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A Review of Rate Coefficients in the H_2-F_2 Chemical Laser System–Supplement (1977)

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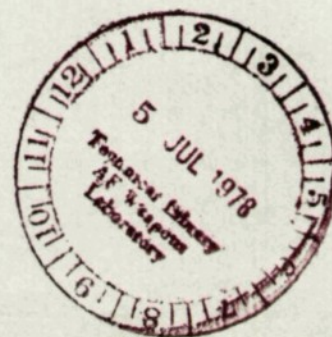The Aerospace Corporation
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This report reviews the literature published since the last report covering this subject appeared: "A Review of Rate Coefficients in the H_2-F_2 Chemical Laser System," N. Cohen and J. F. Bott, TR-0076(6603)-2, The Aerospace Corp. (15 April 1976). Published rate data are summarized and evaluated; a list of "best" estimates of rate coefficients is presented.

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PREFACE

CONTENTS

I. INTRODUCTION

In recent years, the Chemical Kinetics Department of The Aerospace Corporation Aerophysics Laboratory has prepared a series of reports that review the kinetics of hydrogen halide lasers HF, DF, and HCl.[1-3] The most recent of these devoted to the HF system was published in April 1976 and covered the literature through June 1975. Most of the 1976 report and its recommendations still appear to be valid, although kinetic work continues to be done on the HF system, particularly in regard to energy-transfer processes. Therefore, rather than attempting a complete revision of that 1976 report, we present a supplement that includes discussion of work that has appeared during the past two years, with revised conclusions where appropriate. A list of recommended rate coefficients, based on all the literature through September 1977, appears in the Appendix.

II. DISSOCIATION-RECOMBINATION REACTIONS

Recent measurements by Ultee[4] of fluorine atom recombination confirm
previous indications that the rate coefficient is small compared with those
for other atomic species. Ultee used electron spin resonance (esr) to mea-
sure fluorine atom decay at room temperature down a quartz fast-flow system
in which F atoms were produced by microwave discharge through a F_2-
carrier gas mixture. Data were reported at total pressures of 8 to 34 Torr
in mixtures of F_2 and He that consisted of 2 to 10% F_2. A value of
$k = 2.2 \pm 0.3 \times 10^{14} cm^6/mole^2$-sec was reported; preliminary data indicated
$k^{Ar} < k^{He} < k^{F_2}$. This is reasonably consistent with the value of $k^{Ar} =$
$1 \times 10^{14} cm^6/mole^2$-sec recommended by Cohen and Bott.[1] However, in
Ref. 2 it was assumed $k^{He} = k^{Ar}$. In view of Ultee's results, perhaps it
would be more correct to assume that $k^{He} = 2k^{Ar}$.

Previous reports in this series have not dealt with wall recombination
of atomic species. In recent years, several authors have reported measure-
ments of F-atom combination on surfaces. A summary of the existing litera-
ture on this subject is given in Table 1. In general, results indicate a re-
combination coefficient of $10^{-5} - 10^{-4}$ for pyrex, coated or uncoated quartz,
and alumina. Metallic surfaces are somewhat more efficient, with γs rang-
ing from 10^{-4} to 10^{-1}. In several cases, measurements were made over
a sufficient temperature range to report Arrhenius parameters for the re-
combination rate coefficient. For quartz, molybdenum glass, and gold, there
is a slight positive activation energy of about 3 kcal/mole; for copper, there
is a negative activation energy of about 5 kcal/mole. Heterogeneous atom
disappearance can be the result of several processes, including simple diatom
formation catalyzed by the surface and chemisorption of atoms on the surface,
which results in fluorides of the wall material. It is impossible to deduce from
the Arrhenius parameters which type of process is occurring. Either simple
catalysis or wall chemisorption can have a positive or negative activation
energy.

Table 1. Heterogeneous F Atom Loss Probabilities

| Material	T	γ	$\gamma(300)$	Ref.
Alumina	300		$(6.4\pm1.1) \times 10^{-5}$	Nordine and LeGrange[5]
Quartz	300		$(1.5\pm1.0) \times 10^{-4}$	Nordine and LeGrange[5]
Quartz	293		$(0.96\pm0.12) \times 10^{-4}$	Arutyunov et al.[6]
Quartz	295-588	$(1.8\pm0.05) \times 10^{-2} \exp[-(3100\pm400)/RT]$	1.2×10^{-4}	Arutyunov et al.[7]
Quartz				Valance et al.[8]
Pyrex	300		$(1.6\pm0.3) \times 10^{-4}$	Nordine and LeGrange[5]
Pyrex	298		$1.7 \times 10^{-4} - 3.7 \times 10^{-3}$	Pollack and Jones[9]
Boric acid on glass	293		$\sim 3 \times 10^{-4}$	Dodonov et al.[10]
Teflon on quartz	295		$< 7 \times 10^{-5}$	Ganguli and Kaufman[11]
Teflon on quartz	298		3.5×10^{-5}	Ultee[4]
Molybdenum glass	298-583	$(3.9\pm1.0) \times 10^{-2} \exp[-(3300\pm600)/RT]$	1.5×10^{-4}	Arutyunov et al.[7]
Teflon	293-484	$< 2 \times 10^{-5}$		Arutyunov et al.[7]
Copper	293-533	$(2.2\pm0.2) \times 10^{-6} \exp[(4800\pm800)/RT]$	6.9×10^{-3}	Arutyunov et al.[7]
Copper	300-570	$> 1.0 \times 10^{-2}$		Nordine and LeGrange[5]
Gold	293-573	$(8.0\pm0.9) \times 10^{-3} \exp[-(2700\pm400)/RT]$		Arutyunov et al.[7]
Gold	523-543	$(5.7-6.6) \times 10^{-3}$		Arutyunov et al.[7]
Nickel	295-593	$10^{-5} - 10^{-3}$		Arutyunov et al.[7]
Nickel	300		$(7.2\pm0.7) \times 10^{-4}$	Nordine and LeGrange[5]
Aluminum	300-560	$(1.8\pm0.2) \times 10^{-3}$		Nordine and LeGrange[5]
Aluminum Alloy	~ 293		$(1.4\pm0.4) \times 10^{-4}$	Nordine and LeGrange[5]
Brass	300		$> 5 \times 10^{-2}$	Nordine and LeGrange[5]
Zinc	300		$> 2 \times 10^{-1}$	Ultee[4]
KF, LiF on quartz	298		$\sim 1 \times 10^{-4}$	Nordine and LeGrange[5]

There have been no important recent results in H_2 or HF dissociation-recombination. Surface catalyzed recombination of H atoms was reviewed in 1973 by Jones, MacKnight, and Teng.[12]

