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CURRENT STATUS OF HF/DF CHAIN CHEMICAL LASER

Air Force Weapons Laboratory
Kirtland Air Force Base, New Mexico

November 1976

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Final Report

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Air Force Systems Command

Kirtland Air Force Base, NM 87117

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Experimental performance of the $H_2 + F_2$ chain reaction chemical lasers has consistently fallen below the theoretically less advantageous $F + H_2$ cold reaction. This report discusses the current status of chain laser modeling and considers the implications of the computer results. Experimental data have drastically changed the HF(V) V → T,R deactivation rate scale from V to $V^{2.3}$ independent of the deactivating species. A new H + HF(V)

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deactivation rate for $V \geq 3$ has been measured and determined to be approximately 10^{14} cc/mole sec. LAMP computer code results with the new kinetic rates have greatly improved the agreement between theory and experiment. The chain reaction for a chemical laser has been determined to be more efficient in the $DF-CO_2$ transfer laser and the HF pulsed laser.

PREFACE

I am deeply indebted to Capt. Larry Rapagnani for his many hours spent working with the LAMP computer program at AFWL. Many of his calculations entered directly into the conclusions of this report. Of course, the computational and experimental results supplied by the Aerospace Corporation have further aided in making this report possible. Finally, the experimental results offered by TRW and UTRC have supplied many of the justifications I have used in resolving the potential of the chain reaction.

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INTRODUCTION

Computer calculations from a variety of sources have predicted enormous systems advantages for the HF/DF-chain chemical laser (refs. 1 through 3). A thorough discussion of these expectations can be found in AFWL TR-75-201 (ref. 4). Unfortunately, the observed performance has lagged behind that of the theoretically less advantageous cold reaction devices. Several DOD-funded efforts have been conducted to either improve upon this situation or to explain it. It is the purpose of this report to summarize the current status of chain modeling and consider the implications of the results. Although the present discussion will be confined to HF, the basic results should also be applicable to DF. For purposes of brevity in following discussions, it will be assumed that the reader is familiar with the conventional chemical laser terminology. For the uninitiated, definitions are included in appendix A.

1. CHAIN POTENTIAL

It is appropriate to begin a discussion of the chain with a brief explanation of why its use had been thought to be so advantageous compared to the cold reaction. Both systems are based upon the following chemical pumping reactions:

$$F + H_2 \rightarrow HF^* + H \qquad \text{"Cold Reaction"} \qquad (1)$$

$$H + F_2 \rightarrow HF^* + F \qquad \text{"Hot Reaction"} \qquad (2)$$

Cold reaction devices are run under conditions which are selected to utilize only reaction 1. Recent results suggest that this goal may only be partially achieved due to nozzle wall recombination problems (refs. 5 and 6). However, it still appears probable that reaction 1 dominates cold reaction devices. Typical hypothetical chain devices are run with an F to F_2 ratio sufficiently low that nearly one-half of the HF is produced by each pumping reaction.

The first major difference between reactions 1 and 2 is the initial vibrational distributions of the HF*. These have been well characterized by a number of experimenters (refs. 7 through 9). Representative results are shown in figure 1. It is apparent that reaction 2 produces considerably more

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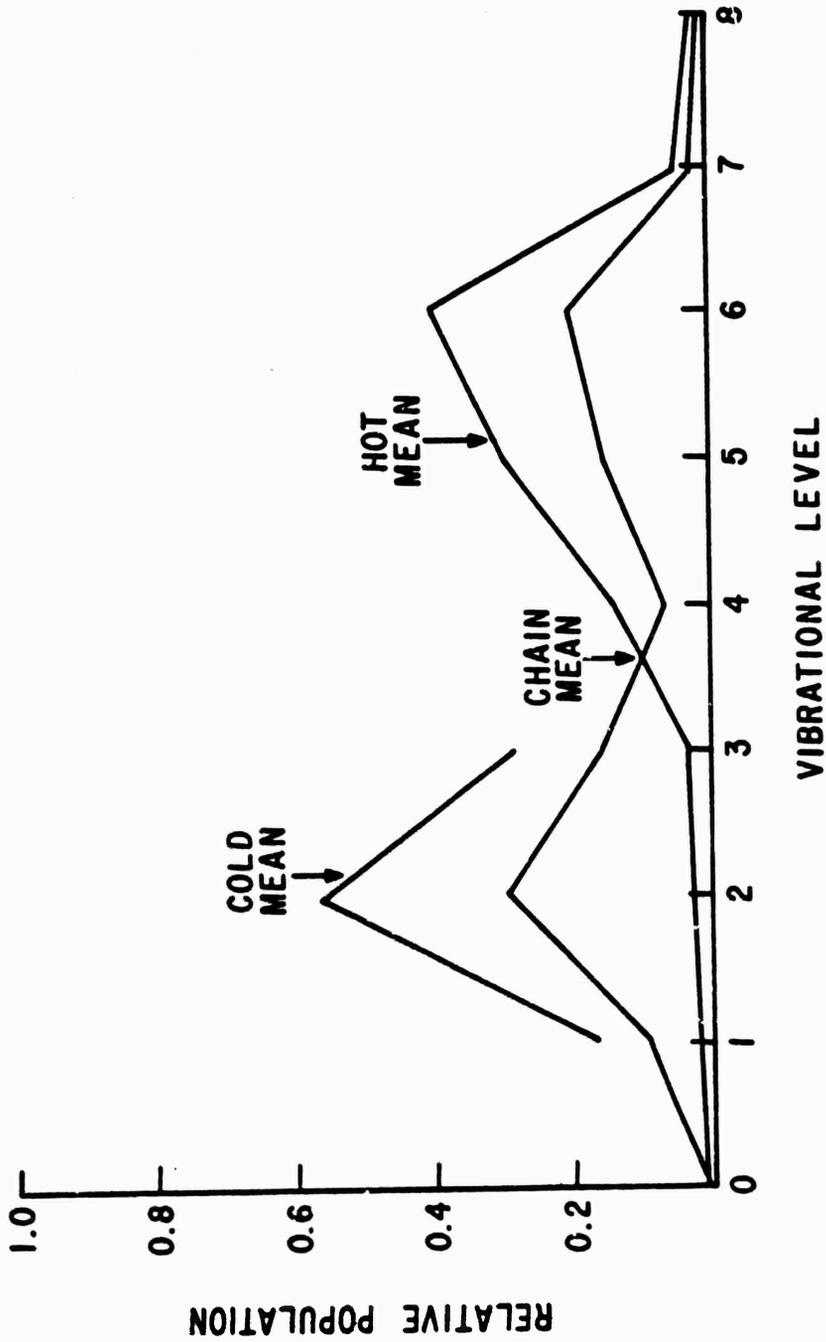
Figure 1. Initial HF Vibrational Distribution
(refs. 7 and 8)

vibrational energy per HF molecule and moreover, that the energy is present in higher vibrational levels. The chain system, of course, consists of an average of reactions 1 and 2 and its initial advantage is also indicated on the figure.

The energetics of the hot, cold, and chain reactions are summarized in table 1. As the table shows, the chain starts with an advantage factor of 1.7 in vibrational energy when compared with the cold reaction. However, note that in addition to starting with more vibrational energy, the chain also releases considerably more heat. In view of the fact that chemical lasers operate at very low efficiency, the net heat release is closer to the total exothermicity rather than the energy initially partitioned into translational and rotational degrees of freedom. For example, a cold reaction device is doing quite well to achieve 1 kJ/gmF. Thus, only 4.5 kcal/mole of the initial 23 kcal/mole is successfully extracted as laser power.

Table 1

CHAIN ENERGETICS

	(kcal/mole HF)		
Hot	E_{tot} =	E_{vib} +	E_{other}
$H + F_2$	102	54.1	47.9
Cold			
$F + H_2$	34.7	22.9	11.8
Chain	68.4	38.5	29.9

The larger heat release handicaps the chain both because it severely damages pressure recovery and because it destroys the partial inversion. It may be anticipated that due to its smaller rotational constant the DF system will be even more susceptible to the latter problem and thus harder to saturate.

An additional potential merit of the chain is that it requires less combustor fuel to produce the lower necessary dissociation factor. Figure 2 (taken from reference 10) shows the varying temperature requirements for different degrees of dissociation at various partial pressures of F_2. The advantages are not immediately obvious, however, because of the variety of heat sinks in a chemical laser combustor. The following factors are significant in heat balance calculations:
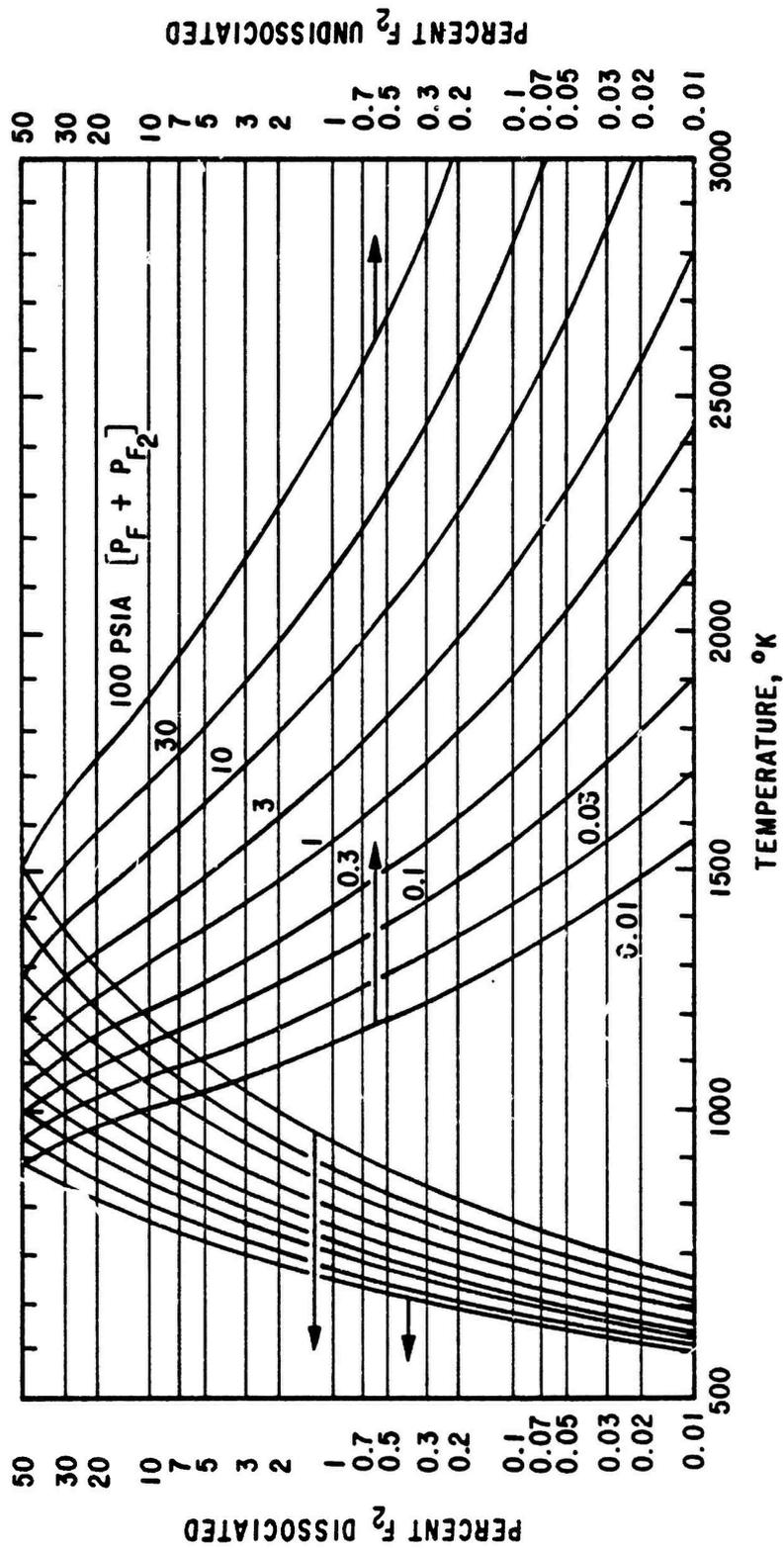
Figure 2. Fluorine Dissociation at Chemical Equilibrium (reproduced from reference 10)

1. F_2 dissociation energy (38 Kcal/mole)
2. Specific heats (Approximately $Cp = 5$ cal/mole°K or $Cp = 7$ cal/mole°K)
3. Combustor/nozzle heat losses ·

The dominant effects are quite different in low and high pressure combustors.

In high pressure applications with totally regeneratively cooled hardware, effects 1 and 2 should predominate. Table 2 shows crude estimates for both cold and chain conditions with a reasonable stoichiometry. Also indicated is a chain case with twice as much diluent. For comparable pressure recovery capabilities this much more diluent may be necessary to compensate for the extra heat release. As the table shows, in pressure recovery applications the advantage of lower dissociation requirements may be substantially reduced by the necessity to heat more combustor diluent.

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Table 2

HIGH PRESSURE COMBUSTOR HEAT BALANCE
</div>

Typical   He/F   =   7.5

Thus, <u>Cold Reaction</u>   1700°K α = 0.99

38 kcal	dissociation
14 kcal	heat: F
<u>105 kcal</u>	heat: He
157 kcal	TOTAL

Requires production of ~ 2.5 moles of DF

<u>Chain Reaction</u>   1100°K α = 0.1

4 kcal	dissociation
1 kcal	heat: F
5 kcal	heat: F_2
<u>60 kcal</u>	heat: He
70 kcal	TOTAL

Requires production of ~ 1.5 mole of DF.

Doubling diluent ratio results in:

Chain Total = 130 kcal

In low pressure cases the importance of combustor/nozzle heat losses will predominate. This is probably irrelevant to the chain since it appears

impossible to achieve sufficiently short extraction lengths at low pressure run conditions. These losses will, however, hurt the cold reaction performance both by increasing deactivation effects and also by the mass of the deactivators.

