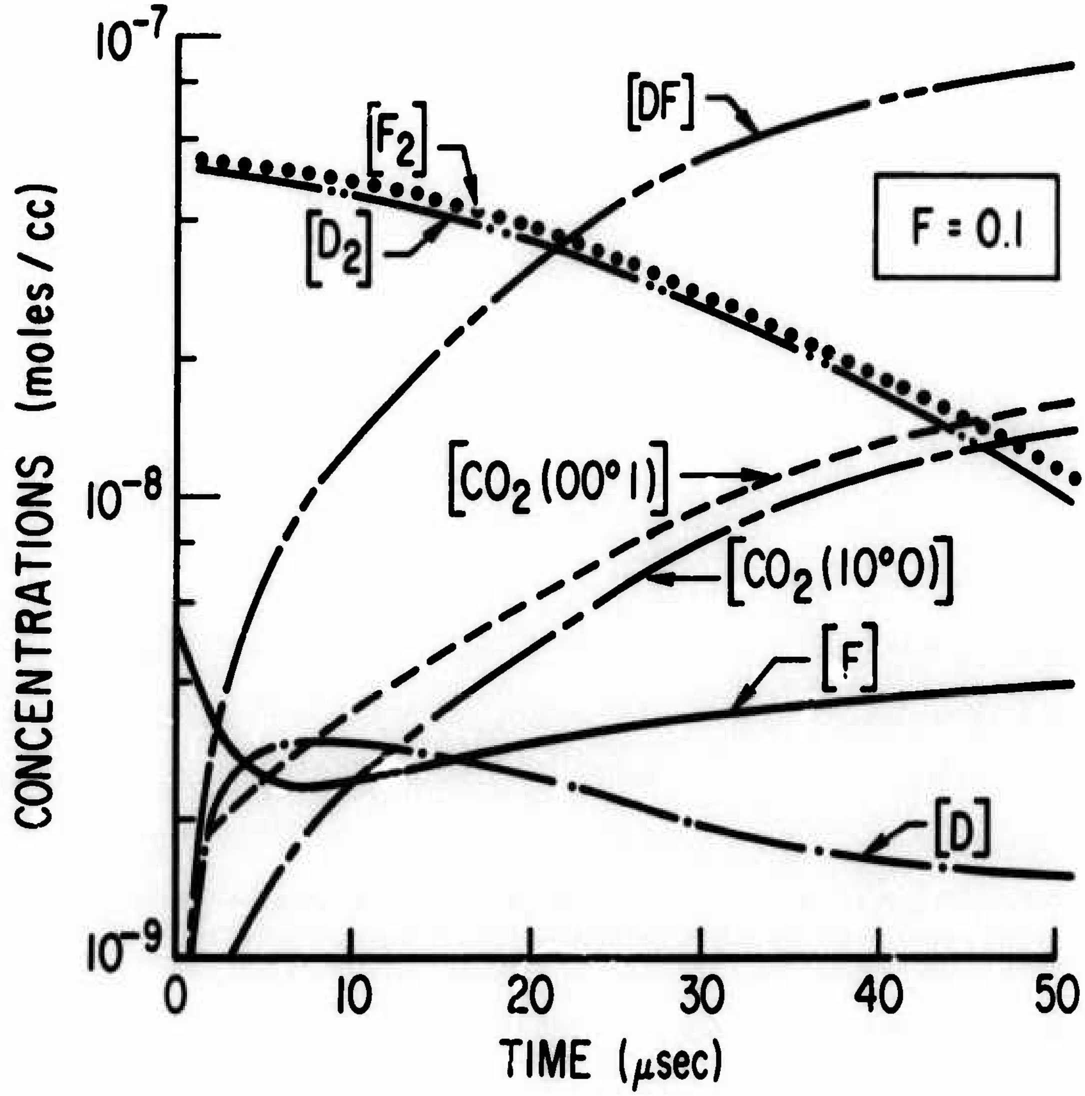

Fig. 8. Time histories of species concentrations for initial F = 0.1.

supply (D_2 and F_2) results in a lower mass transfer rate for Reacts. (4) and (5); this is not the case for F = 0.01. Second, deactivation of DF(v) and of $CO_2(00^01)$ by Reacts. (18) and (19) increases sharply near pulse termination because of the increasing DF and $CO_2(00^01)$ concentrations. Recall that DF is a very efficient collisional deactivator for both DF(v) and $CO_2(00^01)$. Third, the temperature rise resulting from the exothermic chain reaction gives rise to higher concentrations in the (01^10) and $(02^{\ell}0)$ levels of CO_2; therefore, depletion of the lower laser level is less efficient.

The principal differences in mechanisms for the two values of initiation are easily seen in Figs. 7a and 7b. With the higher pumping rate for F = 0.1, the transfer rate is not fast enough to deplete the excited levels of DF; hence, the rate of level filling is higher and a larger DF(v) population results in higher deactivation losses in DF. Pumping for F = 0.01 is slower and is still increasing when the pulse terminates. Although transfer to CO_2 is more efficient with this lower pumping rate, only 50% of the fuel is consumed before pulse termination, as compared to 80% for F = 0.1. Although deactivation in CO_2 is more important for F = 0.01 and is the cause of pulse termination, this is partly offset by the lower rate of deactivation of DF.[3] Hence, even with much less of the fuel consumed during the pulse, the chemical efficiency for F = 0.01 is 6% as compared to 8% for F = 0.01. A more detailed investigation of these mechanisms is now given.

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[3] Lower levels of initiation are often found to give rise to increased importance of mechanisms deactivating the lasing species [43].

In Fig. 9, the time histories of the rate L_r of DF(v) deactivation reactions are shown. For $F = 0.1$, the rapid production of DF(v) in the upper vibrational levels after initiation leads to deactivation of DF by the DF-D_2 VV React. (8). This rate eventually decreases as the concentration of $D_2(v)$ $(v > 0)$ increases relative to DF(v), until the reaction begins to run in reverse near termination, as shown by the dashed curve. The principal catalysts deactivating DF are F and D, React. (6e), and self-relaxation of DF, React. (6c). Catalysts of other VT mechanisms included in the figure are CO_2, React. (6a), He, React. (6b); and D_2, React. (6d).

A lower overall rate of DF deactivation is found when initial $F = 0.01$, and React. (6e) is less significant as a result of the lower F and D concentrations. A slower DF-D_2 VV transfer rate, React. (8), is also found.

With initial $F = 0.1$, the dominant deactivation catalyst for $CO_2(00^01)$ is DF, React. (18c), in Fig. 10. The catalyst for this reaction also contains F and D_2; however, the contribution of these species is at least one order of magnitude less than that of DF for most of the pulse duration. The high concentrations of He and CO_2 cause significant deactivation by Reacts. (18b) and (18a). As a result of our earlier assumption, the relative rates of React. (19) are very similar to those of (18). These deactivation mechanisms are very similar for $F = 0.01$, although the rate is lower as a result of the slower transfer rate and a lower concentration in (00^01).