III. PUMPING REACTIONS

Interest has grown recently in the kinetics of fluorine reactions, and an increasing number of experimental studies have been devoted to such processes. The difficulties of measuring the rate of the $F + H_2$ reaction were discussed in Ref. 1. Since that review was compiled, Goldberg and Schneider[13] have reported a measurement of k_4 for the process

$$F + H_2 \rightarrow HF + H \qquad (4)^*$$

They studied the reaction using a fast-flow reactor at 298 K with esr detection to measure F-atom concentration as a function of distance along the 2.2 cm i.d. quartz flow tube. A microwave discharge through F_2 was the source of F atoms. Calibration indicated that the F_2 was nearly 100% dissociated, which avoided any of the complications that would result from F_2 being present. A value of $k_4 = 1.0 \bullet 0.08 \times 10^{13} \, cm^3 /mole\text{-}sec$ was obtained. This value compares favorably with the value of $1.5 \times 10^{13} \, cm^3 /mole\text{-}sec$ recommended by Cohen and Bott.[1] In the same facility, but under conditions in which the F_2 was not completely dissociated, Goldberg and Schneider measured the value of k_5 for the process

$$H + F_2 \rightarrow HF + F \qquad (5)$$
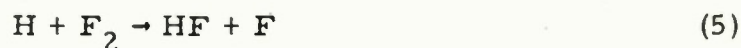
In this case, the system was somewhat more complicated, resulting in greater uncertainty in the results. They reported a value of $k_5 = 2.6 \bullet 0.6 \times 10^{12} \, cm^3 /mole\text{-}sec$. The range of uncertainty encompasses the value of 2.1×10^{12} reported by Albright et al.[14] and recommended by Cohen and Bott.[1]

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*Reactions here are numbered to be consistent with Ref. 1.

Manning et al.[15] studied the hydrogen abstraction reactions by atomic fluorine from a series of hydrocarbons and fluorinated hydrocarbons at 303 K. Neutron bombardment was used to produce ^{18}F from the stable isotope ^{19}F. Pairs of reagents in the presence of an excess of moderator bath were reacted with ^{18}F:

$$^{18}F + RH \rightarrow H^{18}F + R$$

$$^{18}F + C_3F_6 \rightarrow C_3F_6{}^{18}F$$
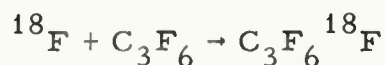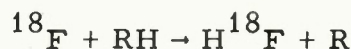
The quantity of $H^{18}F$, measured by radiochemical techniques, was the only variable monitored. Analysis of the data required knowledge of the fraction of hot F atoms that were cooled to thermal temperatures before reaction; this number, a constant for a given series of experiments, was found to be 0.85 ± 0.02. A value of 0.39 was reported for the ratio of rate coefficients k_{F+H_2}/k_{F+CH_4}. Since the best value for k_{F+CH_4} appears to be $4 \pm 1 \times 10^{13} cm^3/mole\text{-}sec$ (see Ref. 1 for discussion), this yields a value of $k_4 = 1.6 \times 10^{13}$, in good agreement with the previously recommended value.

The room-temperature relative distribution of HF(v) formed in reaction (4) has been reasonably well established after several years of continual improvements in experimental techniques. Perry and Polanyi,[16] continuing the careful work carried out in Polanyi's laboratory, used the arrested relaxation infrared chemiluminescence technique to obtain relative rates of production of v = 0....3 of 0.04:0.28:1.0:0.55, in good agreement with the recommendations of Ref. 1. Berry[17] reported a somewhat different distribution of 0.06:0.29:1.0:0.63 by using the quite different technique of measurements of the relative gain coefficients of individual HF laser transitions. He suggested that the discrepancy in results for $k_{4(v=3)} : k_{4(v=2)}$ might in some cases be due to vibrational relaxation of

product HF (cf. Coombe and Pimentel[18]) or differences in translational energies of the reagents.[19] However, Krogh, Stone, and Pimental[20] examined in detail the effects of vibrational relaxation on the results of Coombe and Pimentel and concluded that energy-transfer processes did not interfere with the measurements. Instead, they suggested rotational disequilibrium as a possible source for the discrepancy.

Moehlmann and McDonald[21] obtained very similar results with the arrested relaxation infrared chemiluminescence technique similar to that of Polanyi and co-workers. They reported relative population rates for $v = 1, 2, 3$ to be $0.28:1.0:0.47$. In view of the near agreement among all the experiments save one, it seems best to retain the recommendation of Ref. 1: that $k_{4(1)}:k_{4(2)}:k_{4(3)} = 0.17:0.55:0.28 = 0.31:1.0:0.51$ at room temperature. No measurements of the temperature dependences of these ratios have been reported since the work of Coombe and Pimentel.

The $F + H_2$ reaction (and its isotopic analogs) has been the subject of several theoretical studies in recent years. Connor, Jakubetz, and Manz[22] analyzed the population distributions predicted by one-dimensional trajectory calculations using information theoretic surprisal plots. Kormornicki, George, and Morokuma[23] studied the effect of multiple electronic surfaces on the reactivity of $F + H_2$. Rebentrost and Lester[24] examined nonadiabatic effects of interaction potentials for the various states of the triatomic intermediate in the reaction. Schatz, Bowman, and Kuppermann[25] presented and compared exact quantum, quasi-classical, and semiclassical reaction probabilities and rate coefficients for the collinear reaction. Polanyi and Schreiber,[26] continuing earlier studies by Polanyi and co-workers, reported an extensive series of investigations of the detailed dynamics of the $F + H_2$ reaction on five different potential surfaces; they examined the effect of re-reagent vibrational or translational energy on the product energy distributions. All of these studies can provide useful insights into the fundamental

chemical dynamics of a system such as $F + H_2$. However, inasmuch as they do not provide any information over and above the experimental data necessary for evaluating the rate parameters needed for modeling laser systems, they are not discussed in detail here.

Polanyi, Sloan, and Wanner[27] studied the $H + F_2$ reaction using the arrested-relaxation infrared chemiluminescence technique. They examined the effect on product energy distribution of separately enhanced translational energy (in the H atom) and vibrational-rotational energy (in the F_2 molecule). When the translational energy of the H was increased (by formation of the species in an oven at temperatures up to 2800 K), the excess energy was channeled fully into translational and rotational energy of the products; the vibrational distribution was altered slightly, with the peak of production vibrational energy shifted from HF(v = 6) to HF(v = 5). Heating the F_2 to 900 K produced no measurable effect on the product energy distribution. Although these results are not directly comparable to experiments in which the reagents are all at the same temperature, they do suggest that, if the reagents are thermally equilibrated, there will be a decrease in energy deposited in HF vibration as the reagent temperature is increased. Calculations by Wilkins[28] predict that the fraction of reagent energy channeled into vibration of HF will be almost constant from 300 to 1000 K.