A final advantage that the chain possesses is that the transition probabilities increase with V in the manner shown in figure 3. This rapid rise in principle makes it easier to saturate the upper levels due to the decrease in spontaneous lifetime as V increases. In fact, even this curve understates the case since the anharmonicity aides stimulated emission via the frequency cubed factor.

The above discussion outlines the reasons for interest in the chain reaction. Unfortunately, recent experimental evidence indicates that unfavorable factors negate most, if not all, these positive features.

2. CHAIN HISTORY

a. Pulsed Devices

The successful operation of the chain laser has been clearly demonstrated by its application in pulsed devices. In this case F_2 and H_2 are typically premixed with He diluent and O_2 prereaction inhibitor. The reaction is then initiated by dissociating a fraction of a percent of the F_2 by either photolytic or discharge methods. These approaches were successfully applied by Basov (ref. 11) and Tol'rose (ref. 12) as early as 1969. Later works (ref. 13) have shown a temporal evolution of laser output consistent with chain operation. Flash photolysis studies by Suchard (ref. 14) have indicated that the preponderance of energy is coming from the lower vibrational levels but that it is possible to lase on the upper levels.

The salient features of the pulsed laser data have not been altogether encouraging. In general, the experiments have indeed clearly demonstrated that chain operation is possible. However, they have not produced appreciable power from upper vibrational levels. Moreover, the length and total pulse energies have been substantially shorter than models have predicted. Thus, in summary, in 1973 the pulsed laser data was indicative of fundamental problems in the models of the day.

b. CW Devices

The original CW HF devices used arc heaters to dissociate F_2 (ref. 15). Subsequent innovations developed the use of combustors to achieve the desired
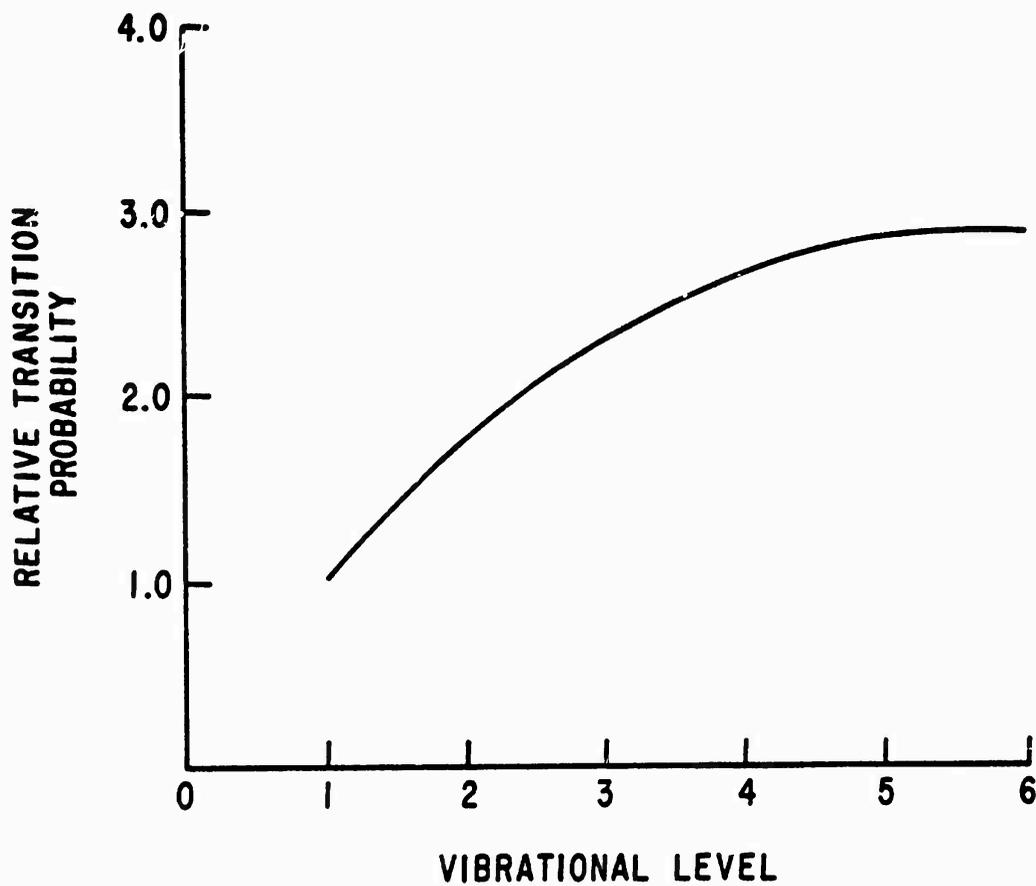
Figure 3. Relative HF Transition Probabilities

F atom levels. In both cases the original hope was that the chain would be the prime operating mode. The results of Project Mesa and the Direct Combustion Laser quickly showed that the best performance was achieved by cold reaction devices (ref. 16). It is quite possible that the causes of these early failures were an inadequate control of the ferocious heat release associated with the chain; so their failures were not really definitive.

Later efforts were somewhat more successful. Among these was the United Technologies work under contract DAAH01-73-C-0682. This work utilized a mass heater to demonstrate CW chain lasing. The results conclusively showed upper level lasing but not the anticipated high specific powers. Unfortunately, the experiments were terminated at this point (ref. 17).

DF/CO_2 transfer devices have always been considerably easier to run than DF ones. Thus, it is not surprising the CW chain operation has been more easily demonstrated in this application than CW-DF. Both Bell Aerospace and TRW have effectively utilized the chain in this mode (refs. 18 and 19). The implications of this success are limited in view of the fact that the observed specific powers are not indicative of DF potential. In fact, the systems are so biased in favor of $DF-CO_2$ transfer that DF deactivation rates are almost negligible.

SECTION II
KINETICS

1. RATES (1972)

In 1972 it was felt that the kinetic rates for the chain laser were ill-understood but that reasonable assumptions predicted a nopeful future. The rate status was extensively reviewed by Cohen (ref. 20). Typically, cold reaction device models overpredicted performance by factors of order two but chain models were off by much larger factors.

The pumping distributions had been measured directly by several investigators with reasonable consistency (figure 1). The absolute pumping rates were much less reliable especially in regard to temperature dependence. Their accepted behavior is shown on figure 4. Although not plotted in the most physical manner, this plot emphasizes the relevant aspects. The main points to note are that the hot reaction is consistently slower than the cold reaction and that it has a very steep temperature dependence. At moderate temperatures the chemistry is sufficiently slow that chain reaction lasers are dominated by reaction rates rather than mixing. This is due to the fact that the hot reaction is nearly an order of magnitude slower than the cold reaction and that a factor of 10 more reactions are typically required to consume the usable fluorine in chain devices. Thus, the chain chemistry is almost two orders of magnitude slower than the cold. The steep temperature dependence has a more unpleasant implication. In a mixing device the temperature rise has only a modest influence on further heating since mixing dominates. In a chain device, on the other hand, the reaction rate feeds back on itself so that fuel consumption can slowly occur and then abruptly rise. This behavior can naturally cause abrupt unmanageable pressure and temperature rises unless very high diluent ratios are used (ref. 21).

In the area of deactivation rates the first-vibrational level rate was already well determined in 1972. The peculiar temperature dependence of the HF rate was also thoroughly characterized. The major unknown was the behavior of deactivation rates with increasing vibrational level. The sum and selection rules for a harmonic oscillator suggested that deactivation processes should be
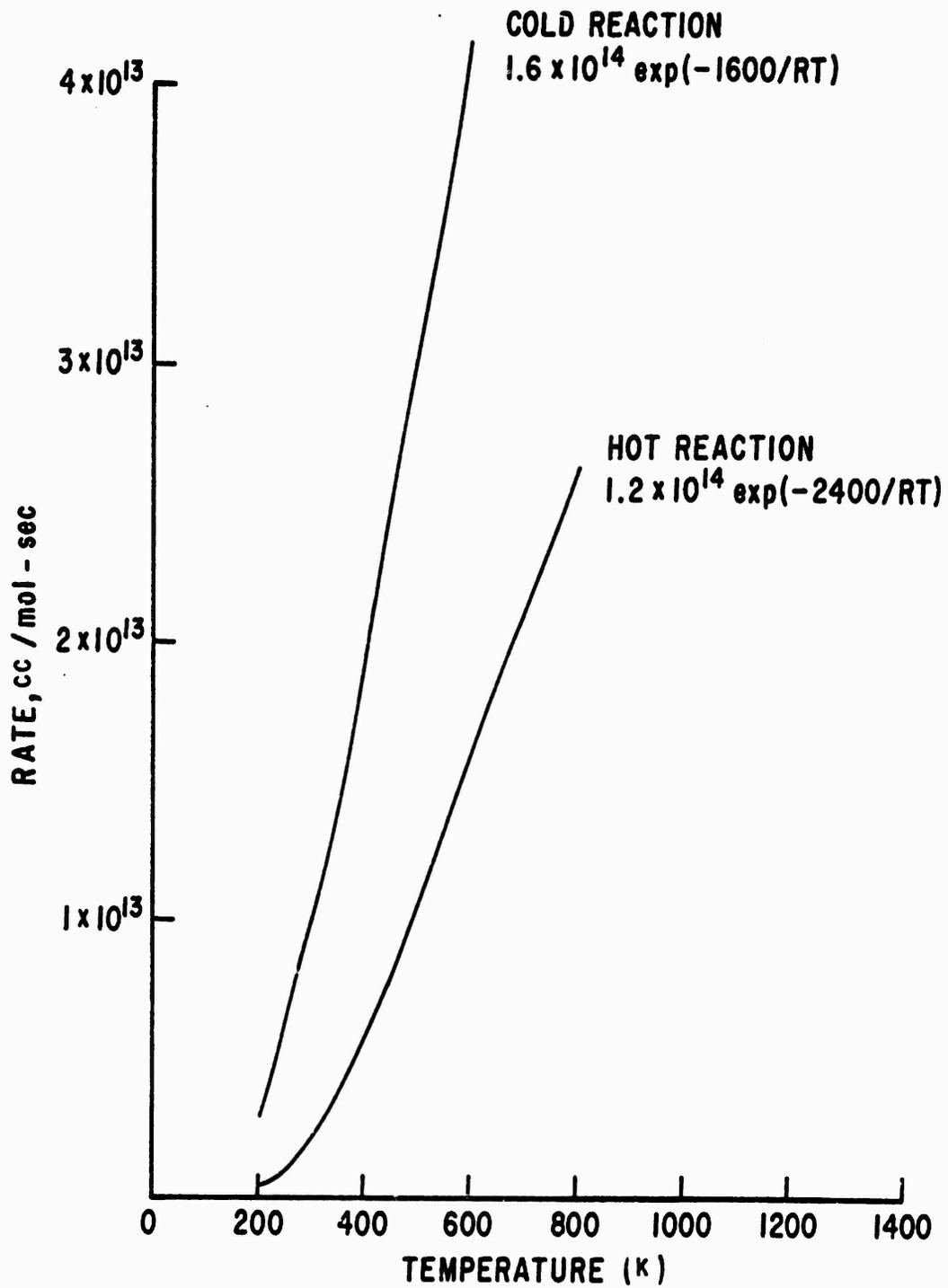
Figure 4. Hot and Cold Reaction Rates

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single quanta and be linear in V. This was a reasonable assumption then, but now has been thoroughly contradicted by a variety of experiments.

The Einstein coefficients were based upon a combination of measurements and computations (refs. 22 and 23). Although substantial uncertainty still exists, there is no evidence to suggest that they are sufficiently in error to impact chain modeling substantially.

2. DEACTIVATION RATES (1976)

Experimental results have universally indicated a rapid growth in deactivation rate with V. Typically, a distribution of HF levels is found to rapidly relax into a vibrational temperature at a rate much faster than linear V dependence could possibly explain (refs. 24 and 25). The empirical work of Kwok and Bott (ref. 26) strongly suggests that a sort of universal VR behavior occurs independent of deactivator. They have suggested that HF rates increase roughly as $V^{2.3}$ independently of deactivating species. Similar types of behavior are necessary to explain data obtained at TRW and UTRC.

The exact causes of this behavior are at present unknown. The most likely possibilities are that multiquantum losses and anharmonicity effects are important. Figure 5 summarizes the various viewpoints. The quantity plotted is the instantaneous rate of vibrational quanta loss in a system consisting of a preponderance of HF(0) with a small amount of HF(v). The linear curve is, of course, the classical result. It should be noted that the $V^{2.3}$ measurements include corrections for V-V terms. However, for the upper levels these are small due to the anharmonicity of HF. For example, the process

$$HF(6) + HF(0) \rightarrow HF(5) + HF(1) \tag{3}$$
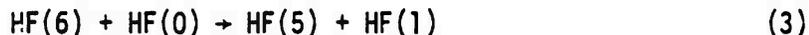
has an energy deficit of 900 cm^{-1} which is 4.5 kT at room temperature. Thus, the process is very unlikely due to its endothermicity.

