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A Review of Rate Coefficients in the H_2-F_2 Chemical Laser System

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FOR THE COMMANDER

Ronald C. Lawson

Ronald C. Lawson, 1st Lt., USAF
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In recent years, considerable effort has been expended at The Aerospace Corporation Aerophysics Laboratory to design theoretical models for computer calculations of the behavior and performance of HF chemical lasers, both pulsed and continuous. In order to perform such calculations, the rate coefficients of the various chemical reactions and energy transfer processes that occur must be known, or at least estimated. To this end, the Chemical Kinetics Department has attempted to maintain an

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up-to-date compilation of the rate coefficients that reflects the best current information available from published and unpublished theoretical and experimental work. When direct information has not been available, theoretical techniques for estimating rate coefficients based on various a priori principles or estimates based on comparison with related reactions with known rate coefficients are applied.

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1. INTRODUCTION

In recent years, considerable effort has been expended at The Aerospace Corporation Aerophysics Laboratory to design theoretical models for computer calculations of the behavior and performance of HF chemical lasers, both pulsed and continuous. In order to perform such calculations, the rate coefficients of the various chemical reactions and energy transfer processes that occur must be known, or at least estimated. To this end, the Chemical Kinetics Department has attempted to maintain an up-to-date compilation of the rate coefficients that reflects the best current information available from published and unpublished theoretical and experimental work. When direct information has not been available, theoretical techniques for estimating rate coefficients based on various a priori principles or estimates based on comparison with related reactions with known rate coefficients are applied.

This report is the sixth of a series prepared by the Chemical Kinetics Department during the past four years in which the kinetics of hydrogen halide laser systems are reviewed [Cohen (1971, 1972, 1974); Cohen and Bott (1975, 1976)]. For the users' convenience, each report is self-contained, obviating recourse to the preceding reports. However, as additional information has become available, or as interests have shifted slightly, certain issues dealt with in earlier reports did not need to be covered again, and, to this extent, these reports are not completely cumulative in scope.

Hydrogen-halide kinetics and energy transfer is a field in which there is great activity, and new results are continually becoming available. Therefore, it is inevitable that information in this report will soon be out-of-date, perhaps before it is disseminated. To minimize this problem, reference is made to unpublished data and reports when appropriate. The assistance of many colleagues who have provided preprints of their work is gratefully acknowledged. The literature survey for this review was completed in June 1975.

The scope of this survey includes all reactions of interest in an H_2-F_2 chemical laser system. Thus, chemical reactions and energy-transfer processes involving other hydrogen- or fluorine-containing compounds have been omitted. In most current chemical kinetics computer programs, rate coefficients are entered in the form $AT^n\exp(-E/RT)$. In this report, therefore, all coefficients have been made to fit this form, even when data or theory suggest a different temperature dependence. The primary purpose here is to present data for computational purposes, rather than to unravel the theoretical significance of the findings. Joint Army, Navy, and Air Force (JANAF) data have been used for thermochemical quantities, with $K_{a,b} = k_a/k_b$ used to express the equilibrium constant in terms of the rate coefficients. Units of cubic centimeters, moles, seconds, and calories are generally used throughout. In fitting data with analytic expressions, particular attention has been given to the temperature range 300 to 1000 K; higher temperatures are not of practical interest, and lower temperatures are largely devoid of data. Extrapolation of the recommended rate coefficients outside of this range should be carried out with caution.

II. DISSOCIATION-RECOMBINATION REACTIONS

A. H_2 DISSOCIATION

Hydrogen dissociation and recombination rates have been widely studied since the first room-temperature measurements were made in 1929. The data have been summarized and reviewed critically by Baulch et al. (1972). Because these reactions are only of slight importance in laser systems, which are generally at low (<500 K) temperatures, all the experimental evidence is not tabulated here. Shock-tube studies of the following reactions have been made by Jacobs, Giedt, and Cohen (1967) in the temperature range 2900 to 4700 K.