The principal mechanism populating the lower lasing level (10^00) is laser action, $\chi_{rad}(J)$, Fig. 11. Reactions (13), (22), and (24) deactivate (11^10) and (030); these levels are supplied by deactivation of (00^01) through

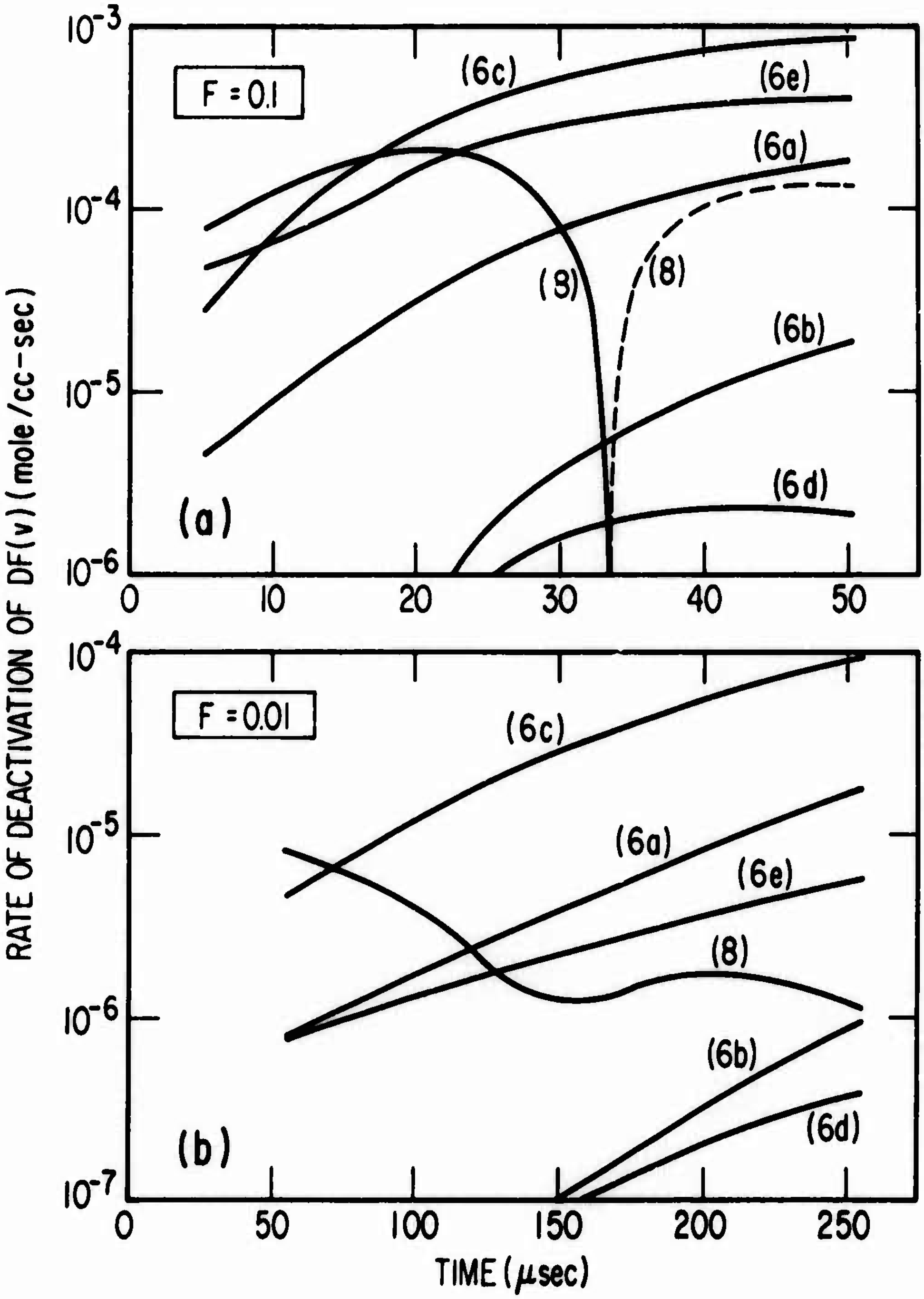

Fig. 9. Time history of the rate L_r of important processes deactivating DF(v). (a) Initial F = 0.1. (b) Initial F = 0.01.

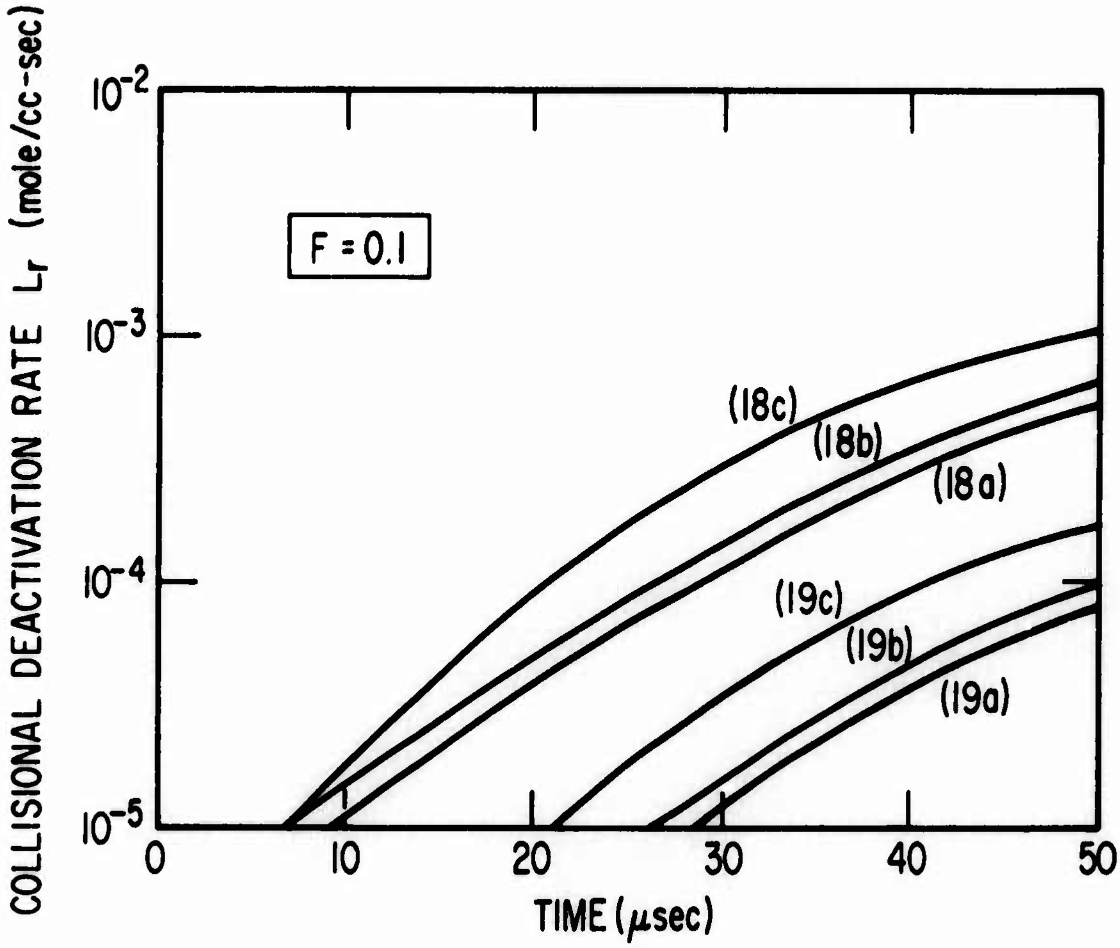

Fig. 10. Time history of the rate L_r of reactions deactivating the upper laser level.