One way to approach the empirically determined $V^{2.3}$ behavior is to assume multiquanta processes are possible. If they were all equally likely, then the net effect is given by the following:

$$\sum_{i=1}^{V} i = \frac{V(V+1)}{2} \tag{4}$$

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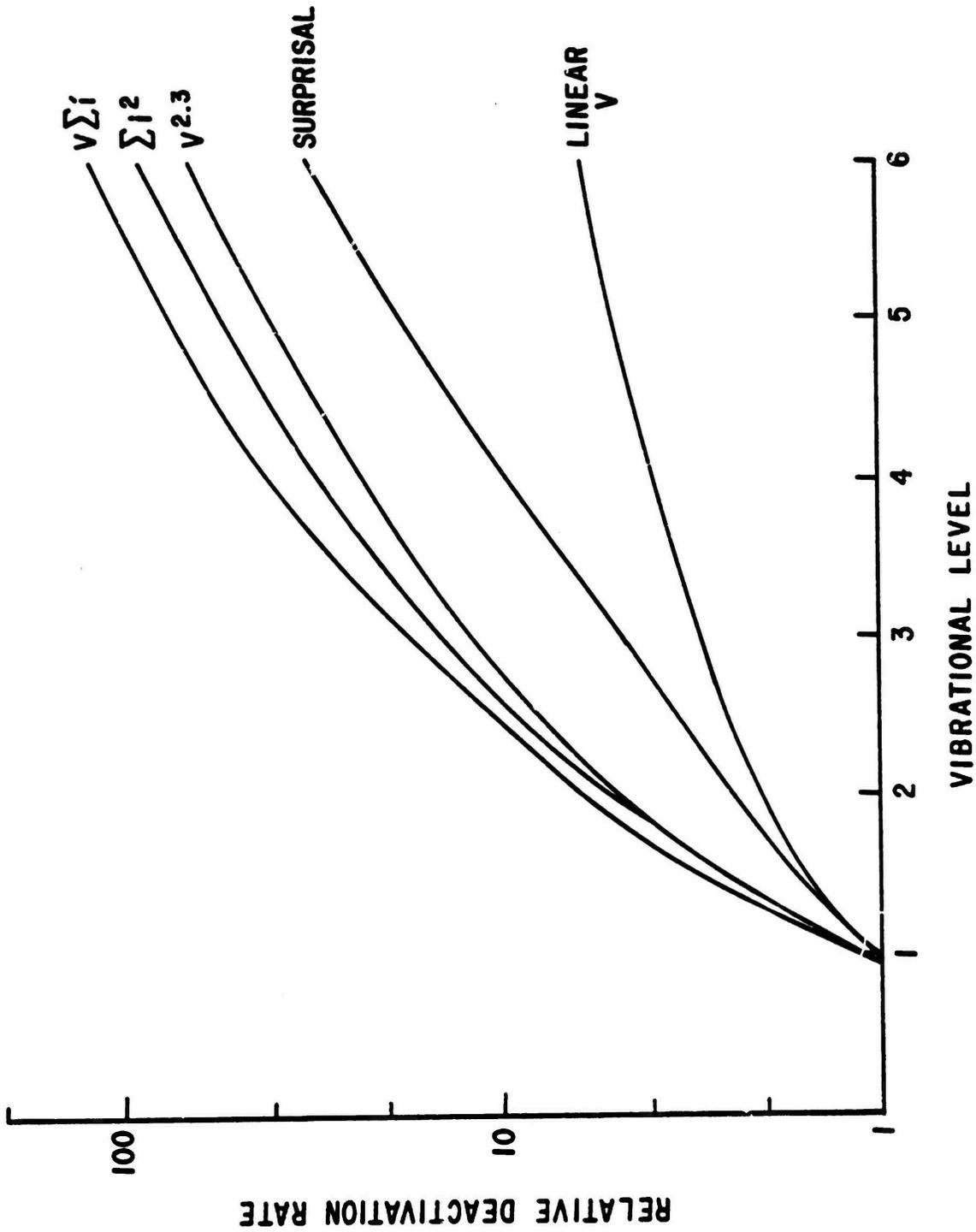
Figure 5. HF/HF Deactivation

Proposed alternatives which have been suggested include

$$V \sum_{i=1}^{V} i = \frac{V^2(V+1)}{2} \tag{5}$$

and

$$\sum_{i=1}^{V} i^2 = \frac{V(V+1)(2V+1)}{6} \tag{6}$$

In addition to the multiquanta loss viewpoint, statistical mechanical viewpoints such as surprisal theory (ref. 27) suggest that the anharmonicity may be quite important. In this formalism, however, multiquanta losses are not significant but simultaneous V-V and V-R,T processes are important. For example, with surprisal theory a significant rate for the following process is predicted:

$$HF(6) + HF(0) \rightarrow HF(3) + HF(2) \tag{7}$$
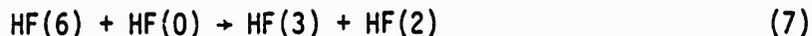
Each of these viewpoints and the available data all suggest that deactivation rates rise strikingly with V. It now appears probable that this phenomenon is due to some combination of the increasing anharmonicity and number of inelastic channels possible as the vibrational level increases. Moreover, it appears likely that a large fraction of the energy is lost via V-R effects. Although the actual mechanism is unclear, it appears that reasonably effective modeling can be performed by assuming that the HF system behaves as if

$$HF(V) + HF(X) \rightarrow HF(V-1) + HF(X) \tag{8}$$

has a rate proportional to $V^{2 \cdot 3}$. Some TRW and UTRC data suggest that even this rate may be too optimistic. UTRC's data is better fit by using multiquanta rates which scale with V (i.e., equivalent to $V^2(V+1)/2$). Notice from figure 5 how closely all these multiquanta viewpoints and $V^{2 \cdot 3}$ match each other in terms of net energy losses. Care must be taken to not exaggerate the significance of this agreement. Emanuel has pointed out at the 1976 Tri-Service

Chemical Laser Conference (ref. 28) that the time evolution of a vibrational population must be properly treated as a complex stochastic process. Thus, viewed in this light, rate packages should be compared by investigating their ability to predict the time evolution of a vibrational ensemble of HF molecules toward equilibrium. It is not at all clear in such cases that $V^{2 \cdot 3}$ single quantum models and multiquanta models will produce equivalent results. Further work remains to be done in this area. Fortunately, it is significant to note that modelers have found that both viewpoints have comparable effects on predicted laser power.

3. H-ATOM RATES (1976)

The H-atom deactivation rate has frequently been proposed as a possible cause of poor chain performance. However, recently Bott has measured a $V=3$ rate much faster than had previously been suspected (ref. 29), 9×10^{13} cc/mole-sec (subsequently revised downward to 6×10^{13}). The most striking aspect of this rate is that it represents an increase of two orders of magnitude over the $V=2$ rate measured in the same experiment. The validity of the measurement appears well established for the following reasons:

   a. The rate correlated properly with H-atom pressures measured with a catalytic probe.
   b. Checks done with undissociated H_2 and with the microwave dissociator running without H_2 ruled out most systematic problems.
   c. Both $V=2$ and $V=3$ H-atom rates were measured in the same system.
   d. The system gave much more modest rates for $V=3$ for other species such as H_2, N_2, CO_2, and O_2.

The rate is extremely fast and the jump at $V=3$ is especially striking. It seems most unlikely that the rate is due to anything other than multiquanta losses or a fast back-reaction. From a molecular standpoint one can infer that the HF($V=3$) molecule is quite similar to HF($V=2$). Using classical vibrating rotator theory from Hertzberg,

$$B_V = \frac{h}{8cu}\left(\frac{1}{\pi r}\right)^2 \tag{9}$$

$$= B_e - \alpha_e(V+1/2) \tag{10}$$

$$\frac{\overline{(1/r^2)}V=2}{\overline{(1/r^2)}V=3} = \frac{B_e - 2.5\,\alpha_e}{B_e - 3.5\,\alpha_e} = 1.04 \qquad (11)$$

Thus, the structure is almost identical.

The threshold behavior of the rate is highly suggestive of a strongly energy-dependent phenomenon involving reactive processes, either an exchange or back-reaction. In fact, at V=3 the JANAF table (ref. 30) values indicate that the V=3 cold reaction is endothermic by roughly 0.6 ± 0.6 kcal/mole. This is only about RT at room temperature. The rotational distributions measured by Polanyi and indicated in figure 6 also support the contention that V=3 is near the backward threshold. The product HF(V=3) molecules actually had less rotational energy than room temperature HF. (Some caution in interpreting this result is necessary since Polanyi's work was not completely rotationally frozen.)

The prime issues are the V scaling and temperature dependence of the rate. It appears most probable that the rate grows even larger for V > 3. This sort of viewpoint is suggested by TRW work under their Reactive Flow contract (ref. 25). Figure 7 shows their data taken under low pressure conditions designed to be pure hot reaction. Although it is improbable that this goal was achieved, it still appears likely that this data represents a case more strongly dominated by H atoms than other experiments. Note the gaps between V=1, 2 and V=3 and V=4, 5, 6. Unlike most data, a vibrational temperature is not apparent. It should be noted that TRW did observe a reasonably good vibrational temperature in their apparatus when they used a low dissociation F_2 run condition. If anything, the TRW data suggests a further increase beyond V=3. They found that even multiquanta HF/HF rates were inadequate to explain their data.

For purposes of comparison, the following versions of the H-atom rate will be used in later modeling:

    1. Multiquantum H (recommended by Dr. Cohen)

$$H + HF(V \geq 3) \rightarrow HF(V-i) + H \quad [\text{for energy } i \text{ such that } V-i \geq 0]$$
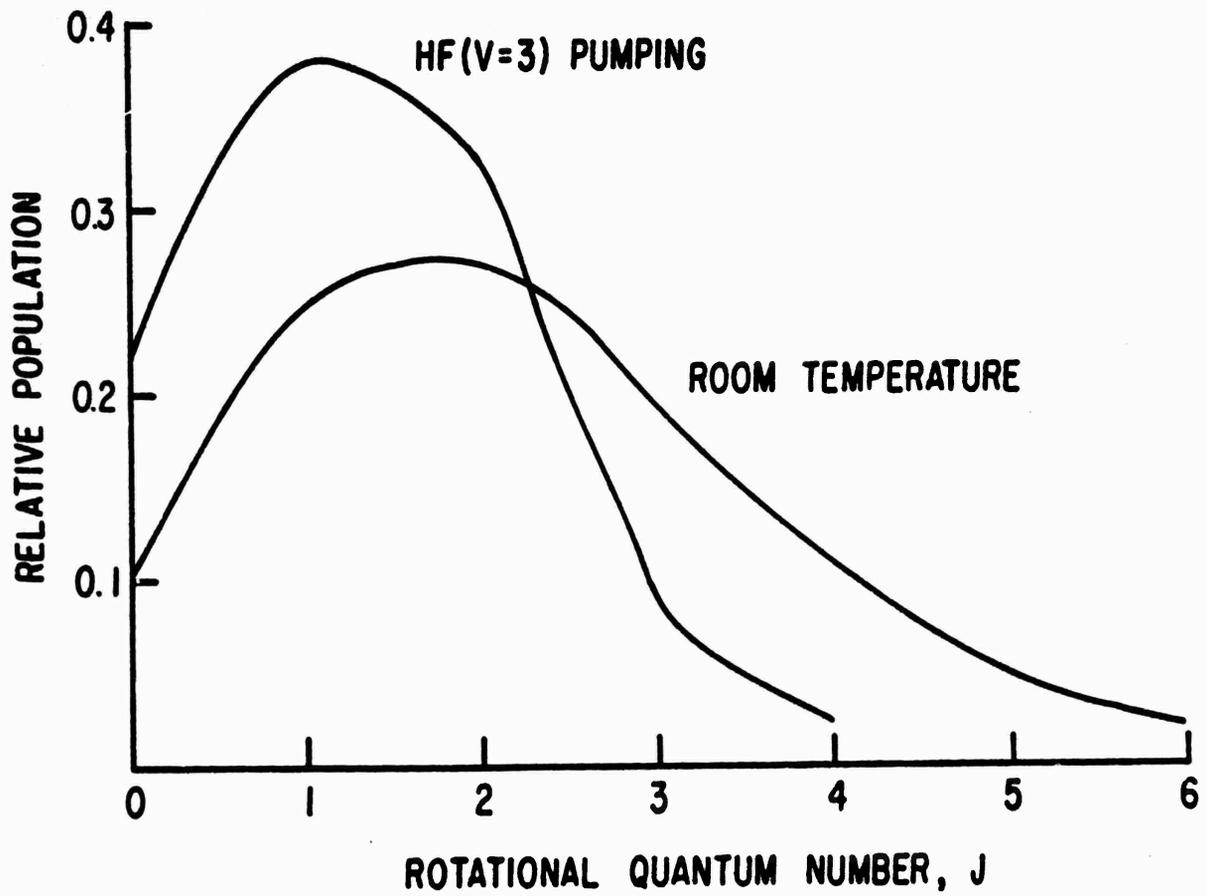
$$10^{14} \text{ cc/mole-sec}$$