IV. ENERGY-TRANSFER PROCESSES

There are two persistent problem areas in HF vibrational relaxation:
(1) relaxation by H atoms, and (2) self-relaxation by a combination of V-V
and V-R, T energy transfer. These processes continue to demand attention
because (1) they are the fastest deactivation processes in the HF system,
and therefore are principal factors in the loss of laser power; and (2) they
are the most difficult to resolve experimentally, particularly when upper
vibrational levels of HF are involved.

A. HF SELF RELAXATION

Recently, Wilkins[29] completed the first three-dimensional trajectory
study of HF-HF interactions. Because his studies provide a convenient
unified framework in which to consider all the possible HF-HF processes,
a summary of his conclusions is presented first. The experimental data
are reviewed and discussed here in the context of the theoretical studies.

An important conclusion of the trajectory studies is that a favored
process in the collision between two HF molecules, one of which is vibra-
tionally excited, is the internal conversion of vibrational-to-rotational energy,
with negligible energy being transferred to the collision partner. For a
given pair of molecules, $HF(v_1, J_1)$ and $HF(v_2, J_2)$, collision products are
$HF(v_1 - \Delta v_1, J_1')$ and $HF(v_2, J_2)$, with Δv_1 varying from 1 to v_1 and J_1' varying
over a half dozen states from the highest one energetically possible on down,
all with approximately equal probability. The resulting J_1' states are sum-
marized in Table 2 for $J_1 = 2$, the most probable state at 300 K. The un-
certainties in the rate coefficients reflect the statistically small number of
trajectories giving the indicated product states. Within the uncertainties, it
appears that the rate coefficients are all approximately equal: between 1 and
7×10^{12} cm^3/mole-sec for any given process. The rate coefficients are
listed in Table 3 for the J-specific coefficients summed over all J states and

Table 2. Theoretical Vibrational-to-Rotational Rate Coefficients and Product Channels for $HF(v_1, J_1) + HF(v_2, J_2) \rightleftarrows HF(v_1', J_1') + HF(v_2', J_2')$ at $T = 300$, $v_2 = v_2' = 0$, $J_1 = 2$[a]

v_1	v_1'	J_1'	$10^{12} k(v_1, J_1, v_2, J_2; v_1', J_1', v_2', J_2')$[b]	$10^{13} k(v_1, v_2; v_1', v_2')$[c]	Most Probable J_1'
1	0	16–10	4.0 ± 2.5	3.0	14
2	1	16–10	2.5 ± 2.0	2.4	14
2	0	21–16	3.5 ± 2.5	1.5	20
3	2	15–10	4.0 ± 3.5	1.5	14
3	1	20–16	2.5 ± 2.0	1.7	20
3	0	26–21	3.0 ± 2.5	1.1	24

[a]Data based on that in Tables 2 and 7 of Ref. 29.

[b]These rate coefficients for Boltzmann distribution of J_2 at 300 K.

[c]Values obtained by summing the numbers of the previous column over all rotational states after taking into account the rotational state populations at equilibrium.

Table 3. Theoretical Rate Coefficients $k_{v_1,v_2;v_1',v_2'}$ for Vibrational-to-Rotational Energy Transfer in $HF(v_1) + HF(v_2)$ Collisions at T = 300 K[a]

$v_1 + v_2$ \ $v_1' + v_2'$	5 + 0	4 + 0	3 + 0	2 + 0	1 + 0	0 + 0	Overall Rate Coefficients[b,c]
6 + 0	18.0 ± 2.6	8.9 ± 1.9	7.5 ± 1.7	8.5 ± 1.9	5.6 ± 1.6	8.5 ± 1.9	58.0 ± 3.0
5 + 0		19.0 ± 2.6	7.1 ± 1.7	11.0 ± 2.1	7.1 ± 1.7	9.4 ± 1.9	53.6 ± 3.2
4 + 0			17.0 ± 2.5	14.0 ± 2.3	8.9 ± 1.9	9.9 ± 2.0	49.8 ± 3.2
3 + 0				15.0 ± 2.4	17.0 ± 2.5	11.0 ± 2.0	43.0 ± 3.2
2 + 0					24.0 ± 2.8	15.0 ± 2.4	39.0 ± 3.1
1 + 0						30.0 ± 3.0	30.0 ± 3.0

[a] From Wilkins, Ref. 29, Table 7.

[b] $k_{v_1 v_2; v_1', v_2'}$ in units of 10^{12} cm^3 mole^{-1}/sec^{-1}.

[c] The overall rate coefficient is the summation of $k_{v_1 v_2; v_1', v_2'}$ over the v_1' levels.

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weighted according to the Boltzmann populations of rotational levels at 300 K. The table shows that a collision between HF(v) and HF(0) will give HF(v′) + HF(0), where v′ varies from v-1 to 0. Single-quantum transitions, i.e., v′ = v-1, are the most probable. Multiquantum transitions are about one-half as likely as single-quantum transitions, but there is little difference between the probabilities of losing 2, 3...v quanta. Similar results are obtained when both HF molecules are vibrationally excited, except that now there is a considerably larger number of possible exit channels. One or both molecules can lose vibrational energy, which is converted intramolecularly to rotational energy. For example, the vibrational energy lost by each molecule is largely converted to rotational energy of that same molecule. The probability of both molecules losing vibrational energy appears to be smaller than that for only one molecule to lose vibrational energy. However, there is no simple correlation between the change in v and the rate coefficients.

Unlike V-R, T energy transfer, in which large Δv processes were observed with high probability, in V-V exchange, the trajectory calculations predicted that only $\Delta v = 1$ is likely. Furthermore, the probabilities for HF(v) + HF(v′) → HF(v - 1) + HF(v′ + 1) were found to decrease with increasing v. Within approximately 25%, the results of Wilkins for V-V exchange (up to v = 5) can be summarized by the expressions[*]

$$k_{1, v; 0, v+1} \cong 3.6 \times 10^{15} T^{-1} v^{-1} \qquad \text{(A)}$$

$$k_{v, v; v-1, v+1} \cong 3 \times 10^{15} T^{-1} v^{-1} \qquad v > 1 \qquad \text{(B)}$$

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[*]R. L. Wilkins, private communication.

In processes of this sort, the rotational states of the HF molecules change during collision; thus, ΔE for any process is considerably smaller than what would be calculated by assuming no change in rotational energy across the reaction. (It should be stressed that the above two analytic expressions for k represent simple, approximate fits to the results of the trajectory calculations; the v dependences have no theoretical significance.)