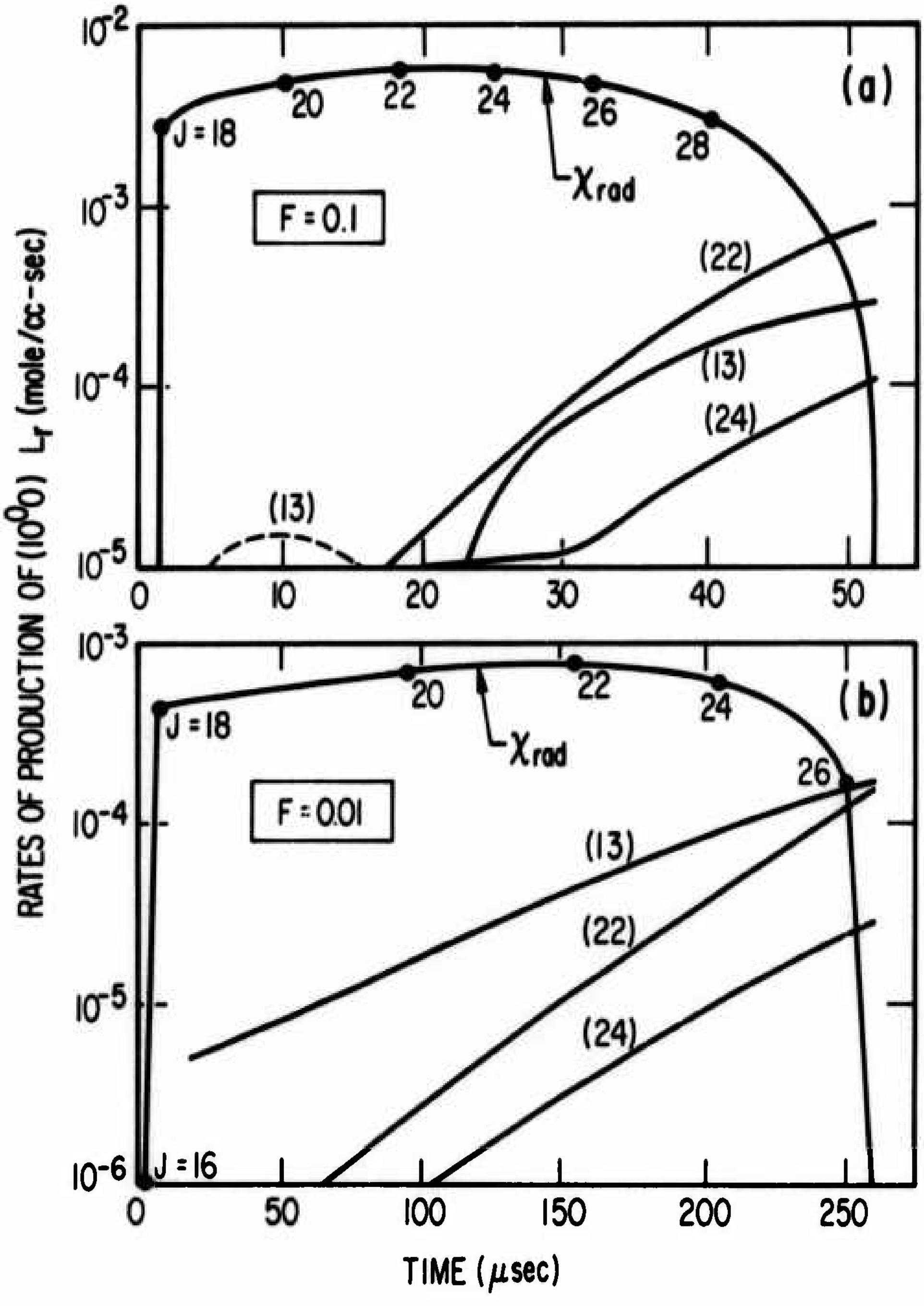

Fig. 11. Kinetic mechanisms that produce $CO_2(10^00)$. The time of a shift in the lasing transition to a new value of J is labeled with the new J. (a) Initial F = 0.1. (b) Initial F = 0.01.

Reacts. (18) and (19). The increased rate of React. (13) relative to Reacts. (22) and (24) for F = 0.01, as compared to F = 0.1, is a result of the slower rate of transfer to (00^01) and thus a lower concentration in this level and a higher concentration in the ground state.

Collisional processes that deactivate the lower laser level for F = 0.1, Fig. 12, and for F = 0.01 are similar. Deactivation of (10^00) to $(02^{\ell}0)$ through React. (25^{ℓ}) is the major mechanism that empties the lower level. The intramolecular VV reaction $(10^00) \rightarrow (01^10)$, React. (26), is also an important process, especially for M = He, React. (26b). The decrease during the reaction in the efficiency of the intermolecular VV process, React. (16), is a result of the increase in temperature and equilibrium population of (01^10).

Since deactivation of (10^00) is closely linked to the $(02^{\ell}0)$ levels which in turn deactivate through (01^10) to the ground state, we examine those processes that depopulate $(02^{\ell}0)$ in Fig. 13 for F = 0.1. Again, He is the principal deactivation catalyst, React. $(28^{\ell}b)$. Other intramolecular VV catalysts CO_2, Reacts $(28^{\ell}a)$, and D_2 and D, React. $(28^{\ell}c)$, contribute very little to the equilibration of these levels. Reactions (17^{ℓ}) are significant early in the pulse as VV deactivation processes, but near termination the increased population of (01^10) and the higher temperature cause these reactions to transfer matter in the reverse direction. The relative rates of these reactions for initial F = 0.01 are similar to those shown in Fig. 13.

In the present model, deactivation rate coefficients for $(02^{\ell}0)$ by VT and intramolecular VV processes are based on measurements of VT