Figure 6. HF(V=3) Rotational Distribution
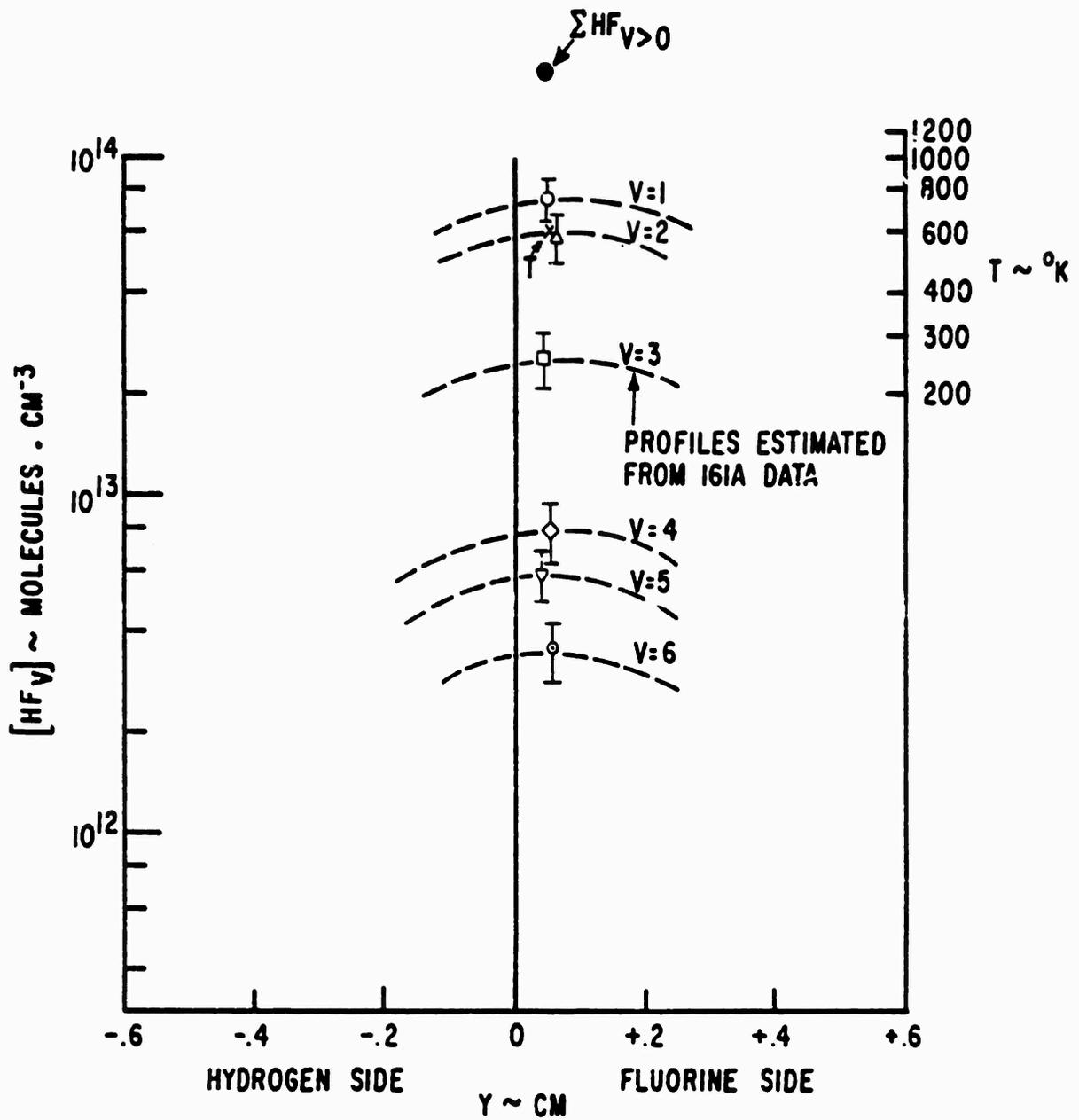
Figure 7. TRW Reactive Flow Data
(Reproduced from reference 35)

2. Modified H (conservative estimate)

$$H + HF(V \geq 3) \rightarrow HF(0) + H$$
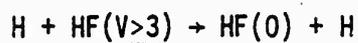
$$10^{14} \text{ cc/mole-sec}$$

3. Fast back-reaction

$$H + HF(V \geq 3) \rightarrow H_2 + F$$
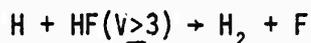
$$10^{14} \text{ cc/mole-sec}$$

In the absence of any information, these rates are assumed to be temperature independent. If the behavior is due to a reaction the most likely probability is that the rate increases with temperature. Thus, for suitable chain conditions both the assumed vibrational dependence and temperature dependence is too optimistic. The value 10^{14} is used because this is the initial value reported by Aerospace. It has been revised downward to 6×10^{13} since the calculations in this report were completed. In general, versions 2 and 3 produce comparable effects. Version 2 is used in an attempt to conservatively estimate the H atom impact on modeling. It is likely that rate 2 is too optimistic in its effects on V=4, 5 and 6.

SECTION III

MODELING

1. ASSUMPTIONS

The modeling of any chemical laser system necessarily involves a number of assumptions. Typically, the chain is given the benefit of the doubt by making optimistic assumptions. The major models used were DESALE III scheduled mixing calculations performed by Norm Cohen of Aerospace and both premixed and mixing LAMP runs performed by Capt. Rapagnani of AFWL.

The first major issue in any modeling effort is the optical extraction scheme. The DESALE III calculations used a communicating cavity. All LAMP runs assumed simple Fabry-Perot noncommunicating optics. The validity of this assumption is open to some question. However, at least in the case of unstable resonators, it appears probable that nature "finds" a mode which is more optimistic than the perfect communicating cavity and that really the assumption of perfect communication represents a position of extreme pessimism.

The scale of the device was assumed to result in an operating gain of 10^{-3} cm^{-1}. This choice appears to be practical for both small scale closed cavity hardware and large scale devices with usable unstable resonators. It appears to be impractical to substantially improve upon this value without either requiring excessively large devices or unreasonably small outcoupling fractions.

The issues of fluid mechanical problems such as choking and pressure gradients are ignored in most of the following calculations. Furthermore, the utopian assumption of constant pressure run conditions has been made for simplicity. The details of DESALE and LAMP are well documented and will not be discussed further here.

2. VALIDITY OF CURRENT RATES

A variety of efforts have contributed to an improved understanding of the chain system. It is desirable to review the basis and internal consistency of these efforts before actually applying the results. In the interest of brevity, the discussions will be quite laconic so it is recommended that the interested reader consult the appropriate references.

a. Kinetic Experiments

By using a very rarefied partial pressure of HF and a multiple photon cascading technique, Bott (Aerospace Corporation) has succeeded in studying deactivation of HF V=2 and V=3 levels by a variety of deactivators. This technique is responsible for the detection of the fast V=3 H-atom rate and has supported the $V^{2.3}$ behavior for many other species (ref. 29). Indications of this trend are shown in figure 8

Kwok (Aerospace Corporation) has studied upper level deactivation of HF by assorted buffer gases in large flow tube experiments (ref. 31). He has utilized both steady state and kinetic modes of operation and achieved consistent results. His data further substantiate the $V^{2.3}$ behavior, but have not verified the H-atom rate as of this writing.

Boedecker (UTRC) (ref. 32) has utilized a mass heater to conduct steady state flow tube experiments. The results have been consistent with a rapid multiquanta self deactivation of the HF and preliminary results are suggestive of rapid H-atom effects. Studies of both $\Delta V=1$ and $\Delta V=3$ emission and HF(0) absorption have produced consistent results and provided convincing evidence that the Einstein coefficients currently used are quite reasonable. An additional result of this work is the indication that the hot reaction may be a factor of 2 to 3 times slower than Albright's value at room temperature. Figure 9 shows the typical results that were obtained.

Hinchen (UTRC) has performed work using a frequency-doubled ruby laser to dissociate F_2 photolytically and studied the H_2/F_2 reaction fluorescence. The results are basically consistent with Boedecker's especially the fast HF/HF rates and the slow hot reaction rate.

TRW's reactive flow work has been conducted at low pressure utilizing either arc-heated H_2 or F_2. The results showed a very rapid decline in upper level population even when initiated with H atoms. The upper level populations fall even faster than multiquantum HF/HF rates could explain. Bearing in mind that the total experimental pressure was only 5 torr and that ψ was typically 50, it is clear that extremely fast rates are necessary to produce the observed distributions of figure 7. Figure 10 shows another interesting feature of the TRW work. Note the non-Boltzmann upper rotational levels. There is either evidence of a hot boundary layer or indirect evidence of V-R processes, probably the latter.
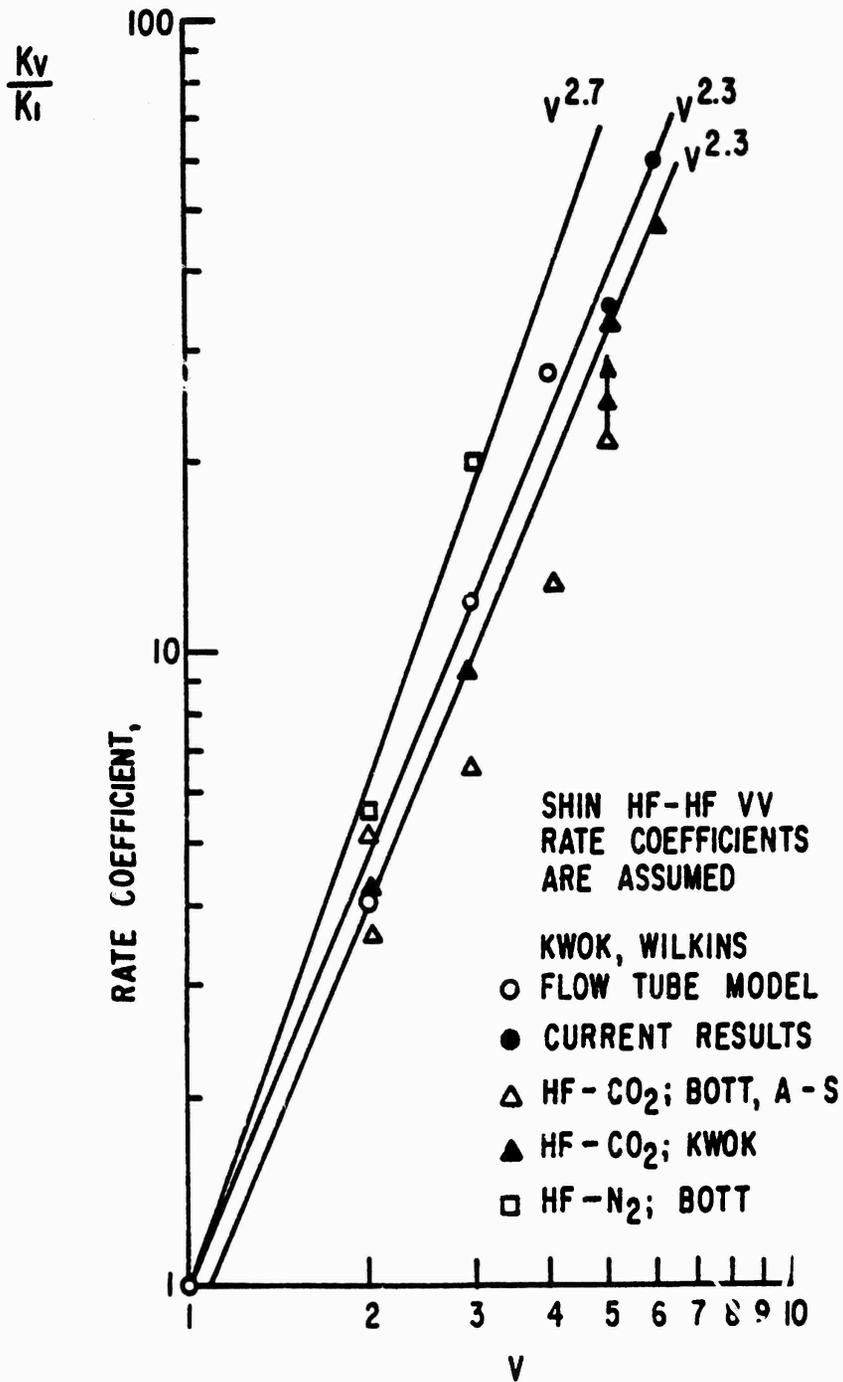
Figure 8. Aerospace Empirical V Law
(reproduced from Aerospace briefing)