The results of Wilkins for V-V and V-R, T transfer[29] taken together suggest that, for small v, both kinds of processes are approximately equally probable, contrary to earlier assumptions that V-V was considerably faster than V-T. For example, in collisions between HF(v=1) and HF(v=1), Wilkins reported the rate coefficients given in Table 4 for the various possible exit channels.

Table 4. Calculated Rate Coefficients for
$$HF(1) + HF(1) \rightarrow HF(v_1') + HF(v_2')$$

v_1'	v_2'	$10^{13} k_{v_1, v_2; v_1', v_2'}$	
1	0	4.1 ± 1.3	V-R, T
0	0	1.5 ± 0.9	
0	2	1.2 ± 0.2	V-V

Furthermore, whereas the overall V-R, T rates increase with v, the V-V rates decrease.

In experiments designed to measure the V-V rate of HF relaxation that have been conducted to date, one observes the decay of [HF(v)], which

is due to two competing processes, a V-V exchange (endothermic) and a V-R, T transfer (exothermic)

$$HF(v) + HF(0) \rightarrow HF(v-\Delta v) + HF(1) \qquad (V-V)$$

$$HF(v, J) + HF(0) \rightarrow HF(v', J') + HF(0) \qquad (V-R, T)$$
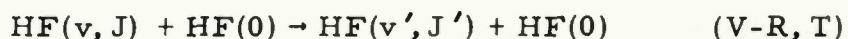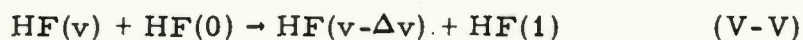
where the J' index is inserted as a reminder that large ΔJ changes are predicted. In order to extract the V-V rate, the experimenter must correct the observed relaxation rate for the expected contribution from V-R, T processes. In early work, it was assumed that the harmonic oscillator rule obeyed; viz., $k_{v, v-1} = vk_{1, 0}$. More recently, it has been realized that the v-dependence is stronger than linear; Kwok[30] has suggested an exponent of 2.3 based on experimental data in several HF-M systems. Wilkins' numerical results quantitatively reinforce Kwok's suggestion that the corrections from V-R, T processes are large, and may, in fact, represent the larger contribution to the relaxation rate. Furthermore, Wilkins' finding that the V-V processes involve changes of rotational state means that one cannot use the simple, rotation-independent equilibrium constant for the V-V process in order to convert the endothermic rate coefficient into an exothermic one. For example, the equilibrium constant for $HF(3) + HF(0) \rightleftharpoons HF(2) + HF(1)$, if it is assumed that species do not change rotational states, is 0.19. However, Wilkins' calculations predict that rotational states do change and, therefore, the endothermicity of the reaction is considerably smaller than if they didn't, which results in an equilibrium constant of 0.66. (In other words, the reaction in the exothermic direction is only 1.52 times faster than in the endothermic direction, rather than 5.2 times faster.)

The calculations of Wilkins have not, in most cases, been directly verified by clean experiments. However, there are considerable experimental data that strongly indicate the presence of high rotational energy

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levels in HF systems, which is what would be expected if his results are correct. (Wilkins also found that R-R relaxation rates decrease noticeably with increasing J. Therefore, although low rotational levels relax rapidly, high levels do not, and this contributes further to the perturbations that his predicted V-R, T energy-transfer processes would cause.) Experiments are being planned in the Aerophysics Laboratory that will establish definitively the existence of nonequilibrium populations of high rotational states of HF, and, if possible, measure their relaxation rates.

If Wilkins' calculations are verified by experiments, there will be two important consequences: (1) the extraction of V-V and V-R, T rate coefficients from experimental HF relaxation data will be even more complicated than was previously believed, and (2) computer codes that do not treat individual rotational levels and do not allow for rotational nonequilibrium may prove inadequate for some types of laser modeling.

Kwok and Wilkins* are working on a model that incorporates rotational nonequilibrium but in a simplified manner so as not to require the full rotational manifold for every vibrational level. Their model approximates the full rotational structure by incorporating six or seven discrete levels at high J (for $v = 0$, they retain J=10 through 16) and by assuming rotational equilibrium always holds for the lower J levels. The justification for this is that the previous calculations of Wilkins show that rotational relaxation is fast for low J levels but slow for upper J levels.

Since the literature search for Ref. 1 was completed, another major experimental study on HF-HF relaxation has been reported. Poole and Smith[31] determined rate coefficients for the transfer of energy from HF($v = 2...7$) to HF(0), H_2, D_2, and HD at room temperature. Data were obtained by monitoring chemiluminescence quenching in a 10 liter bulb into which concentric flows of $H_2/H/Ar$ and $F_2/Ar/Quencher$ were admitted.

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*M. A. Kwok and R. L. Wilkins, private communication.

Experiments were conducted at total pressures of 3.9 Torr, with the re-
agents on the order of 1 part in 10^3-10^4. First overtone emission was
monitored for $v = 2....7$. Quenching of emission was observed as a func-
tion of pressure of added quenching gas. Rate coefficients for deactivation
by the quencher were obtained relative to the sum of all HF(v) loss processes
in the absence of added quencher (i.e., due, principally, to spontaneous
radiation and, to a lesser extent, deactivation by Ar, H_2, F_2, and HF
formed in the reaction). The deactivation rate coefficients given in Table 5
were obtained for M=HF, H_2, D_2, and HD.

Table 5. Measured Deactivation Rate Coefficients for HF(v)
by HF, H_2, and D_2 at Room Temperature

v level	$10^{-12}k$, cm^3/mole-sec							
	HF^a	H_2^a	D_2^a	HD^a	HF^b	HF^c	HF^d	HF^e
2	7.8	0.13	0.16	0.72	10	11	15	10
3	11	0.09	0.35	3.1	16	12	30	
4	19	0.13	0.72	1.3		>32	26	
5	28	0.3	1.9	0.78	35	>48		
6	31	0.6	4.9	0.78	59			
7	~26	0.96	3.7					

[a] Results of Poole and Smith[31]
[b] Results of Kwok and Wilkins,[32] Kwok and Cohen,[33] and Kwok (private communication)
[c] Results of Airey and Smith[34]
[d] Results of Osgood, Sackett, and Javan[35]
[e] Results of Bott[36]

The results up through $v = 5$ obtained by Poole and Smith and by Kwok and
co-workers are in fairly good agreement. As noted earlier, Kwok has
maintained that HF V-V relaxation in the presence of several diatomic and

polyatomic species obeys a v dependence law of approximately $v^{2.3}$. The results of Poole and Smith for HF relaxation in the presence of HF, H_2, and D_2 also fit a similar expression (although it is not possible to choose between, say, v^2 and $v^{2.3}$).