$$H + H + Ar \rightleftharpoons H_2 + Ar \tag{1a}$$

$$H + H + H_2 \rightleftharpoons H_2 + H_2 \tag{1b}$$

$$H + H + H \rightleftharpoons H_2 + H \tag{1c}$$

Their review of previous shock-tube data showed that the results of various experimenters disagreed by factors of about 3, 5, and 10, respectively, for Ar, H, and H_2 as chaperone gases. (The shock-tube experiments actually involved the measurement of hydrogen dissociation. However, it has been customary to report the results in terms of a recombination rate.) In all three cases, their results lie in the middle of the range of values. They reported $k_{1a} = 10^{18}T^{-1}$, $k_{1b} = 2.5\ k_{1a}$, and $k_{1c} = 20\ k_{1a}$. Their values for k_{1a} and k_{1b}, extrapolated to room temperature, yield 3.3 and 8.2×10^{15} cc/mol-sec, respectively. In four decades, the room temperature value of k_{1b} has ranged from 0.2 to 72×10^{15}. Most recently, Ham, Trainor, and Kaufman (1970) [see also Trainor, Ham, and Kaufman (1973)] have measured k_{1a} and k_{1b} in a flow system using an isothermal catalytic probe over the temperature range of 77 to 300 K and found temperature dependencies of $T^{-0.81}$ and approximately $T^{-0.61}$, respectively, with values at 300 K of 3.3 and 2.9×10^{15} cc^2/mol^2-sec. Their results, extrapolated to the temperature range of the experiments of Jacobs, Giedt, and Cohen (1967), agree with the results of the latter workers within 35%. Because the lower temperatures are of more interest in laser chemistry, the results of Ham, Trainor, and Kaufman (1970) are weighted heavily. The expressions $k_{1a} = 6.2 \times 10^{17}\ T^{-0.95}$ and $k_{1b} = 9.4 \times 10^{16} T^{-0.61}$ fit both high- and low-temperature data within about 10%. The numerous results are not tabulated here; further citations are given by Baulch (1972).

Of the several room-temperature measurements of k_{1c}, the most reliable seems to be that of Bennett and Blackmore (1968). They obtained an upper limit of 2.5×10^{15} cc^2/mol^2-sec in a discharge flow system using esr for atom detection, suggesting that k_{1c} has a maximum value somewhere in the temperature range 1000 to 3000 K and is relatively unimportant at low temperatures. The expression $k_{1c} = 1.2 \times 10^{14} T^{1/2}$ is consistent with the upper limit of Bennett and Blackmore (1968) and agrees with the low-temperature end of the shock-tube experiments of Jacobs, Giedt, and Cohen (1967). Therefore, it is probably a reasonable expression in the temperature range of interest, although it is not useful above 3000 K. This expression is recommended in Appendix I, subject to modification when more experimental data become available.

B. F_2 DISSOCIATION

A thorough critical review of the dissociation-recombination of F_2 and Cl_2 was published by Lloyd (1971); repetition of his work has been kept to a minimum here.

In recent years, several shock-tube determinations have been made of the rate of F_2 dissociation (Table 1).