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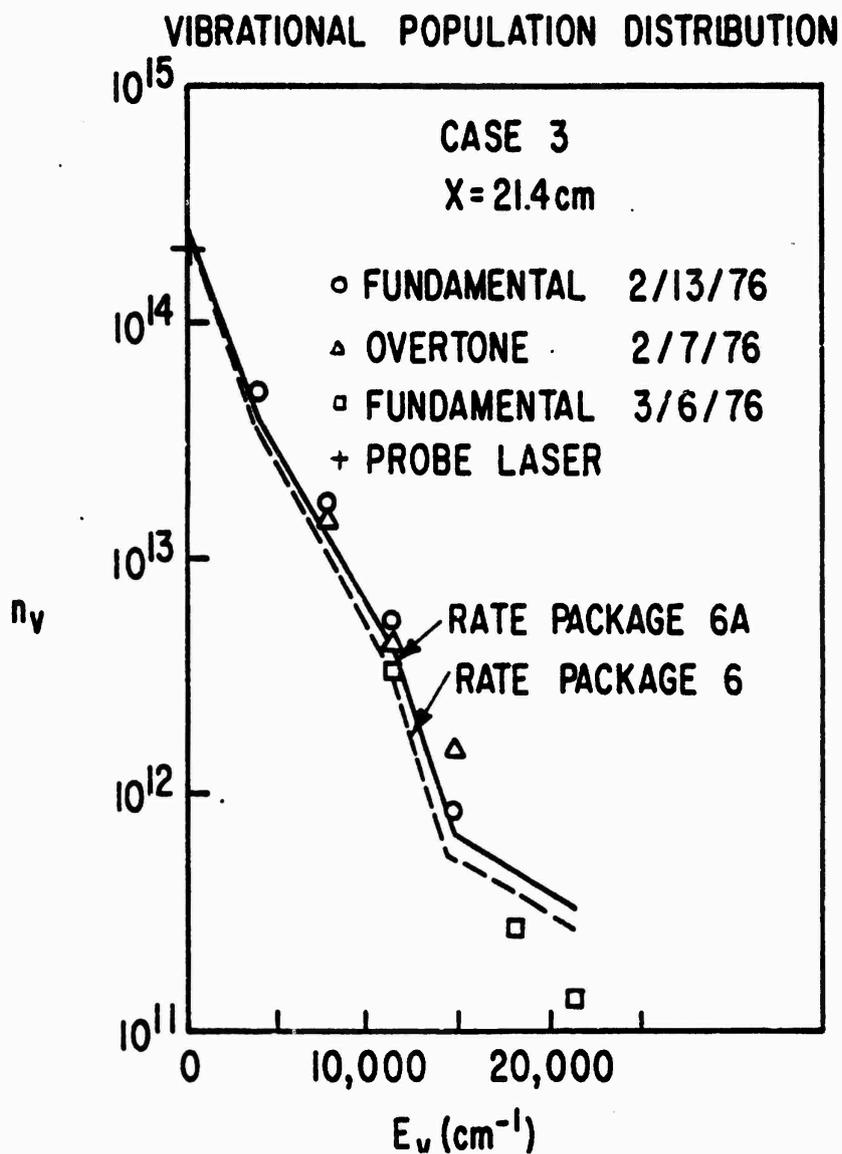
Figure 9. UTRC Flow Tube Data
(reproduced from UTRC briefing chart)
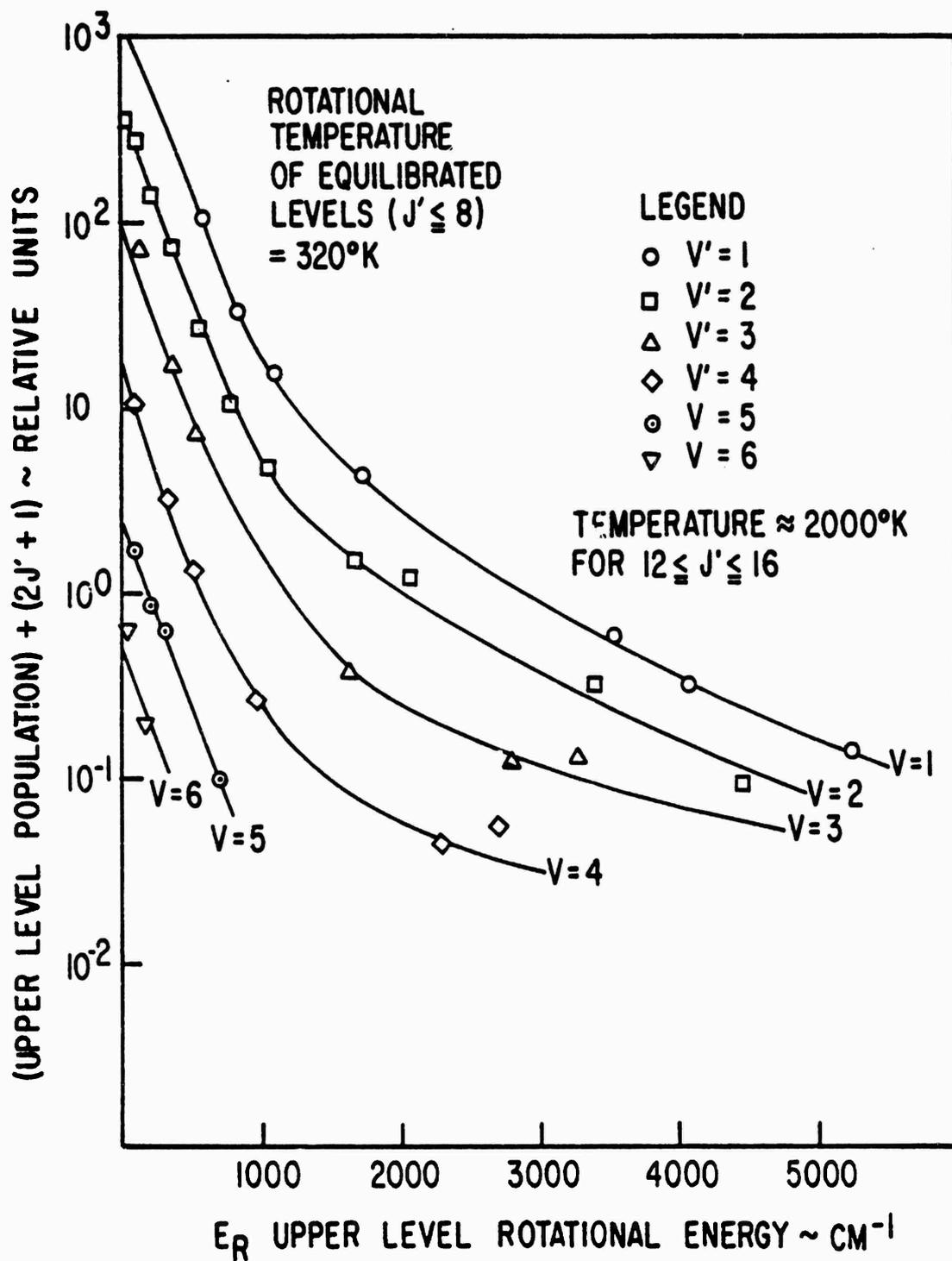
Figure 10. TRW Reactive Flow Data
(reproduced from reference 35)

b. Pulsed Laser Experiments

Several experimenters have succeeded in observing upper level lasing in pulsed devices. A first speculation might be that this should be impossible in view of the fast H-atom rate. Such is not the case. Close examination reveals that these experiments were run at low pressures with small dissociation factors. For example, in Suchard's work the total pressure was only 50 torr. Using his assumptions, only about 20 microns of H atoms were present. Utilizing the rate discussed earlier, it is easily shown that the V=3 rate for the H atom corresponds to roughly a 10 μsec deactivation time. The pulse only lasted about 25 μsec, thus presenting no significant problem.

In fact, given the low dissociation factors involved, it becomes probable that after a few chain cycles the HF/HF rates will dominate HF/H rates. With an initial dissociation level less than one percent this will certainly be true by the time a few percent of the F_2 is consumed. Aerospace Corporation has successfully modeled both pulse amplitudes and lengths by just assuming the $V^{2.3}$ behavior and ignoring the H-atom rate entirely (ref. 33).

c. DF/CO_2 Transfer

Work done at Bell Aerospace (ref. 34) and TRW (ref. 19) has definitely employed the chain successfully. The following analysis shows that the stoichiometries are sufficiently skewed in favor of transfer that the results are not useful in accessing DF chain performance. Typical run conditions were as follows:

$$[CO_2]/[D] = 20\text{-}60$$

$$[CO_2]/[DF] = 4\text{-}\infty$$

The DF/CO_2 transfer rate is

$$K_T(V=1) = 2 \times 10^{12} cm^3/mole\text{-}sec$$

Using the empirical correlation observed by Bott (ref. 35) and shown in figure 11 leads to an estimated transfer rate:

$$K_T(V=4) = 1.4 \times 10^{13} cm^3/mole\text{-}sec$$
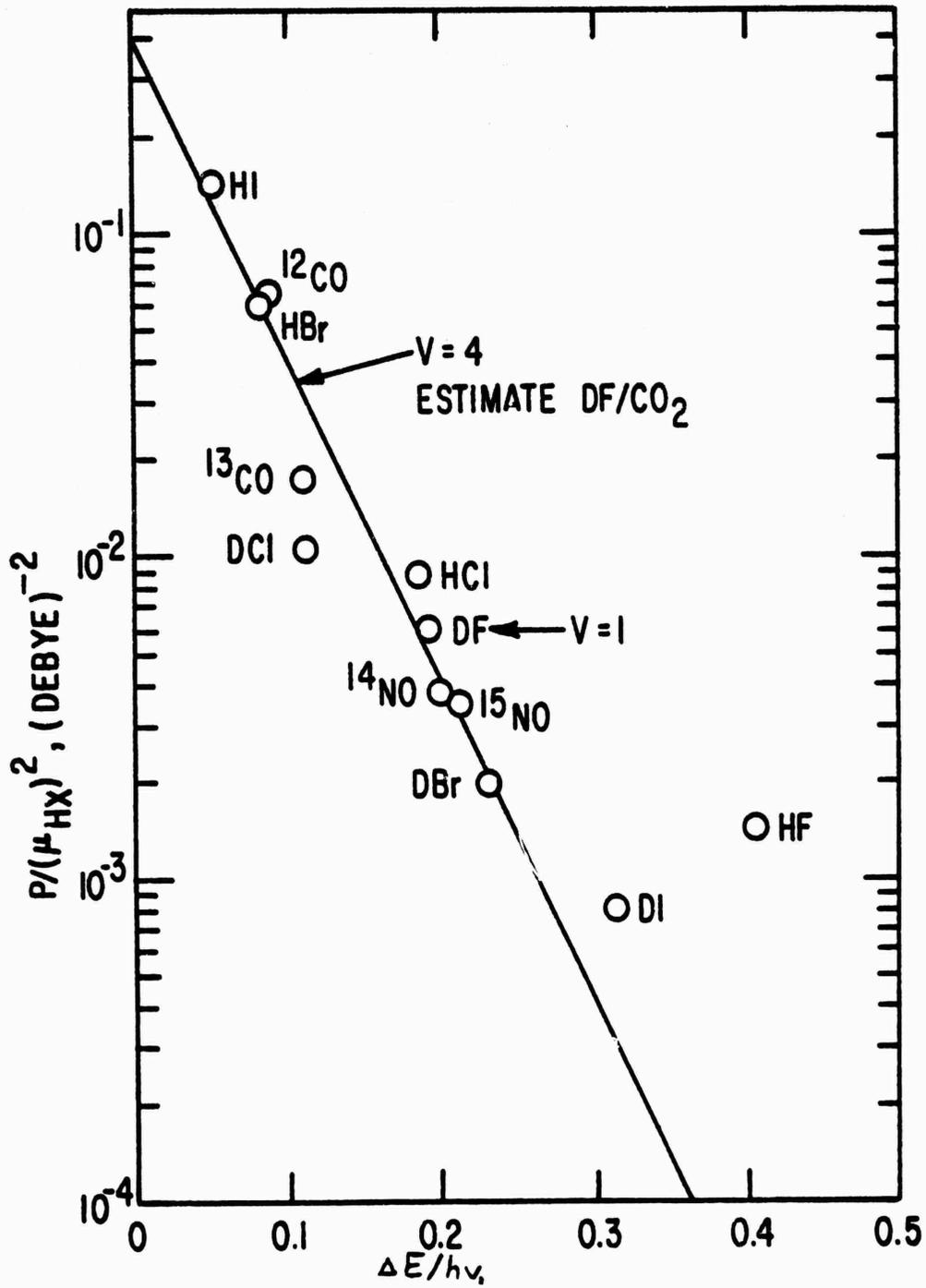
Figure 11. CO_2 Empirical Correlation
(reproduced from reference 35)

Thus, in the case of a D-atom rate $= 5 \times 10^{13}$, we have

$$\frac{[CO_2]}{[D]} \frac{K_T(V=4)}{K_D} = 6 - 20$$

Thus, the D atom is relatively unimportant. Somewhat more significantly, the DF rate gives

$$\frac{[CO_2]}{[DF]} \frac{K_T(V=4)}{K_{DF-DF}(V=4)} = 5 - \infty$$

It should also be noted that under constant pressure conditions this ratio increases roughly as temperature squared. The magnitude of these ratios clearly shows that transfer is a more rapid process than deactivation even with the new fast rates.

3. TEST CASES

The use of models is always a perilous business as past history suggests. With this caveat in mind the reader is cautioned that absolute numbers may be fallacious but trends and relative numbers should provide a useful guide. With this viewpoint, a number of computer calculations have been made with the newer rates.

Table 3 shows the run conditions used extensively by UTRC in calculations that they performed while investigating theoretical chain performance. Figure 12 shows the basis used by UTRC in making this selection. These conditions were selected as a compromise between lasing zone length and pressure recovery capabilities. It should be noted that UTRC later abandoned this set of conditions because of the near impossibility of controlling the heat release with so low a diluent ratio. However, the chain benefits substantially from rapid cycling so from a standpoint of comprehension this is an instructive case. Furthermore, by using large amounts of base relief or a small radius cylindrical laser it may be possible to achieve this case if pressure recovery is not an issue. An important assumption made is that no combustor deactivators are present.

Table 3

BASELINE CHAIN RUN CONDITIONS

Cavity Flow Conditions

	Primary	Secondary
P(Torr)	20	20
T(K)	150	75
U (cm/sec)	212,000	212,000
Mixing Length (cm)	5	5

Gas Composition

Species	Mole Fraction
F_2 (primary)	0.0695
F (primary)	0.007
He (primary)	0.638
H_2 (secondary)	0.073
He (secondary)	0.212

Threshold gain = $10^{-3} cm^{-1}$
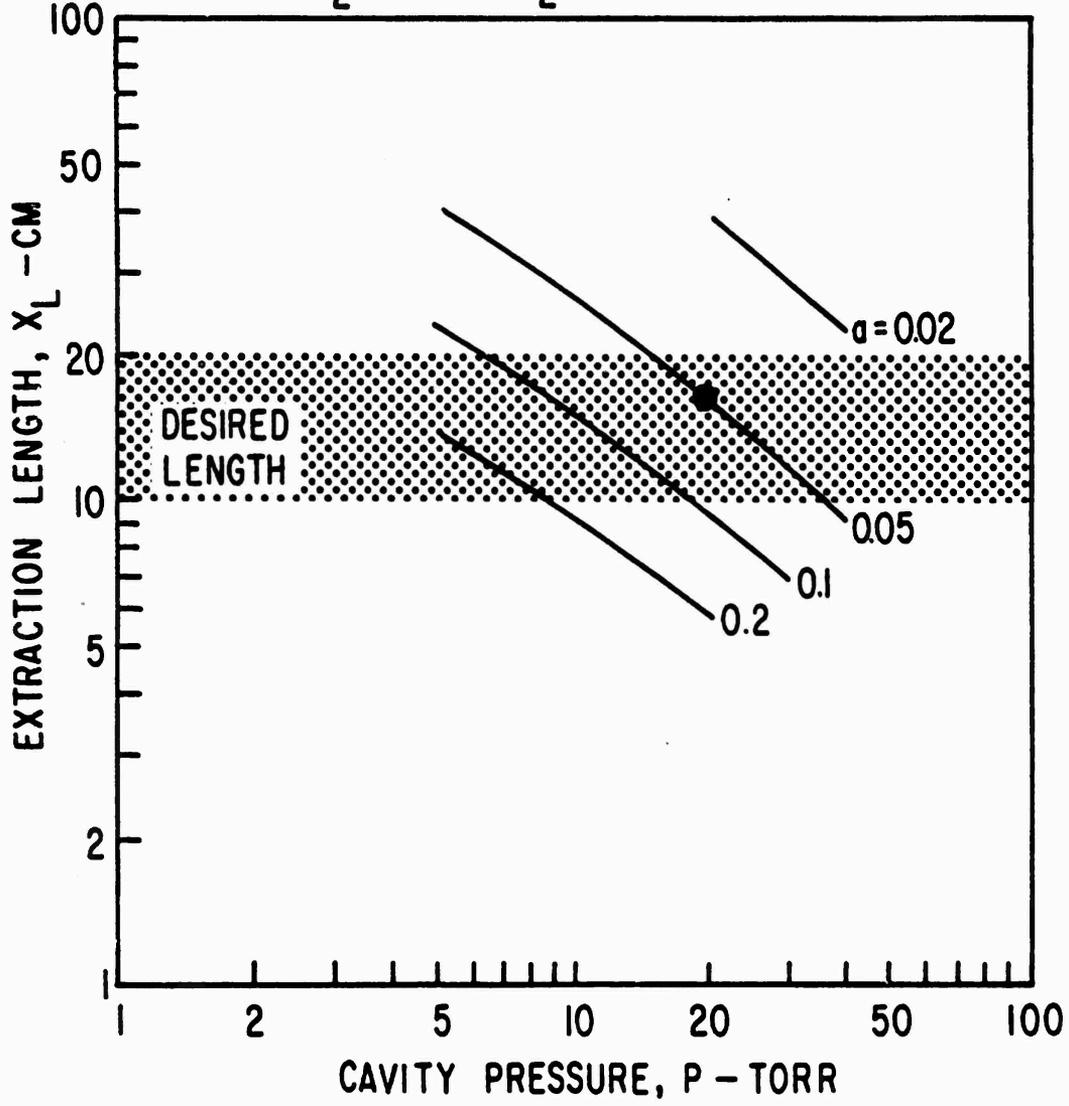
Figure 12. Variation of Extraction Length with Cavity Pressure
(reproduced from reference 3, UTRC)