The preceding brief discussion should have clarified several important points:

1. There are insufficient experimental data with which to evaluate individual rate coefficients for each V-V and V-R,T process involved in HF-HF energy exchange.

2. The data that are available are not entirely consistent.

3. Theoretical calculations provide a framework within which such individual rate coefficients can be estimated, but the results are largely unverified by experiment.

Hence, we are forced to combine experiment and theory in a somewhat arbitrary manner in order to arrive at a set of rate coefficients that can be recommended for computer modeling. In Table 6, we present a possible means of selecting V-V and V-R,T rate coefficients that is based on the overall experimental deactivation data listed in Table 5 and on the predictions of the calculations of Wilkins.[29] These rate coefficients are all highly tentative at this time. It should be noted that they differ somewhat from the recommendations of Cohen and Bott:[1]

1. The V-V rate coefficients of Ref. 1 were assumed to be independent of v. The values given here are inversely proportional to v.

2. In Ref. 1, it was assumed that only single-quantum V-R,T deactivation occurred, and those rate coefficients were scaled as 1:8:28:25:5 for v=1,2,3,4, and 5. Here, we permit multiquantum deactivations to occur with 0.5 the probability of single quantum transitions, and assume that the total V-R,T deactivations scale as 1:6:7:17:30:50.

The effect of the change in V-V rates is expected to be very slight in predicting total laser power output, although it might affect noticeably the spectral distribution. The effect of increased V-R,T deactivations will mean considerably less power predicted in all cases. Because the justification for

Table 6. Estimation of HF(v) + HF(0) V-V and V-R, T Rate Coefficients

v	Experimental Overall Disappearance Rate Coefficient, k_{exp} [a]	k_{v-v} [b]	Σk_{V-RT} Total V-RT [c]	$k_{v,v-1}, k_{v,v-2} \cdots k_{v,0}$ Individual k_{V-RT} [d]
	(all k's in units of $10^{12} cm^3/mole-sec$)			
2	10-12	6.0	6	4, 2
3	11-12	4.0	7	4, 2, 2
4	20	3.0	17	6, 3, 3, 3
5	28-35	2.4	~30	10, 5, 5, 5, 5
6	31-59	2.0	~50	14, 7, 7, 7, 7, 7

[a] Based on experimental data of Bott, [36] Kwok and co-workers, [32,33] and Poole and Smith. [31]

[b] Based on Equation (A) of text, which is in turn based on Wilkins' calculations. [29]

[c] Obtained by subtracting k_{v-v} of column 3 from k_{exp} of column 2.

[d] Obtained by assuming that single-quantum deactivation is twice as likely as any given multi-quantum deactivation, and that all of the latter are equally probable (based on results of Wilkins [29]).

this model is so tenuous, confirmation by comparison with experimental laser data is recommended.

For purposes of this review, the best approach appears to be to rely on the use of a model that retains rotational equilibrium; there are not sufficient data to justify the construction of the full model with separate rotational levels. However, this is done with the recognition that continued developments in laser science and technology may render this approach inadequate in another year or two.

B.   H ATOMS

Bott and Heidner[37-40] have extended their work on HF relaxation by H and D atoms discussed in Ref. 1. They used the same basic procedure of laser-induced fluorescence measurements in a discharge flow-tube apparatus to study rates of removal of HF(v=1,2,3) at 295 K by H atoms, and the rate of removal of HF(3) by both H and D atoms at 295, 240, and 200 K. Their results for removal by H atoms at 295 K are given in Table 7 (from Ref. 39).

Table 7.   Experimental Removal Rate Coefficients
for HF(v) by H at T = 295 K

v	$k(cm^3/mole\text{-}sec)$	k_v/k_1
1	$(1.4 \pm 0.4) \times 10^{11}$	1.0
2	$(5 \pm 2) \times 10^{11}$	3.6
3	$(6.3 \pm 1.5) \times 10^{13}$	450

Removal rates for HF(3) by H and D atoms at different temperatures are given in Table 8.

Table 8. Experimental Removal Rates for HF(3)
by H and D Atoms

	10^{13} k, cm^3/mole-sec		
	295 K	240 K	200 K
HF(3) + H	6.3 ± 1.5	6.5 ± 0.6	10.2 ± 1.2
HF(3) + D	5.9 ± 0.5		7.9 ± 1.2

The removal of HF(v) by H atoms can be attributed to one or more possible processes, as Bott and Heidner have discussed:

$$HF(v) + H \rightleftharpoons HF(v') + H \qquad v' < v \qquad\qquad (6\text{-}d)$$

$$HF(v) + H \rightleftharpoons H_2 + F \qquad\qquad\qquad (\text{-}4)$$

The atom exchange process to form H_2 is exothermic for $v = 3$, but not for $v = 1$ or 2 (assuming H_2 formed in its vibrational ground state). The large increase in removal rates in going from $v = 1$ to $v = 3$ suggests a contribution from the atom exchange process. As Bott and Heidner have noted, the experimental rate coefficient can be interpreted as the sum

$$k_{exp} = \sum_{v'} k^H_{6(v=3, v')} + Ak_{-4(v=3)}$$

where A is between 0.7 and 1.0. From the kinetic and thermochemical data for the reaction of $F + H_2$, and the known vibrational distribution of product HF, one can calculate that $k_{-4(v=3)}$ should be 1.4×10^{13}, which is about 22% of the total removal rate. This suggests a value of between 4.9 and 5.3 $\times 10^{13}$ for the vibrational deactivation processes, i.e., for the sum $\sum_{v'} k^H_{6(v=3, v')}$ where $v' = 0$, 1, 2. For modeling purposes, it is necessary to

know the relative distribution among the various values of v'. For example, the effect on calculated laser performance of the third level that is being deactivated principally to the second level will be considerably different from the effect of deactivation all the way to the zero level. Calculations made in this Laboratory indicate that, under some conditions, the assumption that $\Delta v = 3$ in the relaxation of HF(v=3) by H atoms results in a prediction of approximately one-third of the power predicted under the assumption of single-quantum deactivation for all HF(v). In both cases, it must be assumed that the overall deactivation rate of HF(v=3) is equal to the experimentally measured value for HF(3) deactivation. Since the severe effects of the multi-quantum assumption seem to disagree with experience, we assume that the very large rate for deactivation of HF(3) is associated with single-quantum deactivation only, assigning the rate by arbitrarily selecting a value of 0.9 for A. Thus

$$k_{exp} = k_{6(v=3, \ v'=2)}^{H} + 0.9 k_{-4(v=3)}$$

where, from figures given above, $k_{6(v=3, \ v'=2)}^{H} = 5 \times 10^{13} \text{cm}^3/\text{mole-sec}$.