$$F_2 + M \rightleftharpoons F + F + M \qquad (2)$$

Table 1. Fluorine Dissociation Rate Coefficient

$$F_2 + M \xrightarrow{k_2} 2F + M$$

$$k_2 = A \exp(-E/RT)$$

M	T, K	$P\tau_{HF-M}$, μsec-atm	k, cc/mole-sec	Reference
HF	350	0.014	2×10^{12}	Airey and Fried (1971)
	1400-4100	$6.1 \times 10^{-4} \exp(4/T^{1/3})$	$6.6 \times 10^{2} T^{2.45}$	Solomon et al. (1971)
	1350-4000	$1.0 \times 10^{-2} \exp(4.4/T^{1/3})$	$1.1 \times 10^{5} T^{2.12}$	Bott and Cohen (1971)
	350	0.025	1.1×10^{12}	Stephens and Cool (1972)
	294	0.015	1.6×10^{12}	Hancock and Green (1972)
	295-1000	$(1 \exp(-43/T^{1/3}))$	$(1 \times 10^{14} T^{-1} + 1.7 \times 10^{5} T^{2})$	Bott and Cohen (1972)
	290	0.025	9.5×10^{11}	Osgood, Javan, and Sackett, (1972, 1974)
	350-750	$1.9 \exp(-29/T^{1/3})$	$(2.4 \times 10^{14} T^{-1} + 7.1 \times 10^{8} T)$	Fried, Wilson, and Taylor (1973)
	295-1000	$8.0 \exp(-38.9/T^{1/3})$	$(3 \times 10^{14} T^{-1} + 1.5 \times 10^{5} T^{2})$	Hinchen (1973a, 1973b)
	297-670	$5.7 \exp(-19/T^{1/3})$	$(4.2 \times 10^{14} T^{-1} + 1.5 \times 10^{5} T^{2})$	Lucht and Cool (1974)
	1500-5000	$5.7 \times 10^{-1} \exp(42.0/T^{1/3})$	$2.8 \times 10^{4} T^{2.1}$	Vasil'ev et al. (1973)
	600-2400	$(5.5 \times 10^{6} T^{-2} + 4.4 \times 10^{-3} T)^{-1}$	$(4.4 \times 10^{14} T^{-1} + 4 \times 10^{5} T^{2})$	Blair, Breshears, and Schott (1973)
	1400-2600	$0.026 \exp(21.4/T^{1/3})$	$3.6 \times 10^{6} T^{1.78}$	Just and Rimpel (1972)
	300	0.022	1.1×10^{12}	Ahl and Cool (1973)
	350	0.027	0.9×10^{12}	Ahl and Cool (1973)
Ar	1350-4000	$1.6 \times 10^{-3} \exp(112/T^{1/3})$	$8.5 \times 10^{-4} T^{4.01}$	Bott and Cohen (1973)
	1500-5000	$8.5 \times 10^{-3} \exp(99.47/T^{1/3})$	$0.06 T^{1.41}$	Vasil'ev et al. (1973)
	800-2400	$[90 \exp(-85/T^{1/3}) + 10^{-2}]^{-1}$	$1.7 T^{1.05}$	Blair, Breshears, and Schott (1973)
	350	>4	$< 8 \times 10^{9}$	Airey and Fried (1971)
	295	>22	$< 1.1 \times 10^{9}$	Hinchen (1973a)
	295	>22	1.1×10^{9}	Hancock and Green (1972a)
He	1350-4000	$1.9 \times 10^{-4} \exp(117/T^{1/3})$	$5.5 \times 10^{-3} T^{4.46}$	Bott and Cohen (1973)
	295	>22	$< 1.1 \times 10^{9}$	Hinchen (1973a)
F	1400-4100	$3.4 \times 10^{-5} \exp(64/T^{1/3})$	$3.2 \times 10^{4} T^{2.85}$	Solomon et al. (1973)
	1900-3300	$2.5 \times 10^{-6} T$	3.2×10^{11}	Bott and Cohen (1973b)
	295	0.026	8×10^{12}	Blauer and Solomon (1973)
	1500-2400	$3.9 \times 10^{-4} \exp(46/T^{1/3})$	$6.8 \times 10^{4} T^{2.40}$	Blair, Breshears, and Schott (1973)
	295	0.014	1.7×10^{11}	Quigley and Wolga (1974)
F_2	350	>1	2.5×10^{10}	Airey and Fried (1971)
	350	>11	$< 2 \times 10^{9}$	Fried, Wilson, and Taylor (1973)
H_2	295-610	$5.3 \times 10^{3} T^{-1.28}$	$3.6 \times 10^{4} T^{2.28}$	Bott (1974)
	1400-4000	$.026 \exp(4.4/T^{1/3})$	$4.4 \times 10^{4} T^{2.12}$	Bott and Cohen (1972)

Although the numerical values of the rate coefficient have generally been in agreement, within the experimental uncertainties of the various determinations, the temperature dependencies of the rate coefficient have been noticeably inconsistent. The various results are summarized in Table 1. The rate coefficients calculated from shock-tube data are plotted (Fig. 1); the recombination rate coefficients have been calculated and extrapolated to lower temperatures (Fig. 2). The extent to which the F_2 bond energy exceeds the average experimental activation energy is disconcerting. This discrepancy becomes important when calculating the rate coefficient for F + F recombination from $K_{4,-4}$ and k_4 and extrapolating the results to low temperatures. The problem is compounded by the uncertainty in the bond dissociation energy of F_2.