The results of calculations performed by Aerospace Corporation are shown in tables 4 and 5. In addition to the basic chain case, several other conditions were assumed. These included

    1. Varying chain pressure and temperature

    2. Cold cases with the same stoichiometry except $\alpha = 1.0$

From table 4 it is apparent that with any set of kinetics the higher temperature and pressure is necessary to obtain a realistic lasing zone. It also shows that the chain does not benefit from lower pressures. Note that still higher temperature runs did not significantly change specific power. From the results it is apparent that the faster V-T ra. .s cause approximately a factor of two drop in specific power. The H-atom r. .e used had an even more devastating effect. In later calculations variations on the assumed H-atom rate will be considered. These will indicate that as long as it is a multiquantum process it will predominate. In the event that the H atom were a single quantum process (most unlikely in view of its threshold nature) the V-Ts will be dominant and result 5 would be most realistic.

Table 4

DESALE III HF COLD CALCULATIONS

		20 Torr L_{mix} = 5cm		4 Torr L_{mix} = 2cm	
		T - 130K	T = 100K	T = 130K	T = 100K
1.	Baseline	140 kJ/lb at 2.2cm	145 kJ/lb at 3.2cm	490 kJ/lb at 7.5cm	475 kJ/lb at 136cm
2.	Kwok	115 kJ/lb at 1.7cm			
3.	HF(V) + H	90 kJ/lb at 1.3cm			
4.	Both 2 & 3	85 kJ/lb at 1.1cm	85 kJ/lb at 2cm	360 kJ/lb at 5.5cm	400 kJ/lb at 11.3cm
5.	Multiquanta V-T	120 kJ/lb at 1.8cm			

Table 5

LAMP RUN CONDITIONS

I.   High Performance Cold Case:

T = 120K   P = 4 Torr

Species	Mole Fraction
Primary	
DF	0.065
F	0.132
He	0.203
Secondary	
H_2	0.203

II. Baseline Chain Case:

T = 300K   P = 20 Torr

Species	Mole Fraction
Primary	
F_2	0.070
F	0.007
He	0.600
DF	0.040
Secondary	
H_2	0.073
He	0.21

III. Practical Pressure Recovery Chain Case:

T = 300K   P = 20 Torr

Species	Mole Fraction
Primary	
F	0.003
F_2	0.030
He	0.442
DF	0.025
Secondary	
H_2	0.080
He	0.420

IV. Practical Pressure Recovery Cold Case:

T = 150K   P = 20 Torr

Species	Mole Fraction
Primary	
F	0.052
He	0.387
DF	0.046

Secondary

H_2	0.129
He	0.387

Table 5 shows cold reaction calculations. Notice the relative insensitivity to deactivation rates. Note also that the predicted low pressure performance is much better than the chain. These values must be discounted to some extent because no combustor DF was assumed. The high pressure cold efficiency is somewhat lower than the chain but the improved pressure recovery may actually make the cold condition more desirable than the chain one.

Although illuminating, the conditions considered in table 6 were replaced with more feasible ones for the final LAMP runs and are presented in table 5. Notice that combustor produced DF is now also included. First some premixed studies were done to assess the general impact of the rates. These are shown in table 7. The basic kinetics used were as follows:

1. Baseline kinetics
2. V-T scales as V^2 (too optimistic in all likelihood)
3. Mod H: $HF(V) + H \rightarrow HF(0) + H$: 0^{14} for $V \geq 3$
4. Full H: 10^{14}

$$H + HF(V) \rightarrow HF(V-M) + H: 10^{14} \text{ for } V-M \geq 3$$
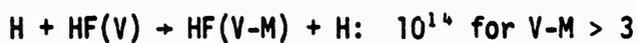
5. Slow pumping: divide Albright's rate by a factor of 2.

Table 7 clearly shows that in the limit of instantaneous mixing the chain devices are still sensitive to deactivation rates. The cold reaction devices on the other hand are quite insensitive. Furthermore, their predicted specific power is much higher. In actuality, it is probable that the V^2 assumption is too optimistic. Furthermore, the Mod-H assumption is more optimistic than other plausible interactions. For instance, calculations which assumed fast back-reactions produced worse chain predictions. Naturally, the Full H-assumption really negated upper level output. The reader should not get the idea that the Premixed Baseline Chain numbers are really indicative of chain performance. As figure 13 indicates, the required area expansion and temperature rise are fluid mechanically unreasonable. Furthermore, the production of 20 torr of premixed

Table 6

DESALE III HF CHAIN CALCULATIONS

	20 Torr $L_{mix} = 5cm$		4 Torr $L_{mix} = 2cm$	
	T - 170K	T - 130K	T - 170K	T - 130K
1. Baseline $H_1^-(V) + H$ $K = 10^{12}$ HF-HF VT αV H.O. V-V rates	470 kJ/lb at 37cm	340 kJ/lb at 111cm	454 kJ/lb at 157cm	> 112 kJ/lb > 250 cm
2. Kwok HF-HF VT* 1:8:28:25:25:25		180 kJ/lb at 88cm		
3. HF(V) + H for $\Delta V \geq 3$ $K = 10^{14}$	185 kJ/lb at 24cm	120 kJ/lb at 82cm	175 kJ/lb at 97cm	
4. Both 2 and 3	140 kJ/lb at 22cm	62 kJ/lb at 71cm	135 kJ/lb at 88cm	47 kJ/lb at 64cm
5. Multiquanta V-T		185 kJ/lb at 89cm		

*More optimistic than current estimates.

Table 7

PREMIXED LAMP RESULTS

Kinetics Baseline Chain	Specific Power kJ/lb
1. Baseline	453
2. V^2-VT	378
3. Mod H	315
4. Full H	224
5. V^2 + Mod H	271
6. 5 Above + Slow pumping	182

High Performance Cold

	kJ/lb
1. Baseline	612
2. V^2 + Mod H	574

Practical Pressure Recovery Chain

1. Baseline	260
2. V^2 - VT + Mod H	130
3. V^2 - VT + Back Reaction	115

Practical Pressure Recovery Cold

|	
1. Baseline	263
2. V^2-VT + Mod H	243
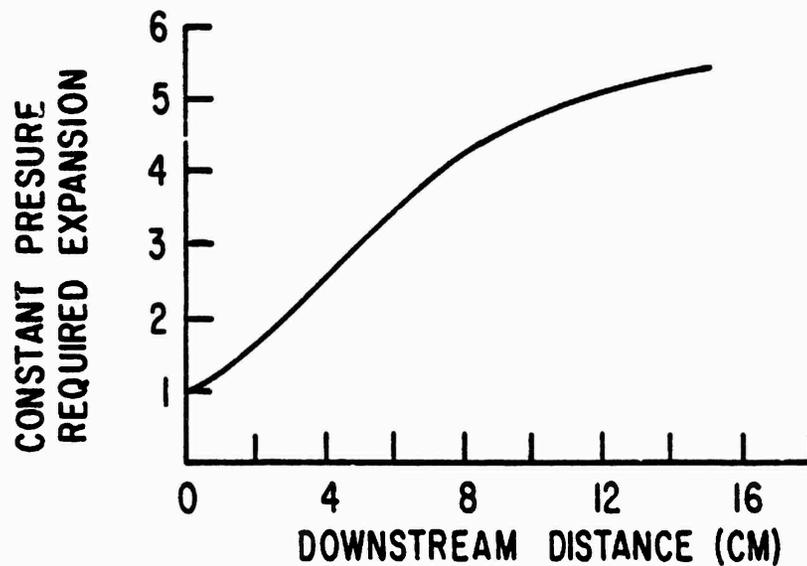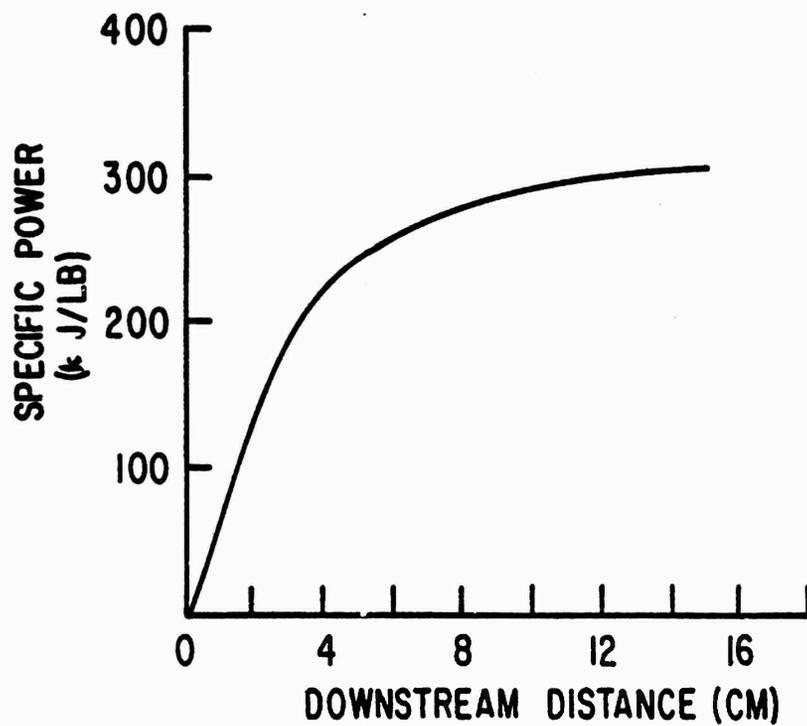
Figure 13. Baseline Premixed LAMP Calculations

gases with an α of 0.1 is an absurdity with current technology. Clearly, assessments must be made with mixing runs and reasonable diluent ratios.

Several such calculations were made with selected kinetics and run conditions. Table 8 shows the results. These were done by using calculated temperature and velocity profiles for the CLV and include F-atom wall recombination. Although somewhat reduced nozzle spacings were used, both cold cases are too conservative in that neither trip nor 3-D mixing are exploited. These should be of much less benefit to the reaction-limited chain than the mixing limited cold systems.

The somewhat unrealistic assumption was made that the calculated CLV profiles scaled with pressure. Thus, for instance, the 20 torr and 60 torr chain cases were assumed to have the same nozzle exit temperature profiles and percentage of DF. In the cold cases the more realistic temperature profiles were considerably less favorable than the assumed premixed temperatures in table 5.

The results indicate that the highest specific powers still are associated with low pressure fast mixing cold devices. Notice how much the cold case benefits as the pressure is reduced from 4 to 2 torr. In essence the cold reaction is benefiting in two ways from the lower pressure. First its deactivation rates are dropping because of the lower pressure. Second its pumping rate is increasing because the mixing is speeding up. At lower pressures the chain, on the other hand, benefits from the lower deactivation but its pumping slows down by a comparable amount so the net effect is nearly canceled. The effect is especially insidious on the upper levels since at 300 K the H-atom deactivation rate is actually 30 times faster than the hot reaction. Unless the H-atom rate has a negative temperature dependence it appears the H-atom rate is much faster over the entire operating range. It is thus almost hopeless to manipulate temperature or α and achieve much improvement. Notice also that eventually even the chain begins to be bothered by high pressure.

In the pressure recovery region the chain looks somewhat more competitive. But, it must be recalled that these calculations are too pessimistic in their mixing rates. Furthermore, even without this factor in the example cited, 35 kJ/lb may well be as good as the 69 kJ/lb when the added heat release associated with the chain is taken into account. Naturally, the usual criteria is that a minimum pressure recovery be achieved. Thus, the mass through-put and diluent ratio of the practical chain case is still too low and would have to

Table 8

MIXING LAMP RESULTS

Practical Pressure Recovery Chain Case:

(Spacing F-F Centerline = 1.6 mm)

	Specific Power kJ/lb
Baseline Kinetics (20 Torr)	147 kJ/lb
V^2 + Mod H (20 Torr)	69 kJ/lb
V^2 + Mod H (40 Torr)	67 kJ/lb
V^2 + Mod H (60 Torr)	37 kJ/lb

Practical Pressure Recovery Cold Case:

(Spacing F-F Centerline = 1.6 mm)

V^2 + Mod H (20 Torr)	35 kJ/lb

High Performance Cold Case:

(Spacing F-F Centerline = 1.6 mm)

Baseline Kinetics (4 Torr)	212 kJ/lb
V^2 + Mod H (4 Torr)	132 kJ/lb
V^2 + Mod H (2 Torr)	213 kJ/lb

be further increased to match the cold. This would probably cause a decline in specific power and furthermore, would be disadvantageous from a systems standpoint because of the He storage requirements. An analytical assessment of this point is very difficult because no actual system would operate at constant pressure. To properly solve the problem, the cavity contour would have to be known. In actual pressure recovery applications, constant pressure operation would not even be desirable.