Even after these assumptions have been made, there is still some ambiguity in the nature of the deactivation process. Deactivation could be a result of a nonreactive, inelastic collision, in which the HF molecule remains intact but loses vibrational energy; or a result of a reactive collision, in which the F atom is transferred to the incoming free H atom. Experiments cannot distinguish between the two possibilities, although isotopic labeling with D atoms should provide a good indication of what is taking place in the H/HF system. Wilkins' trajectory calculations can, in principle, distinguish between the two processes. However, there is still some uncertainty in the shape of the potential energy surface for the H-F-H system. Wilkins has studied the effect of barrier height on the rate of deactivation of

HF(v) by H atoms. He found, for example, the approximate deactivation
rates for HF(v=3) given in Table 9.

Table 9. Theoretical Deactivation Rates for HF(v=3)
by H Atoms for Different Assumed Poten-
tial Energy Surface Barrier Heights

Barrier Height, kcal/mole	k, cm^3/mole-sec
1.5	1.5×10^{13}
2.5	2.0×10^{12}
3.5	2.0×10^{11}
40.0	2.5×10^{12}

As the barrier height increases, the contribution from reactive processes
decreases, but the contribution from nonreactive scattering increases, so
that the total rate does not decrease monotonically with barrier height.

No measurements have been made on the relaxation of HF from vibra-
tional levels higher than the third. We assume that the same large rate
coefficient as was found for $v = 3 \rightarrow v = 2$ applies for all $v \rightarrow v-1$ for $v = 3$. We
assume further that multiquantum relaxation occurs with the same rate as
was found for the deactivation of the $v = 2$ level. (The accuracy of this
estimate cannot be important, inasmuch as the assumed rate coefficient is
so much smaller than that for the single quantum process.) However, the
experimental disappearance rate is divided by 2, which is the number of
possible exit channels for the case of $v = 2$. The assumed deactivation coeffi-
cients are given in Table 10. The rates for $v \geq 3$ are considerably faster than
the earlier results of Kwok and Wilkins;[1,42] however, at present we consider
these to be the more reliable.

Table 10. Suggested Deactivation Rate Coefficients for HF(v) by H Atoms

$$HF(v) + H \rightleftharpoons HF(v') + H$$

$$k = A \times 10^{12} \exp(-700/RT)\,cm^3/mole\text{-}sec$$

v	v′	A	Ref.
1	0	1.5	Heidner and Bott[39]
2	1, 0	1.8	Heidner and Bott;[39] with assumption that both possible exit channels are equally probable.
3	2	360.0	Heidner and Bott;[39] experimental rate is corrected for contribution from H_2 + F formation and then assumed to represent single quantum deactivation.
4	3		
5	4	360.0	Assumed same as for v = 3
6	5		
4	2, 1, 0		
5	3, 2, 1, 0	1.8	Assumed same as for v = 2
6	4, 3, 2, 1, 0		

C.   DF

Recently, Wilkins* completed trajectory studies of the HF-DF system, in which V-V and V-R, T processes with either or both species (HF and DF) vibrationally excited were taken into account. As is the case in many of the energy-transfer processes involving upper vibrational levels of HF in colli-sion with HF, these theoretical results have not been verified by experimental studies and should be used with due caution. We expect, however, that the

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*R. L. Wilkins, private communication.

basic trends of relaxation probabilities as a function of varying vibrational level should be reasonably accurate, and we rely on them in the following suggested rate coefficients.

The experimental data on which the recommended value of the V-R,T process

$$HF(1) + DF(0) \rightarrow HF(0) + DF(0)$$

is based were outlined in Ref. 1. Wilkins calculated the overall rate coefficients given in Table 11 for HF(v) + DF(0) (where "overall" means summed over all possible j states).

Table 11. Theoretical Overall Rate Coefficients
for HF(v) + DF(0)

		$HF(v) + DF(0) \rightleftharpoons HF(v') + DF(0)$	
v	v'	$k_{v,v'}, 10^{12} cm^3/mole\text{-}sec$	$\sum_{v'} k_{v'}, 10^{12} cm^3/mole\text{-}sec$
1	0	3.6	3.6
2	0	2.0	4.1
2	1	2.1	
3	0	1.5	
3	1	1.5	4.7
3	2	1.7	
4	0	1.1	
4	1	1.3	
4	2	1.1	5.0
4	3	1.5	

A monotonic increase with v, although not large, is shown in the last column. For computational ease, and in view of the uncertainties in the theoretical results, we assume that these values are constant with increasing v, And that the channels into the various v' are all equally probable. Column 3 shows that the latter approximation is sufficiently accurate for most purposes. Thus, the recommended rate coefficient for the process

$$HF(v) + DF(0) \rightarrow HF(v') + DF(0) \tag{6-f}$$

is

$$k_6^{DF} = \frac{1}{v} (1.9 \times 10^{14}T^{-1} + 1.3 \times 10^2 T^3)$$

The results of Wilkins for V-V energy transfer in the case of HF(v) colliding with DF(0) shows that the probability of energy transfer increases significantly with v; his results are given in Table 12.

Table 12.   Theoretical V-V Energy Transfer Rate
Coefficients for HF(v) + DF(0) → HF(v-1)
+ DF(1)

v	k, 10^{12}cm^3/mole-sec
1	1.6 ± 0.9
2	2.2 ± 1.0
3	3.1 ± 1.2
4	4.4 ± 1.4

Within the uncertainty of the calculations, a linear dependence on v seems appropriate. Hence, the recommended rate coefficients are $k_8 = 6 \times 10^{11}v$ cm^3/mole-sec, where reaction 8 is

$$HF(v) + DF(0) \rightleftharpoons HF(v-1) + DF(1) \tag{8}$$

D. DEACTIVATION OF UPPER LEVELS BY OTHER CHAPERONES

Bott[41] studied the vibrational relaxation of HF(v=1, 2, 3) in the presence of H_2, N_2, and CO_2; some results were also reported for relaxation by O_2 and HCl. The results are summarized in Table 13.

Table 13. Experimental Rate Coefficients for Vibrational Relaxation of HF(v=1, 2, 3)

v	$10^{-12} k$, cm^3/mole-sec									
	H_2^a		N_2		CO_2		O_2		HCl	
	k_v	k_v/k_1	k_v	k_v/k_1	k_v	k_v/k_1	k_v	k_v/k_1	k_v	k_v/k_1
1	0.71	1.0	0.0027	1.0	0.73	1.0	0.0008	1.0	0.32	1.0
2	1.37	1.9	0.015	5.6	3.7	5.0				
3	2.86	4.0	0.056	20.0	7.0	9.6	0.014	16.7	7.48	23.5

^{a}For H_2, the experiments yield the relaxation rate in the endothermic direction, i.e., $HF(v) + H_2(0) = HF(v-1) + H_2(1)$. The figures given are for the reverse, exothermic direction, assuming no changes in rotational energy levels of either molecule. See also Table 5 for other data for relaxation by H_2.