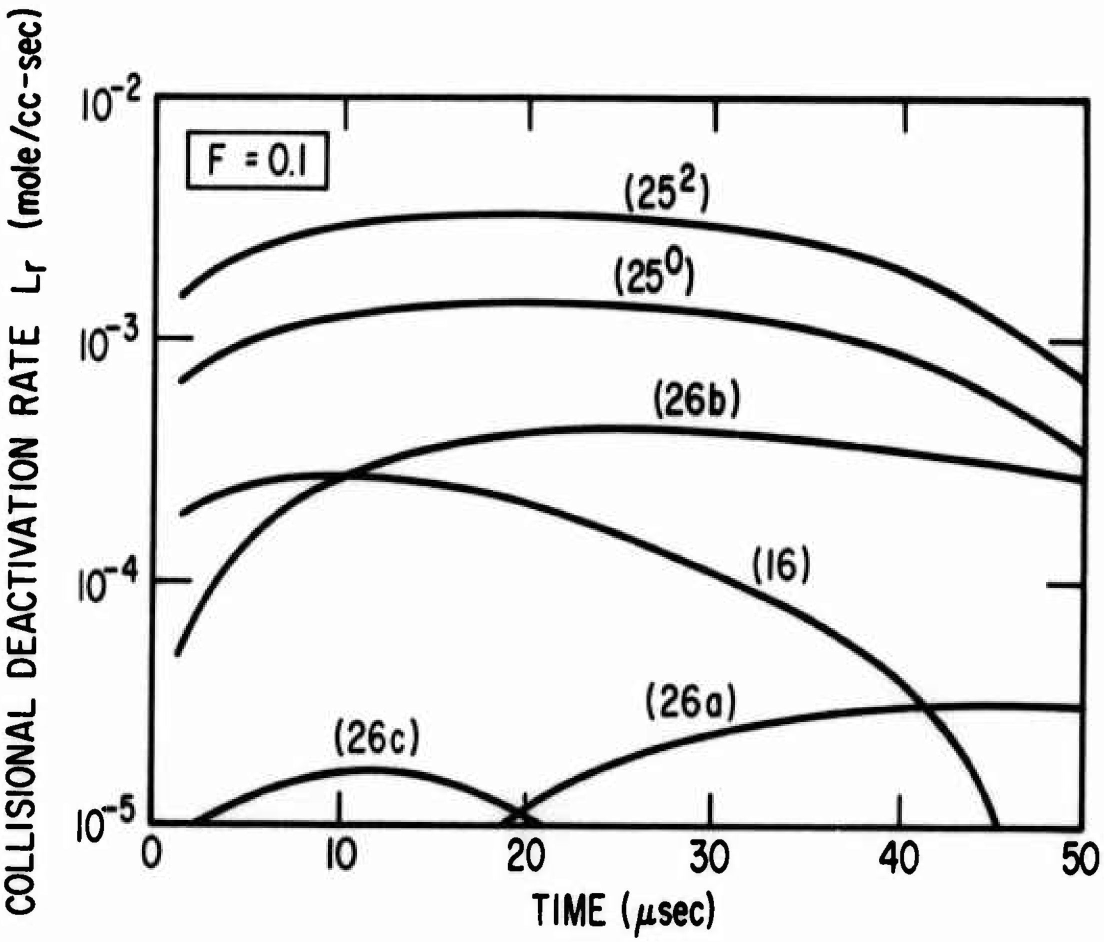

Fig. 12. Kinetic mechanisms that empty $CO_2(10^00)$.

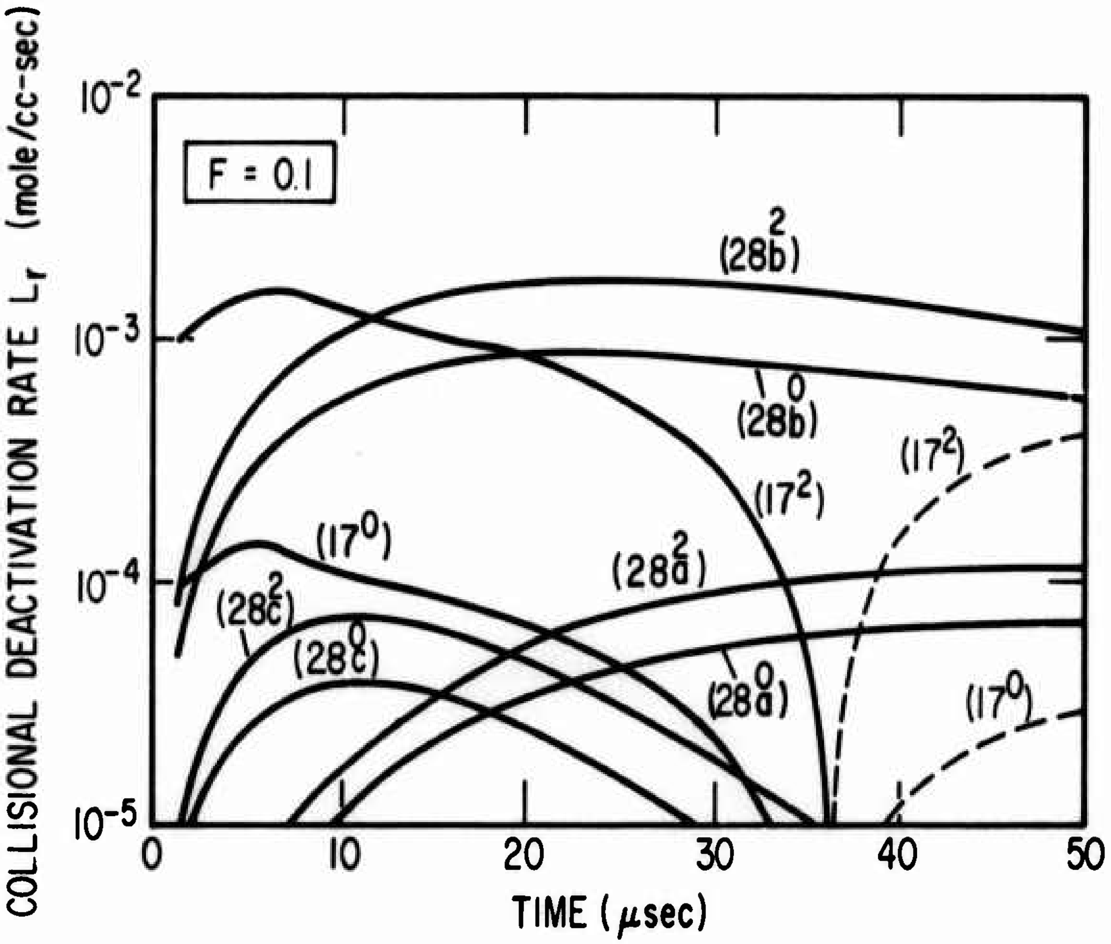

Fig. 13. Collisional processes that equilibriate $(02^{\ell}0)$.

deactivation of (01^10). Therefore, the VT mechanisms that equilibrate (01^10), React. (29), are comparable in importance to the corresponding VT mechanisms that equilibrate $(02^{\ell}0)$, React. (28^{ℓ}). For the mixtures considered in this study, we also find that state (10^00) and all levels below it are very near equilibrium throughout the reaction.

C. EFFECT OF VARIATIONS IN UNCERTAIN RATE COEFFICIENTS

The variations in rate coefficients from the standard are selected to include the major uncertainties, at the time of this study (early 1972), in rates of dominant processes. Of course, the degree of uncertainty of a rate coefficient is only speculative and significant changes in the initial mixture composition can change the relative importance of dominant mechanisms. Hence, the following variations only give an indication of the sensitivity of laser performance to some of the more important mechanisms. The effect of these changes on the peak power $P_{L_{max}}$, pulse energy, and pulse duration are shown in Table V.