Although a critical review of the bond strength of F_2 is outside the scope of this report, it is evident that the possible uncertainty in such a fundamental datum leads to ambiguities in several thermochemical and kinetic values important to this study. In 1968, a National Bureau of Standards committee recommended 37.76 kcal/mol for $D^o_{298}(F_2)$; since 1965, the JANAF committee has recommended 37.72 ± 0.8 kcal/mol. (The dissociation energy at 0 K, D^o_0, in either case is 1.0 kcal/mol smaller.) Here, 38 kcal/mol is used; in view of the uncertainties, a third significant figure is unnecessary.

With a value of 38 kcal/mol for $D^o_{298}(F_2)$, all of the shock-tube values for the activation energy of F_2 dissociation in an Ar bath lead to a strongly negative temperature dependence for F-atom recombination, which results in unreasonably large values near 300 K. Therefore, for calculations, we prefer the theoretical value calculated by Shui, Appleton, and Keck (1971). Their results agree numerically with the shock-tube data of Johnson and Britton (1964) but lead to an activation energy of 35.1 kcal/mol and a pre-exponential factor of $10^{13.7}$. Until direct measurements near 300 K are available, $k_4^{Ar} = 10^{13.7} \exp(-35,100/RT)$ is recommended, which implies

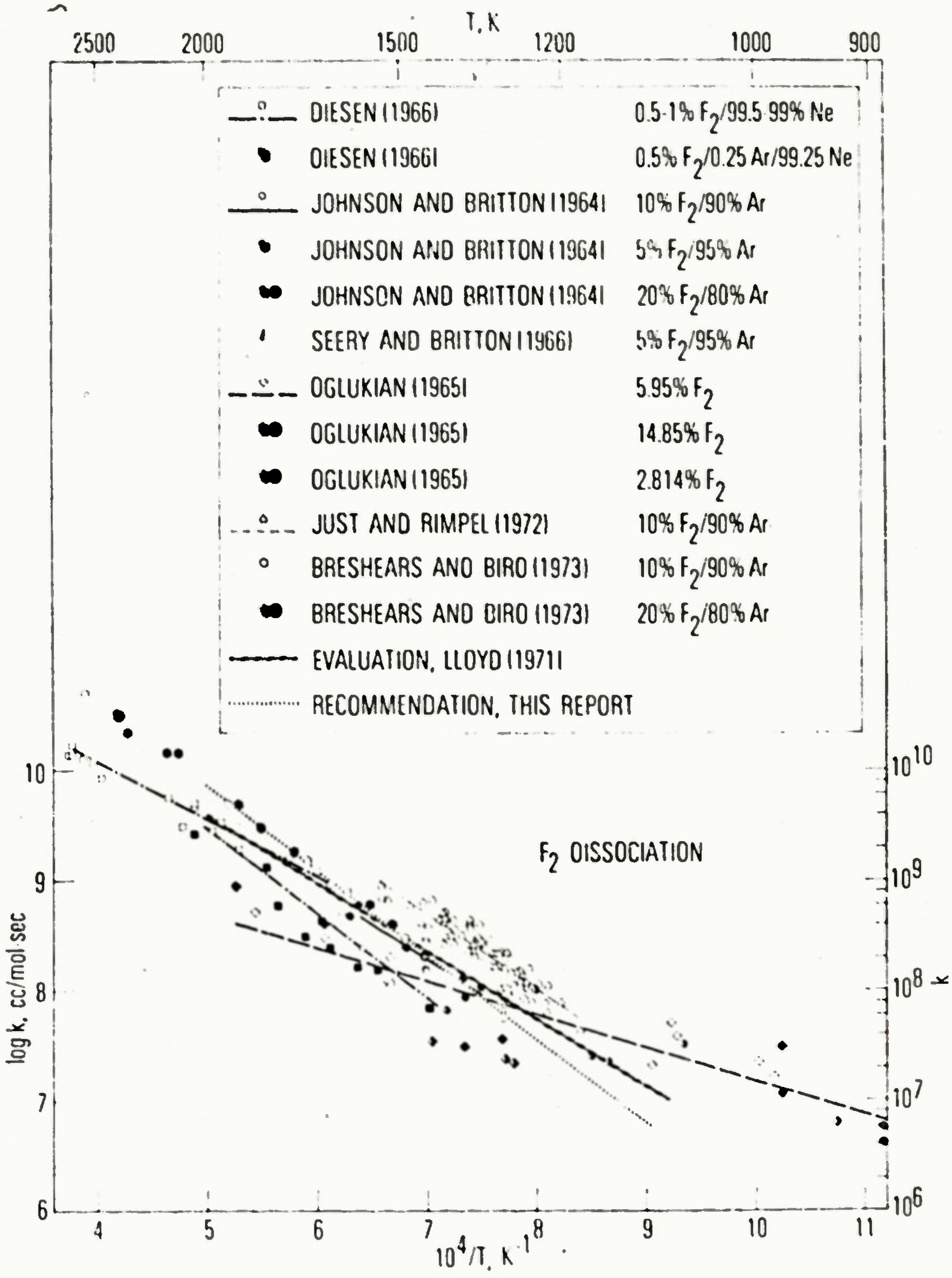

Fig. 1. Experimental Measurements of F_2 Dissociation Rate Coefficient k_1 Versus $10^3/T$

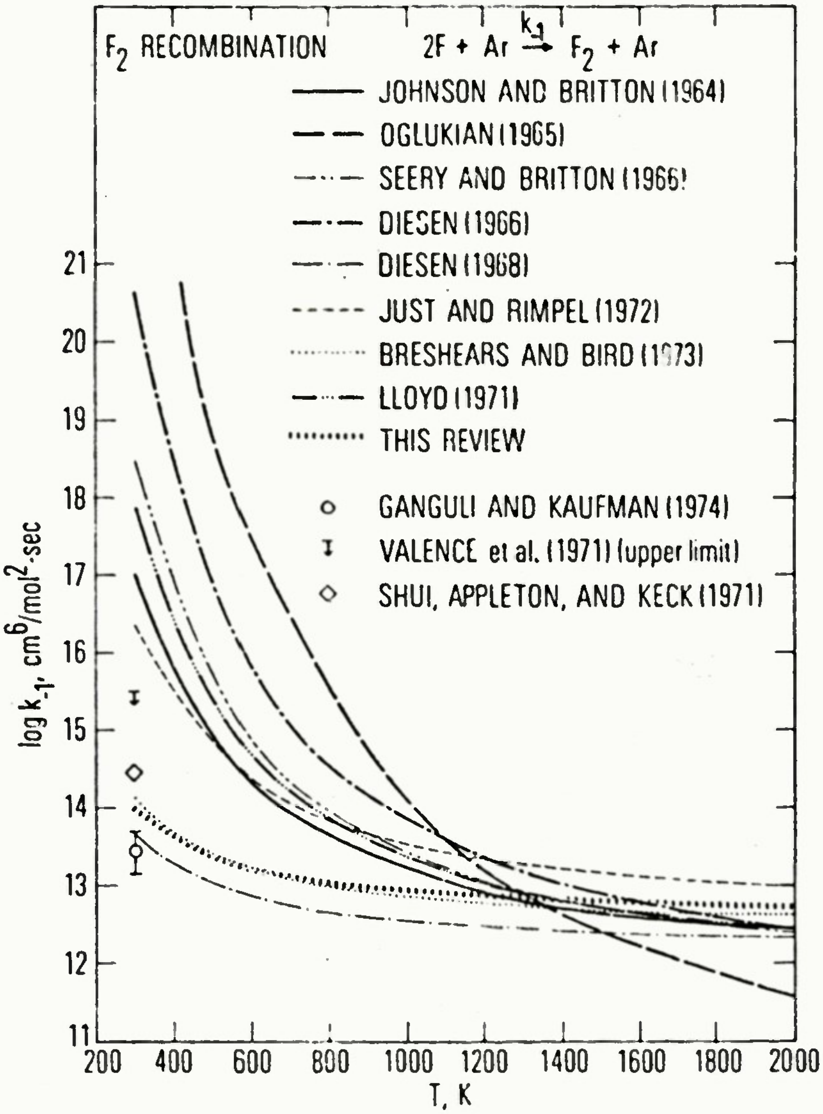

Fig. 2. F + F Recombination Rate Coefficient k_{-1} Computed From k_1 or Measured Directly Versus T