In view of additional saturation problems, it is likely that DF will fare even worse in the chain/cold comparison. For example, the premixed Practical Pressure Recovery Chain Case gives 130 kJ/lb. But, if the HF rotational constant is changed from its value of 21 cm^{-1} to 11 cm^{-1} and everything else is held constant the power drops to 77 kJ/lb. The premixed cold case, on the other hand, only drops from 243 kJ/lb to 216 kJ/lb.

SECTION IV

IMPLICATIONS

In the last analysis, interest in the chain is based upon the systems potential of the concept. To be attractive, the chain must offer significant systems advantages over demonstrated cold performance. The chain has several unattractive features which underline this necessity for substantial improvement:

a. The requirement for a low α makes the allowable tolerances on combustor temperature quite stringent. Not only will it be difficult to maintain these in an average sense but presumably the sensitivity to combustor nonuniformities will be high.

b. The control of heat release is a critical issue. It will certainly be more difficult than with the cold reaction. Most probably, a larger amount of He will be required. This is a likely disadvantage due to the relative difficulty in storing He.

c. The chain demands F_2. Thus, either F_2 will be used or a complicated and energy consuming system will be required to convert another substance such as NF_3 to the required F_2. This could substantially negate the thermodynamic advantages of requiring only partial dissociation of the F_2 and complicate the system considerably.

1. HIGH PERFORMANCE CW DEVICES

The main potential operating ranges of cold and chain devices are discussed below and the advantages of each discussed. In the course of these discussions the V^2 V-T rates and the Modified H interpretation of the rates will be assumed. It will be assumed that Albright's hot reaction rate is correct. As is always the case in modeling, one can only use one's best educated guess. However, the interest in the chain was stimulated on this basis so it is appropriate to judge it by this criteria. At this time these rates actually appear somewhat optimistic. Moreover, they are reasonably satisfactory in modeling a variety of systems including pulsed lasers and CW cold devices in both high and low pressure regimes. Should they be radically changed, some of the conclusions might be modified but dramatic reversals appear unlikely.

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a. Low Pressure Operation

For purposes of comparison, we first assume that an arbitrary pumping
system is available. In this case, the cold reaction very low pressure devices
are the clear winners. Both the computer codes and experiments suggest that
cold performance in excess of 200 kJ/lb is achieveable. The chain predictions
on the other hand have now dropped below this level even when fluid mechanics
problems have been ignored and premixing assumed. In cases with practical
mixing and diluent assumptions the chain may well lose by a factor in excess
of two. The fundamental problem is that the cold devices profit from low
pressure operation but the chain does not. Thus, barring an extreme change
in rate packages it is unlikely that the chain can match the cold performance
much less vastly exceed it.

b. Limited Pressure Recovery

In those cases where substantial pressure recovery is required the
chain is somewhat more competitive. Unfortunately, the old cases which
produced hundreds of kJs per lb have been drastically reduced to more like
70 kJ/lb. In the sample calculations the chain has an apparent advantage of
roughly a factor of two over the cold. Compensating the chain with enough
diluent and increased mass through-put to match the cold pressure recovery will
probably reduce or eliminate this advantage. This comparison is further in-
fluenced by the fact that trip should further improve the cold relative to the
chain. Thus, with equal pressure recovery the calculations suggest that the
cold and chain devices will produce comparable performance. It is significant
that this calculation is based upon a fairly optimistic set of rates. It is
quite possible that the chain cannot do even this well. The cold values on
the other hand have been demonstrated. Also, as was mentioned earlier, the
switch to DF will probably shift the balance more in favor of the cold because
of the lesser degree of saturation. It therefore appears improbable at this
time that the use of the chain system will result in substantial advantages
over the cold system in this application either.

c. High Pressure Systems

It is not within the scope of this report to discuss the implications
for this type of application. It does appear quite unlikely that the chain
would ever outperform the very low pressure cold devices but it might prove
advantageous in applications where high pressures are required. The predicted

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performance will undoubtedly be severely damaged by unfavorable kinetics. But, standards of comparison will also deteriorate rapidly once passive recovery is inadequate. Thus, a straightforward comparison is extremely difficult.

2. OTHER APPLICATIONS

a. DF/CO$_2$ Transfer

The chain does appear potentially useful in this application. It appears possible to beat the kinetics problems by rapidly transferring the energy to CO$_2$. Furthermore, it may be quite possible to operate at higher pressures because of the relative insensitivity of CO$_2$ to deactivation. Whether running with the chain or even employing the DF/CO$_2$ system at all is viable is an issue which must be resolved by detailed systems studies which lie outside the current scope.

b. Pulsed Devices

In essence, pulsed devices are a special case of C above. Due to the difficulty in dissociating F$_2$ by electrical or photolytic means, they must employ the chain. The current kinetics have substantially resolved the previous flaws of earlier modeling and suggest a continuing potential for high pressure use. Naturally, the nature of the initiator raises another plethora of systems issues which surpass even the earlier problems in their complexity and scope. It certainly is not possible to assess relative merits of these systems here.

In conclusion, the status of chemical laser modeling has improved substantially in recent years. Especially discouraging information has been obtained on upper vibrational level kinetics. The best current assessment is that the CW HF chain device will be substantially outperformed by low pressure HF cold devices. The chain also has lost its substantial advantage over the cold in systems which require moderate pressure recovery. In this case, it appears that at best the chain has a modest lead over the cold. The only application for which chain systems may have substantial advantages are the very high pressure ones. This sort of application is typified by atmospheric pressure pulsed devices. Whether the chain wins on a system basis in these situations is a point which still remains to be resolved.

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APPENDIX A

DEFINITIONS

The following set of standardizing definitions was distributed at the 1976 TRI-SERVICE CHEMICAL LASER CONFERENCE and is reproduced below for reference.

Confusion continues to reign in the chemical laser business due to an inability to communicate results. For this reason, a consistent set of terminology, symbols and units is herein presented for anyone wanting to communicate within the Air Force chemical laser community. Included in this move is a transitional conversion to SI (metric) units. The transitional aspect is that several laser parameters will continue to be reported in parentheses using the classical mixed system of units currently conventional. To accomplish this objective, the following standards are proposed:

I. Laser System Terminology. The structural arrangement of the chemical laser system is shown on figure 14.

II. Parameters, Symbols and Units. Alternate units reportable are included in parentheses.

    A. Device Parameters

        P_c - Combustor or plenum pressure, atm (psia)

        P_L - Laser cavity pressure, torr

        $\dot{m}$ - Flow rates, gm/sec

        T - Temperature, °K

        P - Laser power, kilowatts

        α - Fluorine dissociation fraction

        ψ_c - Total molar combustor diluent ratio

        ψ_L - Total molar cavity diluent ratio

        β_c - Combustor molar diluent ratio

        β_L - Cavity molar diluent ratio

        R_c - Combustor molar mixture ratio

        R_L - Cavity molar mixture ratio

        Ω - $\psi_c + \psi_L$
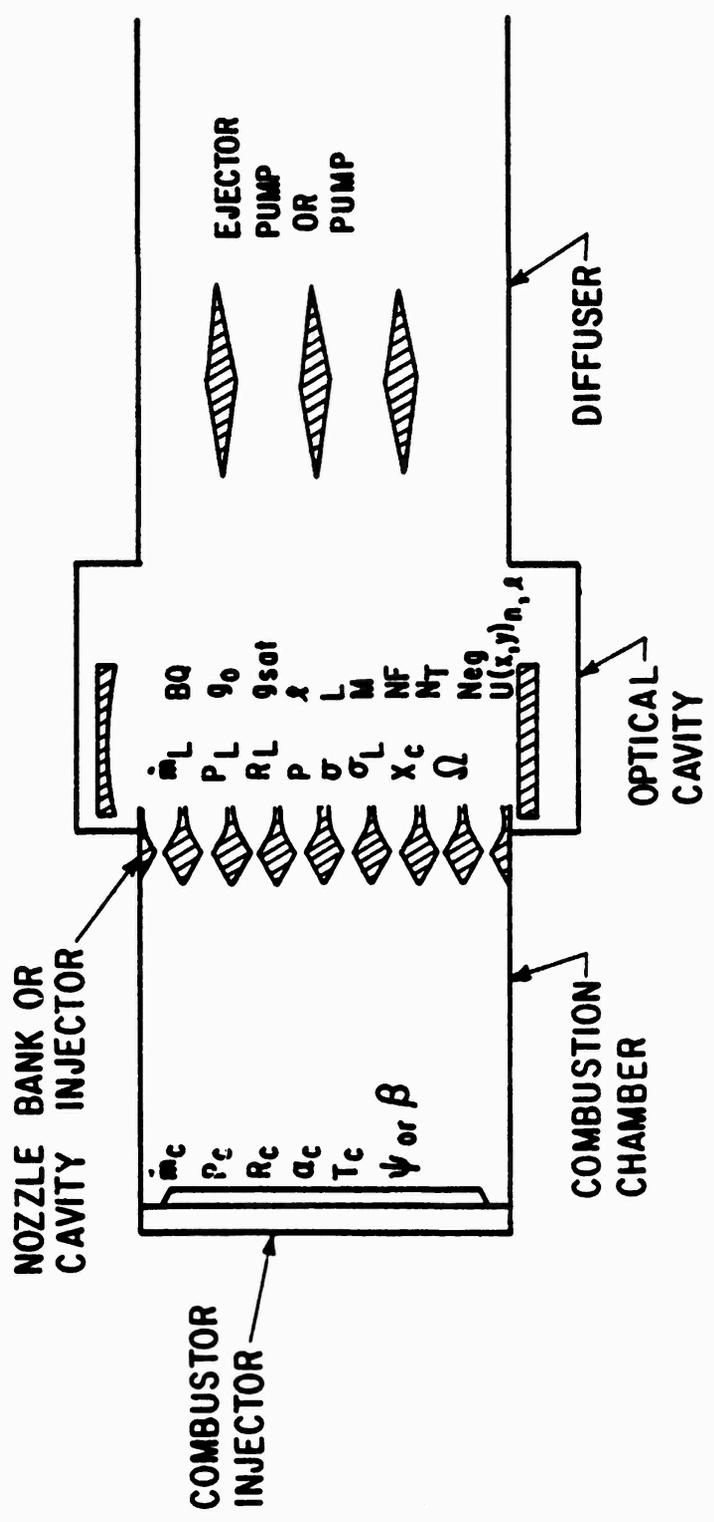
Figure 14. Chemical Laser System

σ - Specific power based on combustor and nozzle mass flows, KJ/Kg (kJ/lb)

σ_L - Specific power based on all laser flows, KJ/Kg (kJ/lb)

σ_s - Specific power based on all laser system flows, KJ/Kg (kJ/lb)

η - Laser efficiency, 10^3 kilojoules/Kg of F

δ - Nozzle power flux, W/cm^2 (kw/in^2)

δ_E - Expanded flow nozzle power flux, W/cm^2 (kw/in^2)

B. Optical Parameters

B.Q. - Beam Quality

g_o - Small signal gain, %/cm

g_{sat} - Saturated gain, %/cm

ℓ - Gain region (nozzle length), meters (cm)

L   - Laser cavity length, meters (cm)

M   - Magnification

NF   - Fresnel Number

N_T - Tube Fresnel Number

Neq   - Equivalent Fresnel Number

$U(x,y)_{n,\ell}$ - Field amplitude distribution where n is the radial mode index and ℓ is the azimuthal mode.

III. Definitions

A. Terminology

<u>Combustor or Plenum Injector</u> - The hardware for injecting gases into the combustion chamber--this may be modified if more than one is in use, i.e., diluent injector or reactant injector.

<u>Combustion Chamber</u> - Combustion Device.

<u>Nozzle Bank or Cavity Injector</u> - If H_2 is injected into the fluorine stream, it is referred to as cavity H_2 injection.

<u>Laser/Optical Cavity</u> - The box containing the active lasing media.

Avoid terminology like oxidizer and fuel and specify reactants and diluents used. We are no longer building rocket engines.

B. Measured Parameters

p_c - Combustion chamber pressure in units of atm.

p_L - Laser cavity pressure in units of torr.

P - Laser power in units of watts.

X_c - Closed or open cavity mirror position, the distance from the nozzle exit plane to the perpendicular line between both mirrors in units of   cm.

C. Computed/Measured Parameters

1. m_{F_2}, m_{H_2}, etc. - Flow rates in units of   grams/sec.
All input flow rates.

m_{F_2} - Remaining fluorine out of the nozzle bank (available for lasing).

2. T_c or any other temperature. - Temperature in degrees Kelvin.

T_c - Static equilibrium temperature in the combustion chamber or plenum based on the JANNAF value of the F_2 bond energy, and including heat losses to the chamber walls, but NOT nozzle bank losses.

3. α - F_2 equilibrium dissociation in the combustion chamber based on T_c above

$$\alpha = \frac{\text{Moles F}}{\text{Moles F} + 2x\ \text{Moles } F_2} = \frac{[F]}{[F] + 2[F_2]}$$

4. σ - Specific power in units of kilojoules/kilogram based on combustor and nozzle flow rate.