The variations from the standard model (Table IV) studied and their principal effects are:

Rate 1 The rate of DF-CO_2 transfer, React. (10), is assumed constant in temperature and equal to 3.82×10^{12} cc/mole-sec for all DF(v). There is some evidence that the negative temperature dependence in the standard model is too strong [87]. When the pumping rate is large relative to the transfer rate, larger deactivation losses occur before transfer from DF(v) to CO_2 takes place. With k_{10} assumed constant, deactivation losses

Table V. Effect of Rate Coefficient Changes on Pulse Characteristics

Rate	F = 0.1			F = 0.01		
	$P_{L_{max}}$ (Watts/cc)	E (joule/liter)	$t_0 + t_c$, (μsec)[a]	$P_{L_{max}}$ (Watts/cc)	E (joule/liter)	$t_0 + t_c$ (μsec)[a]
Standard	65.9	2.33	52.0	8.64	1.71	260
1	86.4	3.04	52.4	9.12	1.82	266
2	104.5	3.49	50.3	9.55	1.91	267
3	65.9	2.35	52.1	8.64	1.70	260
4	66.9	2.70	61.7	9.11	2.05	303
5	65.0	2.29	51.9	8.64	1.71	260
6	65.9	2.33	51.6	8.64	1.70	260
7	63.2	1.94	43.1	7.46	1.25	215
8	108.0	2.32	34.14	17.81	2.07	156
9	70.3	2.65	55.4	9.73	2.02	275
10	67.9	2.42	52.3	8.71	1.73	262
11	59.1	1.81	43.8	8.48	1.66	257
12	64.7	2.18	48.6	8.38	1.61	252
13	66.5	2.37	52.8	8.68	1.72	261

[a] The exact value of t_0 was not determined for each calculation. Typical values of t_0 are 1 and 5 μsec for F=0.1 and 0.01, respectively, and t_0 is normally independent of deactivation mechanisms.

in DF are reduced. Hence, this change gives higher values for the pulse energy and peak power, and the effect is larger for F = 0.1 where the pumping rate is higher.

Rate 2 Transfer for DF(1) is the same as for Rate 1 and $k_{10_v} = vk_{10_1}$ Preliminary experimental evidence indicates that the rate of transfer may increase with v [87]. By comparing these results with those of Rate 1, both $P_{L_{max}}$ and E increase with this change, especially for F = 0.1. The competition between deactivation in DF and transfer to CO_2 indicated earlier is responsible for this behavior.

Rate 3 The efficiency of deactivation of $(00^0 1)$ by D_2 and F, React. (18) and (19), is assumed the same as CO_2-CO_2. The laser pulse characteristics are insensitive to these reactions for our choice of initial concentrations.

Rate 4 Rate 3 is modified such that the efficiency of DF in deactivating $(00^0 1)$ is proportional to T^{-2} as indicated by combining results of Ref. [35] with preliminary results of Cool at 300° K [47]. Of course, this change gives rise to an increase in E and $P_{L_{max}}$, since deactivation is important later in the reaction when the temperature and the DF concentration are both higher.

Rate 5 The rate coefficients for all processes that deactivate $(10^0 0)$ are arbitrarily reduced by a factor of 10. This decrease was not sufficient to cause $(10^0 0)$ to deviate from near equilibrium; therefore, the pulse characteristics are essentially the same as those computed with the standard rate. A much larger decrease in these rate coefficients is necessary before pulse characteristics are substantially altered.

Rate 6 Rate coefficients for Reacts. (13), (22), and (24) are increased by a factor of 10. This change is not large enough to prevent the reactions that relax (10^00) from maintaining the near equilibrium condition; thus, no change is found in pulse characteristics.

Rate 7 Rate coefficients for all processes in Reacts. (18) and (19) are arbitrarily increased by a factor of 2. This pessimistic change is greater than the uncertainty in the rates of these processes and causes a reduction in $P_{L_{max}}$, E, and $t_0 + t_c$.

Rate 8 The overall pumping rates k_4 and k_5 are increased by a factor of 2. As expected, $P_{L_{max}}$ increases and the pulse duration decreases with the faster chain. Again, the competition between deactivation in DF and transfer to CO_2 manifests itself, and no increase in E for $F = 0.1$ is shown while E increases for $F = 0.01$ where this competition is less.

Rate 9 The distribution of $D + F_2$ pumping, Reacts. (5), are assumed to be more sharply peaked near $v = 8$. The new distribution is obtained from Herbelin's new interpretation [88] of recent $H + F_2$ data of Jonathan and co-workers on the basis of revised estimates of the HF matrix elements. The altered distribution is

$$k_5(0): k_5(1): k_5(2): k_5(3): k_5(4): k_5(5): k_5(6): k_5(7):k_5(8):k_5(9) =$$
$$0:0.052:0.065:0.078:0.078:0.208:0.494:0.792: 1.0:0.701$$

With this distribution, React. (5) converts 53% of the available chemical energy into vibrational energy; the standard rate converts 46% of this energy. The values of $P_{L_{max}}$, E, and $t_0 + t_c$ all increase with this change as expected.

Rate 10 All DF-DF VV rate coefficients are taken as 1/4th the binary collision rate. Preliminary experimental measurements by Bott [87] indicate that these rate coefficients may be this large. As in the HF system [43, 44], laser performance is insensitive to these processes.

Rate 11 The rate coefficient for deactivation of DF(v) by D and F is increased by a factor of 10. The effect of this rate increase is more important for F = 0.1 where the F and D concentrations are larger.

Rate 12 The efficiency of CO_2 in deactivating DF is increased by a factor of 10. For these mixture compositions, this change produces a very small decrease in the laser performance characteristics.

Rate 13 The DF-D_2 VV rate coefficients, React. (8), are increased by a factor of 10. Laser performance for these concentrations is insensitive to these reactions.

VI. SUMMARY AND CONCLUSIONS

A kinetic model of a DF-CO_2 chemical transfer laser and a review of the rate coefficient literature needed to formulate this model are presented. The D_2+F_2 portion of this model is applicable for modeling the DF chemical laser. Rate coefficients recommended for the model are listed in Table IV. A computer simulation is used to examine the relative importance of various kinetic mechanisms during lasing. Two initial mixture compositions of XF : 1 F_2 : 1 D_2 : 8 CO_2 : 40 He at 50 torr and 300°K, with initiation levels modeled by setting X = 0.1 and 0.01, are studied. For F = 0.01, a 260-μsec pulse with 6% chemical efficiency is predicted, while the higher level of initiation produces a 52-μsec pulse with 8% chemical efficiency. To the best of our knowledge, this is the first published calculation of a CO_2 lasing system that includes detailed modeling of the rate processes that relax the lower laser level. For the initial compositions considered, the (10^00) level and those below it are near equilibrium. Calculations with other compositions, however, indicate that this is not always true and detailed modeling is sometimes necessary.

The sensitivity of laser performance to variations in uncertain rate coefficients is shown and rate coefficient measurements critical to improved modeling are indicated. The uncertain rate coefficients for the more important mechanisms include:

1. Rate of deactivation of DF(v) by D and F.
2. Overall pumping rate and distribution into vibrational levels of DF by F + D_2 and D + F_2.

3. Rate coefficient for transfer from DF(v) to $CO_2(00^01)$ as a function of T and v.

4. Rate coefficient for collisional deactivation of $CO_2(00^01)$ by DF over a wide temperature range.

5. Rate coefficient for most of the intermolecular and intramolecular VV reactions in CO_2 involving levels (11^10), $(03^\ell0)$, (10^00), and $(02^\ell0)$.

Additional measurements and theoretical estimates of these rate coefficients will improve the ability of theoretical laser models to predict laser performance.