V. ROTATIONAL RELAXATION

For several years, spectral distributions in HF lasers have strongly suggested the presence of nonequilibrium rotational populations. The evidence was avoided as long as possible, not so much because it appeared physically unreasonable as because it appeared computationally intractable on an affordable timescale.

Results of the first direct measurements of rotational relaxation in HF indicated that the process was extremely rapid, with rate coefficients on the order of 10^{14} cm^3/mole-sec.[43-45] The extraction of these rate coefficients from experimental data required some assumptions about the various processes that were taking place in the medium. In general, processes exchanging rotational energy with translational, or transferring rotational energy from one molecule to another, were considered; processes that exchange rotational energy with vibrational energy were neglected. An example of the latter is

$$HF(v=1, J=3) + M \rightleftharpoons HF(v=0, J=16) + M$$

Recent calculations by Wilkins have suggested that such processes can be very rapid, which makes doubtful the rate coefficients that had been deduced from the experimental data. Furthermore, both experimental and theoretical results indicate that rotational relaxation rates decrease with increasing J. Therefore, even if rotational energy transfer were to occur with nearly gas-kinetic frequency for low J, it could be orders of magnitude slower for higher J levels of interest. Calculations by Kerber[*] and by Hough[*] indicate that, even if rotational energy transfer were to occur on every gas-kinetic collision, that would still not be fast enough to maintain rotational equilibrium in a lasing medium.

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[*] R. L. Wilkins, private communication.

The picture, then, appears rather unclear now, although it does appear clear that rotational nonequilibrium is an issue that must be taken into consideration. However, it is not obvious that a model needs to be constructed that treats each rotational level separately. Kwok and Wilkins have been investigating a kinetic model that sets lower rotational levels in equilibrium (on the assumption that energy transfer among them is very rapid), but treats upper levels discretely. The degree of success of this approach has not yet been fully determined.

As noted earlier, the recommended rate coefficients given in the Appendix are based on data interpreted with the assumption of rotational equilibrium. The extent to which this assumption detracts from the usefulness of the computer modeling remains to be seen.

APPENDIX

RECOMMENDED RATE COEFFICIENTS FOR H_2 - F_2

Table A-1. Recommended Rate Coefficients for the H_2-F_2 System

Reaction Number	Reaction	Rate Coefficient, units of cm, mole, sec, cal	M, v, A, g(v)
1a	$H_2(0) + M_1 = 2H + M_1$	$k_{-1a} = 6.2 \times 10^{17} T^{-0.95}$	M = 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	$H_2(0) + H = 2H + H$	$k_{-1c} = 1.2 \times 10^{14} T^{0.5}$	
2	$F_2 + M_2 = 2F + M_2$	$k_2^M = 5 \times 10^{13} A_M \exp(-35,100/RT)$	$A_F = 10$, $A_{F_2} = 2.7$, $A_{He} = 2$; $A_M = 1$, all others
3	$HF(v) + M_3 = H + F + M_3$	$k_{3(v)} = \dfrac{1.2\, A_M}{n+1} \times 10^{19} T^{-1} \exp(-135,100/RT)$	$A_F = A_H = A_{HF} = 5$: $A_M = 1$, 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	$HF(4) + H = H_2(v') + F$	$k_{-4(v=4)} = g(v') \times 1.7 \times 10^{12} \exp(-460/RT)$	$g(0) = g(1) = 0.5$, $v' = 0,1$
4b-2	$HF(5) + H = H_2(v') + F$	$k_{-4(v=5)} = g(v') \times 1.1 \times 10^{13} \exp(-510/RT)$	$g(0) = 0.36$, $g(1) = 0.64$, $v = 0,1$
4b-3	$HF(6) + H = H_2(v') + F$	$k_{-4(v=6)} = g(v') \times 1.9 \times 10^{13} \exp(-580/RT)$	$g(0) = g(1) = 0.22$, $g(2) = 0.56$, $v = 0,1,2$
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	$HF(v) + HF = HF(v') + HF$	$k_{6v}^{HF} = g(v,v')(3 \times 10^{14} T^{-1} + 3.5 \times 10^4 T^{2.26})$	$g(1,0) = 1$; $g(2,1) = 4$; $g(2,0) = 2$; $g(3,2) = 6$, $g(3,1) = g(3,0) = 1.5$: $g(4,3) = 3$, $g(4,v') = 3$, $v' = 2,1,0$; $g(5,4) = 10$, $g(5,v') = 5$ $v' = 3,2,1,0$; $g(6,5) = 14$, $g(6,v') = 7$, $v' = 4 \ldots 0$

[a] These rate coefficients are evaluated with the assumption that all species are in rotational equilibrium.

Table A-1. Recommended Rate Coefficients for the H_2-F_2 System[a] (Continued)

Reaction Number	Reaction	Rate Coefficient, units of cm, mole, sec, cal	M, v, A, g(v)
6b	$HF(v) + H_2 = HF(v') + H_2$	$k_{6v}^{H_2} = 6 \times 10^7 \, Tv$	$v' = v - 1$
6c	$HF(v) + M_4 = HF(v-1) + M_4$	$k_{6v}^{M_4} = 7.7 \times 10^{-7} A_M v \, T^5$	$A_{Ar} = A_{F_2} = 1; A_{He} = 2$
6d	$HF(v) + H = HF(v') + H$	$k_{6(v,v')}^{H} = g(v,v') \times 1.5 \times 10^{12} \exp(-700/RT)$	$g(1,0) = 1; g(2,1) = g(2,0) = 1.8; g(v,v-1) = 360, v = 3 \ldots 6;$ $g(v,v-n) = 1.8, v = 3 \ldots 6, n = 2 \ldots v$
6e	$HF(v) + F = HF(v-1) + F$	$k_{6(v)}^{F} = 1.6 \times 10^{13} v \exp(-2700/RT)$	
6f	$HF(v) + DF = HF(v') + DF$	$k_6^{DF} = \frac{1}{v}(1.9 \times 10^{14} T^{-1} + 1.3 \times 10^2 T^3)$	$0 \le v' < v, \; DF = \sum_{v} DF(v)$
7a	$H_2(v) + M_5 = H_2(v-1) + M_5$	$k_7^{M_5} = 2.5 \times 10^{-4} T^{4.3} A_{M_5} v$	$A_{H_2} = 4, A_{Ar} = 1; v = 1 \ldots$
7b	$H_2(v) + H = H_2(v-1) + H$	$k_7^{H} = 2 \times 10^{13} \exp(-2720/RT)$	$v = 1 \ldots$
8	$HF(v) + DF(0) = HF(v-1) + DF(1)$	$k_8 = 6 \times 10^{11} v$	$v = 1 \ldots 6$
9	$HF(v) + HF(v') = HF(v+1) + HF(v'-1)$	$k_{9(v,1:v+1,0)} = 3.6 \times 10^{15} T^{-1} v^{-1}$ $k_{9(v,v':v+1,v'-1)} = 3 \times 10^{15} T^{-1} v^{-1}$	$v = 1 \ldots 6, v' = 1$ $v = 1 \ldots 6; v' = 1$
10	$HF(v-n) + H_2(v'+n) = HF(v) + H_2(v')$	$k_{10} = 8 \times 10^{11} v$	$v = 1 \ldots 6; n = 1 \ldots v$
11	$HF(v) + N_2(0) = HF(v-1) + N_2(1)$	$k_{11} = v^2(11 \, T^3 + 2.4 \times 10^9)$	$v = 1 \ldots$