σ_L - Specific power in units of kilojoules/kilogram based on total flow rates up to cavity, i.e., combustor, cavity, flushes, purges, etc.

σ_S - Specific power in units of kilojoules/kilogram based on all laser system flows, i.e., everything in σ_L calculation but also including ejector, gas generator, etc.

5. Mole Ratios, not Weight Ratios.

R_c - Mixture ratio into the combustion chamber

$$R_c = \frac{\text{Moles oxidizer}}{\text{Moles Fuel}} = \frac{[F_2]}{[\text{Combustor Fuel}]}$$

R_L - Mixture ratio into the laser cavity

$$R_L = \frac{\text{Moles cavity fuel}}{\text{Moles fluorine as all } F_2} = \frac{[H_2]}{[F_2] + \frac{1}{2}[F]}$$

ψ_c - Total molar combustor diluent ratio

$$\psi_c = \frac{\text{Moles diluent} + \text{Moles other}}{\text{Moles fluorine as all } F_2} = \frac{[He] + [Other]}{[F_2] + \frac{1}{2}[F]}$$

ψ_L - Total molar cavity diluent ratio

$$\psi_L = \frac{\text{Moles diluent} + \text{Moles other}}{\text{Moles fluorine as all } F_2} = \frac{[He] + [Other]}{[F_2] + \frac{1}{2}[F]}$$

β_c - Combustor diluent ratio

$$\beta_c = \frac{\text{Moles diluent}}{\text{Moles fluorine as all } F_2} = \frac{[He]}{[F_2] + \frac{1}{2}[F]}$$

β_L - Cavity diluent ratio

$$\beta_L = \frac{\text{Moles diluent}}{\text{Moles fluorine as all } F_2} = \frac{[He]}{[F_2] + \frac{1}{2}[F]}$$

Ω - Total laser molar diluent ratio

$$\Omega = \psi_L + \psi_c$$

η - Laser efficiency in units of 10^3 kilojoules/Kg of fluorine. This is a measure of how efficiently a given nozzle is utilizing the available fluorine atoms generated in the combustor.

δ - Nozzle power flux in units of watts/square cm. This parameter is an important scaling parameter and is calculated simply by the total laser output power divided by the exit nozzle bank area including any base relief required.

δ_E- Nozzle power flux in an expended duct in units of watts/square cm. This parameter is calculated based on the area occupied by the fully expanded flow resulting from a scalable nozzle bank including any base relief required.

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SI - International System of Units

Base Units	Some Derived Units	Some Prefixes
metre (m)	energy-joule (J)	tera (T) 10^{12}
kilogram (kg)	force-newton (N)	giga (G) 10^9
second (s)	frequency-Hertz (Hz)	mega (M) 10^6
ampere (A)	power-watt (W)	kilo (k) 10^3
kelvin (K)	pressure-pascal (Pa)	
Mole (mol)		
candela (cd)		

To convert from	to	Multiply by (*=exact)
atmosphere	pascal	1.013 250 E+05
British thermal unit (International Table)	joule	1.055 056 E+03
calorie (thermochemical)	joule	4.184*
Celsius	kelvin	add 273.15*
electron volt	joule	1.602 19E-19
erg	joule	1.00* E-07
Farenheit	kelvin	$(f_f + 459.67)/1.8$
foot	metre	0.3048*
foot^3	m^3	2.831 685 E-02
gallon (U.S. liquid)	m^3	3.785 412 E-03
inch	metre	2.54 * E-02
inch^2	m^2	6.451 6 * E-04
kilowatt-hour	joule	3.60 * E+06
lambert	candela/m^2	$1/\Pi$ * E+04
langley	joule/m^2	4.184 * E+04
mile (U.S. statute)	metre	1.609 344 * E+03
pound-force	newton	4.448 222
pound-force-foot	newton-metre	1.355 818
lb/in^2(psi)	pascal	6.894 757 E+03
pound-mass	kg	4.535 924 E-01
torr (mmHg, 0°C)	pascal	1.333 224 E+02
yard	metre	0.9144*

Hybrid Units:

|		
kJ/lb	kJ/kg	2.204 622
kW/in^2	W/cm^2	1.550 003 E+02

APPENDIX B

KINETIC RATES

The rates recommended by Aerospace Corporation for modeling HF systems in reference 3b are included in table 9 for reference. Since that TR was prepared, several significant modifications appear appropriate.

If it is assumed that V-T rates are single quanta, then the appropriate rates for 6a should scale roughly as $V^{2.3}$. This remark is also probably applicable to 6b, 6c, 6e, and 6f. The implications for 7a and 7b are less clear. Fortunately, these two rates are only important for lower levels, so leaving them unmodified probably has little significance.

As an alternative which is probably more realistic, but more complex, either multiquanta or surprisal theory V-T rates can be used. It appears that the results do not differ drastically from the $V^{2.3}$ effects. This may be because both viewpoints predict that a system loses energy at the same rate. In cases with vibrational temperatures, this may suffice to produce comparable effects.

The V-V transfer rates are really quite difficult to estimate. Still, rate 9 does appear a bit unreasonable. Since the endothermicity for

$$HF(0) + HF(2) \rightarrow HF(1) + HF(1) \text{ is } 180 cm^{-1}$$

while that of

$$HF(0) + HF(6) \rightarrow HF(1) + HF(5) \text{ is } 900 cm^{-1}$$
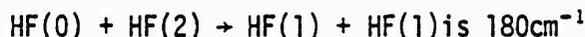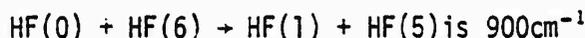
they certainly should not have the same rate. Notice also, that detailed balance will imply a really fast reverse rate. The recommendations in LAMP appear more reasonable and hence were used in earlier calculations. The rates used were the following: (Note Cohen suggested rates similar to this in 72.)

$$K = A/T$$

$$HF(X) + HF(X) \rightarrow HF(X-1) + HF(X+1) \quad A$$
$$X=1 \rightarrow 5 \qquad 8.4E15$$
$$HF(X) + HF(X+1) \rightarrow HF(X-1) + HF(X+2) \quad A$$
$$X=1 \rightarrow 4 \qquad 4.2E15$$

Table 9

RECOMMENDED RATE COEFFICIENTS FOR H_2-F_2 SYSTEM (ref. 36)

Reaction Number (as it appears in text)		Rate Coefficient, cc, mol, sec, cal	M, v, A, g(v)
1a	$H_2(0) + M_1 \; ; \; 2H + M_1$	$k_{-1a} = 6.2 \times 10^3 T^{-0.95}$	M_1 = all species except H and H_2
1b	$H_2(0) + H_2 \; ; \; 2H + H_2$	$k_{-1b} = 9.4 \times 10^{16} T^{-0.61}$	
1c	$H_2(0) + H \; ; \; 2H + H$	$k_{-1c} = 1.2 \times 10^{17} T^{0.5}$	
2	$F_2 + M_2 \; ; \; 2F + M_2$	$k_2^{M_2} = 5 \times 10^{13} A_M \exp(-35,100/RT)$	$A_F = 10; \; A_{F_2} = 2.7; \; A_M = 1$ all others
3	$HF(v) + M_3 \; ; \; H + F + M_3$	$k_3(v) = \left(\frac{1.2 A_M}{n+1}\right) \times 10^{19} T^{-1} \exp[(-135100 + E_v - E_0)/RT]$	$A_F = A_H = A_{HF} = 5; \; A_M = 1$ for all others; $v = 0 \ldots n$
4	$F + H_2(0) \; ; \; HF(v) + H$	$k_4 = g(v) \times 1.6 \times 10^{14} \exp(-1600/RT)$	$v = 1, 2, 3; \; g(1) = 0.17, \; g(2) = 0.55, \; g(3) = 0.28$
4b-1	$HF(4) + H \; ; \; H_2(v) + F$	$k_{4b} = g(v) \times 7.4 \times 10^{12} \exp(-460/RT)$	$g(0) = g(1) = 0.5; \; v = 0, 1$
4b-2	$HF(5) + H \; ; \; H_2(v) + F$	$k_{4b} = g(v) \times 1.1 \times 10^{13} \exp(-510/RT)$	$g(0) = 0.36, \; g(1) = 0.64; \; v = 0, 1$
4b-3	$HF(6) + H \; ; \; H_2(v) + F$	$k_{4b} = g(v) \times 1.9 \times 10^{14} \exp(-580/RT)$	$g(0) = 0.22, \; g(2) = 0.56; \; v = 0, 1, 2$
5	$H + F_2 \; ; \; HF(v) + F$	$k_5 = g(v) \times 1.2 \times 10^{14} \exp(-2400/RT)$	$g(v) = 0, \; v = 0, 1, 2; \; g(3)=0.08, \; g(4)=0.13, \; g(5)=0.35, \; g(6)=0.44$
6a	$HF(v) + HF \; ; \; HF(v-1) + HF$	$k_{6v}^{HF} = g(v)(3 \times 10^9 T^{-1} + 3.5 \times 10^6 T^{2.26})$	$g(1) = 1, \; g(2)=8, \; g(3)=28, \; g(4)=25, \; g(v)=5$ for $v \ge 5; \; v=1 \ldots$
6b	$HF(v) + H_2 \; ; \; HF(v-1) + H_2$	$k_6^{H_2} = 6 \times 10^7 Tv$	$v = 1 \ldots$
6c	$HF(v) + M_5 \; ; \; HF(v-1) + M_5$	$k_6^{M_5} = 7.7 \times 10^{-7} A_M T^5$	$A_{Ar} + A_{F_2} = 1; \; A_{He} = 2$
6d	$HF(v) + H \; ; \; HF(v') + H$	$k_6^H = A(v) \times 4.5 \times 10^{12} \exp(-700/RT)$	$0 \le v' \le v; \; v = 1 \ldots, \; A(1) = 0.1, \; A(v \ge 1) = 1.$ See table 12 for detailed values for specific v, v'.
6e	$HF(v) + F \; ; \; HF(v-1) + F$	$k_6^F = 1.6 \times 10^{13} v \exp(-2700/RT)$	$v = 1 \ldots$
7a	$H_2(v) + M_3 \; ; \; H_2(v-1) + M_3$	$k_7^{M_3} = 2.5 \times 10^{-5} T^{2.3} A_{M_3} v$	$A_{H_2} = 4, \; A_{Ar} = 1$

Table 9 (Continued)

RECOMMENDED RATE COEFFICIENTS FOR H_2-F_2 SYSTEM (ref. 36)

Reaction Number (as it appears in text)	Reaction	Rate Coefficient, cc, mol, sec, cal	$M, v, A, g(v)$
7b	$H_2(v) + H \underset{\leftarrow}{\overset{\rightarrow}{}} H_2(v-1) + H$	$k_7^H = 2 \times 10^{13} \exp(-2720/RT)$	$v = 1 \ldots$
6f	$HF(v) + DF \underset{\leftarrow}{\overset{\rightarrow}{}} HF(v-1) + DF$	$k_6^{DF} = 1.9 \times 10^{14}T^{-1} + 1.3 \times 10^2T^3$	$DF = \sum_v DF(v)$
8	$HF(v) + DF(v') \underset{\leftarrow}{\overset{\rightarrow}{}} HF(v-1) + DF(v'+1)$	$k_8 = 6 \times 10^{11} v$	$v = 1 \ldots; v' = 0 \ldots 6$
9	$HF(v) + HF(v') \underset{\leftarrow}{\overset{\rightarrow}{}} HF(v+1) + HF(v'-1)$	$k_9 = 3.3 \times 10^{15}T^{-1}$	$6 \geq v' \geq v + 2$
10	$HF(v-n) + H_2(v'+n) \underset{\leftarrow}{\overset{\rightarrow}{}} HF(v) + H_2(v')$	$k_{10} = v(8 \times 10^{11})$	$v = 1 \ldots 6; n = 1 \ldots v$
11	$HF(v) + N_2(0) \underset{\leftarrow}{\overset{\rightarrow}{}} HF(v-1) + N_2(1)$	$k_{11} = v(11T^3 + 2.4 \times 10^9)$	$v = 1 \ldots$

$$HF(X) + HF(X+2) \rightarrow HF(X-1) + HF(X+3) \quad A$$
$$X=1 \rightarrow 3 \qquad\qquad 2.1E15$$
$$HF(X) + HF(X+3) \rightarrow HF(X-1) + HF(X+4) \quad A$$
$$X=1 \rightarrow 2 \qquad\qquad 1.0E15$$
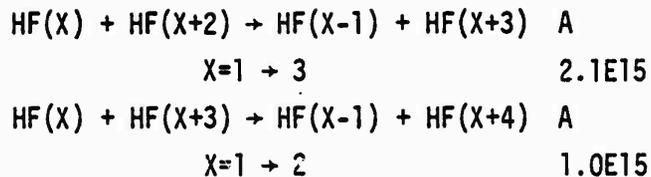
A third viewpoint arising from surprisal theory is that the V-V rates just given above are roughly constant to within a factor of two. Note that this is not what Cohen assumes. He takes the endothermic rates as constant. Surprisal theory suggests that the temperature dependence of both V-T and V-V processed follows the 1-0 behavior fairly well. This is because at typical chemical laser temperatures the theory predicts that the dominant cause of temperature effects is the phase space available to the elastic channel. Naturally surprisal theory also predicts additional V-V processes.

Fortunately computer calculations indicate that predicted power is relatively insensitive to which V-V assumption is made. This statement is especially true for cold reaction devices since only a minor extrapolation from the 2 + 0 rate is required to include all relevant V-V processes. It now appears that a reasonable compromise is to take the exothermic rates as constant and to use the above inverse temperature dependence.

The variety of possible H-atom rates have been discussed earlier and will not be reiterated here.

The UTRC work suggests that the room temperature hot reaction rate is slower than 5. It is also possible that this invalidates the assumed temperature dependence. However, there is supporting evidence for Albright's value so it appears appropriate to just be more suspicious of 5 but still retain it.