Many of the recommended rate coefficients are tentative and subject to reevaluation as more data become available. Nevertheless, the relationship of pumping, transfer, deactivation, and lasing and the competition between deactivation of DF and transfer to CO_2 has been clearly revealed by these calculations.

REFERENCES

[1] J.R. Airey, "Cl + HBr Pulsed Chemical Laser: A Theoretical and Experimental Study," J. Chem. Phys., vol. 52, pp. 156-167, 1970.

[2] G. Emanuel, W.D. Adams, and E.B. Turner, "RESALE - 1: A Chemical Laser Computer Program," El Segundo, Calif.: The Aerospace Corp. Tech. Rept. TR-0172(2776)-1, Mar. 1972, and G. Emanuel and W.D. Adams, "RESALE-2, CO_2, and INHALE," El Segundo, Calif.: The Aeorspace Corp., Tech. Rept. TR-0172(2776)-5, April 1972.

[3] W.S. King and H. Mirels, "Numerical Study of a Diffusion Type Chemical Laser," AAIA Paper No. 72-146, presented at AIAA 10th Aerospace Sci. Meet., San Diego, Calif., Jan. 17-19, 1972.

[4] R.K. Seals, Jr., F. Allario, R.A. Lucht, and H.A. Hassan, "Theory and Experiment of Electric Discharge CO_2 Convection Lasers," AIAA Paper No. 71-588, presented at AIAA 4th Fluid and Plasma Dynamics Conf., Palo Alto, Calif., June 21-23, 1971.

[5] R.L. Taylor and S. Bitterman, "Survey of Vibrational Relaxation Data for Processes Important in the CO_2-N_2 Laser System," Rev. Mod. Phys., vol. 41, pp. 26-47, 1969.

[6] N. Cohen, "A Review of Rate Coefficients for Reactions in the H_2-F_2 Laser System," El Segundo, Calif.: The Aerospace Corp., Tech. Rept. TR-0172(2779)-2, Sept. 1971.

[7] R.W.F. Gross, "Chemically Pumped CO_2 Laser," J. Chem. Phys., vol. 50, pp. 1889-1890, 1969.

REFERENCES (Continued)

[8] T.A. Cool, R.R. Stephens, and T.J. Falk, "A Continuous-Wave Chemically Excited CO_2 Laser," Int. J. of Chem. Kin., vol. 1, pp. 495-497, 1969.

[9] T.A. Cool, T.J. Falk, and R.R. Stephens, "DF-CO_2 and HF-CO_2 Continuous-Wave Chemical Lasers," Appl. Phys. Lett., vol. 15, pp. 318-320, 1969.

[10] T.A. Cool and R.R. Stephens, "Chemical Laser by Fluid Mixing," J. Chem. Phys., vol. 51, pp. 5175-5176, 1969.

[11] T.A. Cool and R.R. Stephens, "Efficient Purely Chemical cw Laser Operation," Appl. Phys. Lett., vol. 16, pp. 55-58, 1970.

[12] T.A. Cool, R.R. Stephens, and J.A. Shirley, "HCl, HF, and DF Partially Inverted cw Chemical Lasers," J. Appl. Phys., vol. 41, pp. 4038-4050, 1970.

[13] T.A. Cool, J.A. Shirley, R.N. Sileo, and R.R. Stephens, "Purely Chemical Laser Operation in the HF, DF, HF-CO_2, and DF-CO_2 Systems, "AIAA Paper No. 71-27, presented at AIAA 9th Aerospace Sci. Meet., January 1971.

[14] N.G. Basov, V.T. Galochkin, V.I. Igoshin, L.V. Kulakov, E.P. Markin, A.I. Nikitin, and A.N. Oraevsky, "Spectra of Stimulated Emission in the Hydrogen-Fluorine Reaction Process and Energy Transfer from DF to CO_2," Appl. Opt., vol. 10, pp. 1814-1820, 1971.

REFERENCES (Continued)

[15] T.J. Falk, "Parametric Studies of the DF-CO_2 Chemical Transfer Laser," Buffalo, N.Y.: Cornell Aeronautical Laboratory, CAL NO. RF-2966-A-1, Final Tech. Rept. F29061-70-C-066, June 1971.

[16] H. Brunet and M. Mabru, "Design of a DF-CO_2 Chemical Laser with Transverse Gas Flow," C.R. Acad. Sc. Paris, vol. 272, pp. 232-235, 1971.

[17] S.N. Suchard, R.L. Kerber, G. Emanuel, and J.S. Whittier, "Effect of H_2 Pressure on Pulsed $H_2 + F_2$ Laser, Experiment and Theory," to be published in J. Chem. Phys. (Dec 1972).

[18] T.A. Jacobs, R.R. Giedt, and N. Cohen, "Recombination Rate of Deuterium Atoms," J. Chem. Phys., vol. 48, pp. 947-948, 1968.

[19] T.A. Jacobs, R.R. Giedt, and N. Cohen, "Kinetics of Decomposition of HF in Shock Waves," J. Chem. Phys., vol. 43, pp. 3688-3693, 1965.

[20] G. Herzberg, Molecular Spectra and Molecular Structure, Princeton, N.J.: D. Van Nostrand Co., Inc., 1950.

[21] R.L. Wilkins, The Aerospace Corp., private communication, 1971.

[22] R.L. Jaffe and J.B. Anderson, "Classical Trajectory Analysis of the Reaction $F + H_2 \rightarrow HF + H$," J. Chem. Phys., vol. 54, pp. 2224-2236, 1971.

REFERENCES (Continued)

[23] J.T. Muckerman, "Monte Carlo Calculations of Energy Partitioning and Isotope Effects in Reactions of Fluorine Atoms with H_2, HD, and D_2," J. Chem. Phys., vol. 54, pp. 1155-1164, 1971.

[24] R.L. Wilkins, "Absolute Rates of the Reactions H_2 + F and F_2 + H," El Segundo, Calif.: The Aerospace Corp., Tech. Rept. TR-0059-(6753-20)-1, March 1971.

[25] J.H. Parker and G.C. Pimentel, "Vibrational Energy Distribution through Chemical Laser Studies. I. Fluorine Atoms Plus Hydrogen or Methane," J. Chem. Phys., vol. 51, pp. 91-96, 1969.

[26] T.P. Schafer, P.E. Siska, J.M. Parson, F.P. Tully, Y.C. Wong, and Y.T. Lee, "Crossed Molecular Beam Study of F_2 + D_2," J. Chem. Phys., vol. 53, pp. 3385-3387, 1970.

[27] K.G. Anlauf, P.E. Charters, D.S. Horne, R.G. MacDonald, D.H. Maylotte, J.C. Polanyi, W.J. Skrlac, D.C. Tardy, and K.B. Woodall, "Translational Energy - Distribution in the Products of Some Exothermic Reactions," J. Chem. Phys., vol. 53, pp. 4091-4092, 1970.

[28] J.C. Polanyi and D.C. Tardy, "Energy Distribution in the Exothermic Reaction F + H_2 and the Endothermic Reaction HF + H^*," J. Chem. Phys., vol. 51, pp. 5717-5719, 1969.

[29] N. Jonathan, C.M. Melliar-Smith, and D.H. Slater, "Initial Vibrational Energy Distributions Determined by Infra-red Chemiluminescence, I. The Reaction of Fluorine Atoms with Hydrogen and Methane," Mol. Phys., vol. 20, pp. 93-102, 1971.