REFERENCES

1. N. Cohen and J. F. Bott, A Review of Rate Coefficients in the H_2-F_2 Chemical Laser System, TR-0076(6603)-2, The Aerospace Corporation, El Segundo, Calif. (15 April 1976).

2. N. Cohen, A Review of Rate Coefficients in the D_2-F_2 Chemical Laser System, TR-0077(2603)-3, The Aerospace Corporation, El Segundo, Calif. (5 August 1977).

3. N. Cohen and J. F. Bott, "Kinetics of Hydrogen Halide Chemical Laser Systems," in Handbook of Chemical Lasers, eds., R. W. F. Gross and J. F. Bott, Wiley-Interscience, New York (1976a).

4. C. J. Ultee, Chem. Phys. Lett. 46, 366 (1977).

5. P. C. Nordine and J. D. LeGrange, AIAA J 14, 644 (1976).

6. V. S. Arutyunov, L. S. Popov, and A. M. Chaikin, Kinet. Katal 17, 286 (1976).

7. V. S. Arutyunov and A. M. Chaikin, React. Kinet. Katal. Lett. 6, 169 (1977).

8. W. Valance, B. Birang, and D. I. MacLean, "Measurement of Fluorine Atom Concentrations and Recombination Rates by ESR Spectroscopy," FRK-116, Boston College (October 1971).

9. T. L. Pollock and W. E. Jones, Can. J. Chem. 51, 2041 (1973).

10. A. F. Dodonov, G. K. Lavroskaya, I. I. Morozov, and V. L. Tal'rose, Dokl. Akad. Nauk SSSR 198, 622 (1972). As reported by Arutynov and Chaikin in Ref. 7.

11. P. S. Ganguli and M. Kaufman, Chem. Phys. Lett. 25, 221 (1974).

12. W. E. Jones, S. D. MacKnight, and L. Teng, Chem. Rev. 73, 407 (1973).

13. I. B. Goldberg and G. R. Schneider, J. Chem. Phys. 65, 147 (1976).

14. R. G. Albright, A. F. Dodonov, G. K. Lavrovskaya, I. I. Morosov, and V. L. Tal'roze, J. Chem. Phys. 50, 3632 (1969).

15. R. G. Manning, E. R. Grant, J. C. Merrill, N. J. Parks, and J. W. Root, Int. J. Chem. Kinet. 7, 39 (1975).

16. D. S. Perry and J. C. Polanyi, J. Chem. Phys. 12, 419 (1976).

17. M. J. Berry, J. Chem. Phys. 59, 6229 (1973).

18. R. D. Coombe and G. C. Pimental, J. Chem. Phys. 59, 251 (1973).

19. J. C. Polanyi and K. B. Woodall, J. Chem. Phys. 57, 1574 (1972).

20. O. D. Krogh, D. K. Stone, and G. C. Pimentel, J. Chem. Phys. 66, 368 (1977).

21. J. G. Moehlmann and J. D. McDonald, J. Chem. Phys. 62, 3061 (1975).

22. J. N. L. Connor, W. Jakubetz, and J. Manz, J. Chem. Phys. 17, 451 (1976).

23. A. Kormornicki, T. F. George, and K. Morokuma, J. Chem. Phys. 65, 4312 (1976).

24. F. Rebentrost and W. A. Lester, Jr., J. Chem. Phys. 63, 3737 (1975).

25. G. C. Schatz, J. M. Bowman, and A. Kuppermann, J. Chem. Phys. 63, 674 (1975).

26. J. C. Polanyi and J. L. Schreiber, Disc. Faraday Soc. 62, 267 (1977).

27. J. C. Polanyi, J. J. Sloan, and J. Wanner, J. Chem. Phys. 13, 1 (1976).

28. R. L. Wilkins, J. Chem. Phys. 58, 2326 (1973).

29. R. L. Wilkins, J. Chem. Phys. 67, 5838 (1978)

30. M. A. Kwok and N. Cohen, 172nd Amer. Chem. Soc. Natl. Mtng, San Francisco, Cal. (September 1976).

31. P. R. Poole and I. W. M. Smith, J. Chem. Soc. Faraday Trans. II, 1434 (1977).

32. M. A. Kwok and R. L. Wilkins, J. Chem. Phys. 63, 2453 (1975).

33. M. A. Kwok and N. Cohen, 172nd ACS National Meeting, San Francisco, California (September 1976).

34. J. R. Airey and I. W. M. Smith, J. Chem. Phys. 57, 1669 (1972).

35. R. M. Osgood, Jr., P. B. Sackett, and A. Javan, J. Chem. Phys. 60, 1464 (1974).

36. J. F. Bott, J. Chem. Phys. 57, 96 (1972).

37. J. F. Bott and R. F. Heidner III, J. Chem. Phys. 68 (1978).

38. R. F. Heidner and J. F. Bott, J. Chem. Phys. 63, 1810 (1975).

39. R. F. Heidner and J. F. Bott, Ber. der Bunsen-Ges. fur physik. Chemie 81, 128 (1977).

40. J. F. Bott and R. F. Heidner III, J. Chem. Phys. 66, 2878 (1977).

41. J. F. Bott, J. Chem. Phys. 65, 4239 (1976).

42. M. A. Kwok and R. L. Wilkins, J. Chem. Phys. 60, 2189 (1974);

43. L. M. Peterson, G. H. Lindquist, and C. B. Arnold, J. Chem. Phys. 61, 3480 (1974).

44. J. J. Hinchen, Appl. Phys. Lett. 27, 672 (1975).

45. J. J. Hinchen and R. H. Hobbs, J. Chem. Phys. 65, 2732 (1976).

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