that k_{-4}^{Ar} at 300 K is $10^{14.0}$. A recent report by Ganguli and Kaufman (1974) suggests log $k_{-4}^{Ar} \approx 13.5$ at 300 K, which is smaller than the recommended value for k_{-4} by a factor of ≤3.

As a result of their recent work, Breshears and Bird (1973) have concluded that $k_4^{F_2}/k_4^{Ar}$ is approximately 2.7 in the temperature range 1400 to 2600 K. However, an examination of Fig. 1, in which all the shock-tube dissociation data are plotted, shows that their data are not greatly sensitive to this ratio; therefore, considerable uncertainty must be assigned to this value. Data on the rate of F_2 dissociation with M = H, H_2, or F are not available. From an analogy with the findings in cases of other homonuclear diatomics such as Cl_2, Br_2, H_2, O_2, and N_2, it is expected that F atoms will exhibit a large efficiency relative to Ar; $k_4^F = 10\ k_4^{Ar}$ is assumed in this report.

If it is assumed that the primary recombination mechanism for F atoms is, as is believed to be the case for I atoms, the radical-molecule mechanism

$$F + M \rightarrow FM^*$$

$$FM^* + F \rightarrow F_2 + M$$

then some qualitative statements can be made regarding the relative efficiencies of H and HF as chaperones. For example, H atoms would be expected to be somewhat more efficient than Ar because the strong H-F bond would favor formation of FM*, where M = H. The effect on HF chaperone efficiency would be much less pronounced. Therefore, in this report, it is tentatively assumed that H atoms are three times as efficient as Ar and that HF is equal to Ar in efficiency. Other species are assumed to have the same efficiency as Ar.

Figure 2 is significant in demonstrating that a relatively small discrepancy in k at shock-tube temperatures can lead to an unacceptably large divergence of extrapolated values at room temperature. When the uncertainty in the F_2 bond dissociation energy (and, therefore, the equilibrium constant) is taken into account, the necessity for a reliable direct measurement at 300 K becomes apparent. For the present, however, it must be accepted that the room-temperature recombination rate is uncertain by at least an order of magnitude.

C. HF DISSOCIATION

The rate of HF dissociation

$$HF + M \rightarrow H + F + M \qquad (3)$$

was first measured by Jacobs, Giedt, and Cohen (1965) in the shock tube at temperatures of 3800 to 5300 K. They reported a rate coefficient for Ar as chaperone in two forms: $k_3^{Ar} = 10^{19.05}T^{-1}\exp(-D_o/RT)$ or $k_3^{Ar} = 10^{22.71}T^{-2}\exp(-D_o/RT)$, where D_o, the dissociation energy at 0 K from v = 0, is currently taken as 135.1 kcal/mol. (At the time of their study, a slightly smaller value of 134.1 kcal/mol was accepted.) Subsequently, Blauer (1968) performed similar shock-tube experiments over the temperature range 3700 to 6100 K and obtained a rate coefficient smaller by about a factor of 2, with a pre-exponential factor of $10^{18.67}T^{-1}$. The two studies were reviewed by Brown (NBS Report No. 10-635), who concluded that there was no basis for preferring one result to the other. Brown assembled all the data of both studies in one plot (Fig. 3).