[30] N. Jonathan, C.M. Melliar-Smith, D. Timlin, and D.H. Slater, "Analysis of Hydrogen Fluoride Infrared Chemiluminescence from Simple Atom-Molecule Reactions," Appl. Opt., vol. 10, pp. 1821-1826, 1971.

[31] N. Jonathan, C.M. Melliar-Smith, S. Okuda, D.H. Slater, and D. Timlin, "Initial Vibrational Energy Level Distributions Determined by Infra-red Chemiluminescence II. The Reaction of Fluorine Atoms with Hydrogen Halides," Mol. Phys., vol. 22, pp. 561-574, 1971.

[32] R. Wilkins, "Monte Carlo Calculations of Reaction Rates and Energy Distributions Among Reaction Products $F + H_2$, $HF + H$," El Segundo, Calif.: The Aerospace Corp., Tech. Rept., TR-0073(3430)-3, 15 Sept. 1972.

[33] R. L. Wilkins, "Monte Carlo Calculations of Reaction Rates II. $H + HF(v) \rightarrow H_2(v') + F$ and $H + FH(v) \rightarrow HF(v') + H$," El Segundo, Calif.: The Aerospace Corp., Tech. Rept. TR-0073(3430)-7, 1972.

[34] J. F. Bott and N. Cohen, "A Shock Tube Study of DF Vibrational Relaxation," to be published in J. Chem. Phys.

REFERENCES (Continued)

[35] R.R. Stephens and T.A. Cool, "Vibrational Energy Transfer and Deexcitation in the HF, DF, HF-CO_2 and DF-CO_2 Systems," submitted to J. Chem. Phys.

[36] J.F. Bott and N. Cohen, "Shock Tube Studies of HF Vibrational Relaxation," J. Chem. Phys., vol. 55, pp. 3698-3706, 1971.

[37] J.F. Bott and N. Cohen, "HF Vibrational Relaxation by F Atoms," J. Chem. Phys., vol. 55, pp. 5124-5125, 1971.

[38] J.A. Blauer, W.C. Solomon, and T.W. Owens, "Collisional Efficiency in Vibrational Excitation of HF and DF," Edwards AFB, Calif.: Air Force Rocket Propulsion Lab., Tech. Rept.

[39] B.A. Ridley and I.W.M. Smith, "The Vibrational Relaxation of HCl ($v = 3$, 2 and 1) by Cl Atoms," Chem. Phys. Lett., vol. 9, pp. 457-459, 1971.

[40] D. Rapp and P. Englander-Golden, "Resonant and Near Resonant Vibration-Vibration Energy Transfer between Molecules in Collisions," J. Chem. Phys., vol. 40, pp. 573-575, 1964.

[41] H.L. Chen and C.B. Moore, "Vibration-Vibration Energy Transfer in Hydrogen Chloride Mixtures," J. Chem. Phys., vol. 54, pp. 4080-4084, 1971.

[42] V.I. Gorshkov, V.V. Gromov, V.I. Igoshin, E.L. Koshelev, E.P. Markin, and A.N. Oraevsky, "Investigation of Vibrational Relaxation in the Hydrogen Chloride Chemical Laser," App. Opt., vol. 10, pp. 1781-1785, 1971.

REFERENCES (Continued)

[43] R.L. Kerber, G. Emanuel, and J.S. Whittier, "Computer Modeling and Parametric Study for a Pulsed $H_2 + F_2$ Laser," Appl. Opt., vol. 11, pp. 1112-1123, 1972.

[44] G. Emanuel and J.S. Whittier, "Closed-Form Solution to Rate Equations for an $F + H_2$ Laser Oscillator," to be published in Appl. Opt.

[45] J.R. Airey and S.F. Fried, "Vibrational Relaxation of Hydrogen Fluoride," Chem. Phys. Lett., vol. 8, pp. 23-26, 1971.

[46] J.L. Stretton, Transfer and Storage of Energy by Molecules, G.M. Burnett and A.M. North, Eds., New York: Wiley-Interscience, 242 pp., 1969.

[47] T.A. Cool, Naval Research Lab., private communication, 1971.

[48] H.L. Chen, J.C. Stephenson, and C.B. Moore, "Laser-Excited Vibrational Fluorescence of HCl and the $HCl-CO_2$ Laser," Chem. Phys. Lett., vol. 2, pp. 593-596, 1968.

[49] A.B. Callear, "Measurement of Energy Transfer in Molecular Collisions," Appl. Opt. Suppl. (Chemical Lasers), vol. 2, pp. 145-170, 1965.

[50] K.F. Herzfeld, "Deactivation of Vibration by Collision in CO_2," Discussions Faraday Soc., vol. 33, pp. 22-27, 1962.

[51] K.F. Herzfeld, "Deactivation of Vibrations by Collision in the Presence of Fermi Resonance," J. Chem. Phys., vol. 47, pp. 743-752, 1967.

REFERENCES (Continued)

[52] C.K. Rhodes, M.J. Kelly, and A. Javan, "Collisional Relaxation of the 10^00 State in Pure CO_2," J. Chem. Phys., vol. 48, pp. 5730-5731, 1968.

[53] R.D. Sharma, "Kinetics of Equilibration of 1388 cm^{-1} Vibrational Level of CO_2," J. Chem. Phys., vol. 49, pp. 5195-5197, 1968.

[54] R.D. Sharma and C.A. Brau, "Near-Resonant Vibrational Energy Transfer in N_2-CO_2 Mixtures," Phys. Rev. Lett., vol. 19, pp. 1273-1275, 1967.

[55] R.D. Sharma and C.A. Brau, "Energy Transfer in Near Resonant Molecular Collisions Due to Long-Range Forces with Application to Transfer of Vibrational Energy from ν_3 Mode of CO_2 to N_2," J. Chem. Phys., vol. 50, pp. 924-930, 1969.

[56] K.N. Seeber, "Radiative and Collisional Transitions between Coupled Vibrational Modes of CO_2," J. Chem. Phys., vol. 55, pp. 5077-5081, 1971.

[57] T.J. Bridges, "Competition, Hysteresis and Reactive Q-Switching in CO_2 Lasers at 10.6 Microns," Appl. Phys. Lett., vol. 9, pp. 174-176, 1966.

[58] R.J. Carbone and W.J. Witteman, "Vibrational Energy Transfer in CO_2 under Laser Conditions with and without Water Vapor," IEEE J. Quantum Electron., vol. QE-5, pp. 442-447, 1969.

REFERENCES (Continued)

[59] Yu. V. Brzhazovskii, L.S. Vasilenko, and V.P. Chebotaev, "Effect of Collisions on the Nature of Saturation of the Vibrational Rotational Transitions of the CO_2 $00^{0}1$-$10^{0}0$ Band," Zh. Eksp. Teor. Fiz., vol. 55, pp. 2095-2102, 1968; also, Sov. Phys. JETP, vol. 28, pp. 1108-1112, 1969.

[60] Yu.V. Brzhazovsky, V.P. Chebotayev, and L.S. Vasilenko, "Collision Effect on the Saturation Character of Vibration-Rotation Transitions for $00^{0}1$-$10^{0}0$ Band of CO_2," IEEE J. Quantum Electron., vol. QE-5, pp. 146-151, 1969.

[61] P.K. Cheo, "Effects of CO_2, He, and N_2 on the Lifetimes of the $00^{0}1$ and $10^{0}0$ CO_2 Laser Levels and on Pulsed Gain at 10.6μ," J. Appl. Phys., vol. 38, pp. 3563-3568, 1967.

[62] P.K. Cheo, "G-1-Relaxation of CO_2 Laser Levels by Collisions with Foreign Gases," IEEE J. Quantum Electron., vol. QE-4, pp. 587-593, 1968.

[63] L.O. Hocker, M.A. Kovacs, C.K. Rhodes, G.W. Flynn and A. Javan, "Vibrational Relaxation Measurements in CO_2 Using an Induced-Fluorescence Technique,"Phys. Rev. Lett., vol. 17, pp. 233-235, 1966.

[64] C.B. Moore, R.E. Wood, B. Hu, and J.T. Yardley, "Vibrational Energy Transfer in CO_2 Lasers,"J. Chem. Phys., vol. 46, pp. 4222-4231, 1967.

REFERENCES (Continued)

[65] J.T. Yardley and C.B. Moore, "Intramolecular Vibration-to-Vibration Energy Transfer in Carbon Dioxide," J. Chem. Phys., vol. 46, pp. 4491-4495, 1967.

[66] J.A.F. Alexander, J.T. Houghton, and W.B. McKnight, "Collisional Relaxation from the ν_3 Vibration of CO_2," J. Phys. B (Proc. Phys. Soc.), vol. 1, pp. 1225-1226, 1968.

[67] W.A. Rosser, Jr., A.D. Wood, and E.T. Gerry, "Deactivation of Vibrationally Excited Carbon Dioxide (ν_3) by Collisions with Carbon Dioxide or with Nitrogen," J. Chem. Phys., vol. 50, pp. 4996-5008, 1969.

[68] W.A. Rosser and E.T. Gerry, "De-excitation of Vibrationally Excited CO_2^* (ν_3) by Collisions with He, O_2 and H_2O," J. Chem. Phys., vol. 51, pp. 2286-2287, 1969.

[69] W.A. Rosser, Jr., and E.T. Gerry, "De-excitation of Vibrationally Excited CO_2 (001) by Collisions with CO_2, H_2, NO, and $C\ell_2$," J. Chem. Phys., vol. 54, pp. 4131-4132, 1971.

[70] J.C. Stephenson, R.E. Wood, and C.B. Moore, "Temperature Dependence of Intra-molecular Vibration → Vibration Energy Transfer in CO_2," J. Chem. Phys., vol. 54, pp. 3097-3102, 1971.

[71] R.S. Chang, R.A. McFarlane and G.J. Wolga, "Vibrational Deactivation of CO_2 by HF and DF at 75 and 100°C, "J. Chem. Phys., vol. 56, pp. 667-669, 1972.

REFERENCES (Continued)

[72] J.T. Houghton, "Fluorescence from the ν_3 Vibration of Carbon Dioxide," Proc. Phys. Soc. (London), vol. 91, p. 439, 1967.

[73] C.J.S.M. Simpson and T.R.D. Chandler, "A Shock Tube Study of Vibrational Relaxation in Pure CO_2 and Mixtures of CO_2 with the Inert Gases, Nitrogen, Deuterium and Hydrogen," Proc. Roy. Soc., Lond., vol. A-317, pp. 265-277, 1970.

[74] P.V. Slobodskaya, "Study of the Relaxation Time of the Vibrational State Corresponding to the 4.3 nm Absorption Band of Carbon Dioxide by Means of a Spectraphone," Opt. Spectra, vol. 22, pp. 14-17, 1967.

[75] T.L. Coltrell, I.M. MacFarlane, and A.W. Read, "Measurement of Vibrational Relaxation Times by the Spectraphone, Systems $CO_2 + N_2$ and $N_2O + N_2$," Trans. Faraday Soc., vol. 63, pp. 2093-2097, 1967.

[76] M. Huetz - Aubert, P. Chevalier, and C. Klapiaz, "Relations entre les temps de relaxation thermiques de vibration determines par differantes methods. Application aux niveaux de vibration (01^10) et (00^01) de CO_2," Compt. Rend., vol. B268, pp. 748-750, 1969.

[77] R. Tripodi, "Interpretation of Spectrophone Results for CO_2," J. Chem. Phys., vol. 52, pp. 3298-3299, 1970.

[78] M. Huetz-Aubert, P. Chevalier, and R. Tripodi, "Phase-Lag Equation for CO_2 in a Spectraphone and Its Application to Deducing the Predominant Vibration-Vibration Transitions," J. Chem. Phys., vol. 54, pp. 2289-2290, 1971.

REFERENCES (Continued)

[79] M. Huetz-Aubert and R. Tripodi, "Rate Equations for the Vibrational Relaxation of CO_2-N_2 or CO_2-Noble Gas Mixtures - Application to Comparison of Spectrophone Data with Results from Other Experimental Techniques," J. Chem. Phys., vol. 55, pp. 5724-5734, 1971.

[80] G.R. Levinson, A.N. Sviridov, V.P. Tychinskiy, and V.G. Frolova, "Measurement of the Lifetimes of the 00°v System of Vibrational Levels of CO_2 Molecules," Radio Engnr. and Electron. Phys., vol. 14, pp. 580-585, 1969.

[81] A.S. Biryukov, R.I. Serikov, and E.S. Trekov, "Measurement of the time of Vibrational Relaxation of the 00^01 level of the CO_2 Molecule," Zh. Eksp. Teor. Fiz., vol. 59, pp. 1513-1517, 1970; also, Sov. Phys. JETP, vol. 32, pp. 825-827, 1971.

[82] R.L. Taylor, M. Camac, and R.M. Feinberg, "Measurements of Vibration-Vibration Coupling in Gas Mixtures," Proc. of 11th Symp. (Intern.) on Combust., Aug. 14-20, 1966, Pittsburg, Pa.: Combustion Inst., pp. 49-65, 1967.

[83] T.L. Cottrell and J.C. McCoubrey, Molecular Energy Transfer in Gases, London: Butterworths Scientific Publications, Ltd., pp. 26-29, 1961.

[84] M. Huety and P. Chevalier, "Determination of Thermal Relaxation Times of Gases by the Impact Tube Method-Measurements for the (01^10) Vibration of Pure CO_2 and CO_2 Mixed with Other Gases," Adv. Molec. Proc., vol. 2, pp. 101-117, 1970.

REFERENCES (Continued)

[85] R.D. Sharma, "Deactivation of Bending Mode of CO_2 by Hydrogen and Deuterium," Everett, Mass.: AVCO Everett Research Lab., Res. Rept. 319, Contract F33615-68-C-1030, January 1969.

[86] T.L. Coltrell and M.A. Day, Molecular Relaxation Processes, New York: Academic Press, Inc., p. 253, 1966.

[87] J.F. Bott, The Aerospace Corp., private communication, 1972.

[88] J. Herbelin and G. Emanuel, "Einstein Coefficients for Diatomic Molecules," El Segundo, Calif.: The Aerospace Corp., Tech. Rept., to be published.