Because of advances in the knowledge of related rate coefficients, it is worthwhile to re-examine the data of Jacobs, Giedt, and Cohen (1967) to determine if their conclusions are still valid. They deduced the value of k_3 by computer modeling the profile of $(HF)/(HF)_o$, where the denominator is the initial HF concentration. Although their model included all five reactions occurring in the system, i.e., HF dissociation-recombination, H_2 dissociation-recombination, F_2 dissociation-recombination, H + HF, and

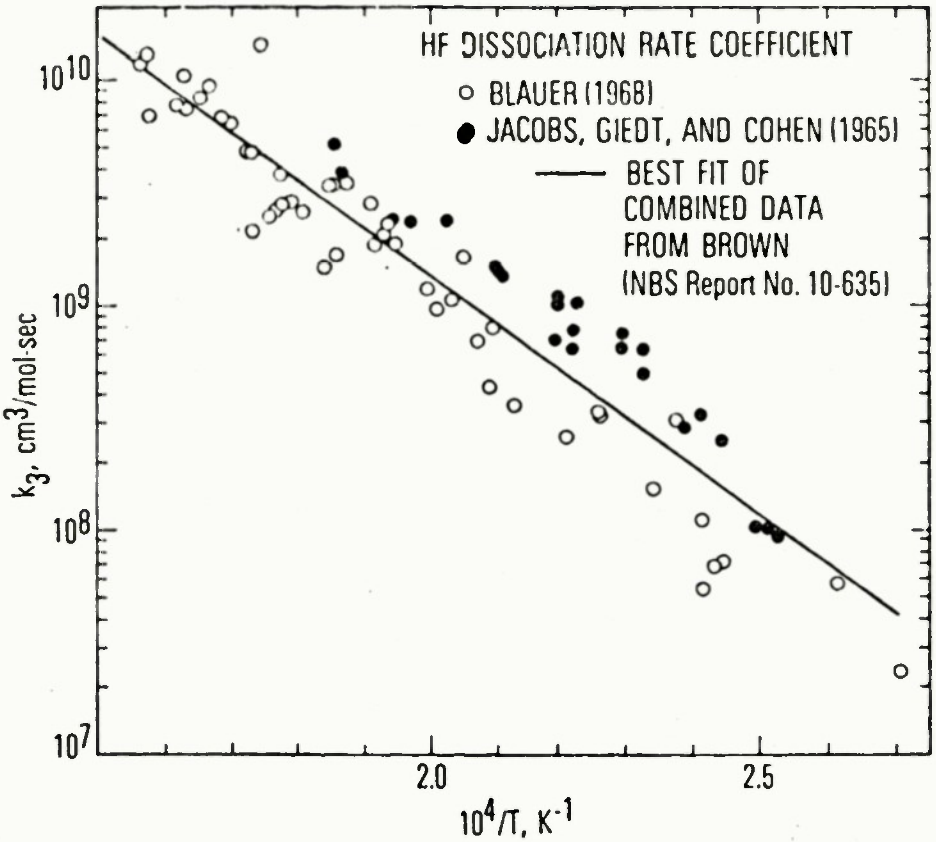

Fig. 3. Experimental Measurements of HF Dissociation Rate Coefficient k_3 Versus $10^3/T$

F + HF, they found that two of the five reactions did not contribute measurably to the overall kinetics and could be ignored. The system of significant reactions, therefore, consists of

$$HF + M_{3,i} \rightleftharpoons H + F + M_{3,i} \qquad (3\text{-}i)$$

$$H + HF \rightleftharpoons H_2 + F \qquad (4)$$

$$H_2 + M_{1,i} \rightleftharpoons H + H + M_{1,i} \qquad (1\text{-}i)$$

Reaction (1) was considered as three separate processes, (1a), (1b), and (1c), as defined earlier, where a, b, and c represent, respectively, M = Ar, H_2, and H. M_3 was assumed to be a weighted average over all species present because no experimental basis was found for assigning different efficiencies to the different species (principally Ar and HF). The value they used for k_4 was 10^{13} exp(-35000/RT), which with currently accepted thermochemical values, implies a value for the reverse rate coefficient, k_{-4}, of $5.5 \times 10^{14} T^{-0.473}$ exp(-6490/RT). At present, the most probable value for k_{-4} is 1.6×10^{14} exp(-1600/RT) (Section II), which yields a value at 4000 K that is 27.5 times larger than that used by Jacobs, Giedt, and Cohen (1967), and at 300 K, it is $10^{5.36}$ times as large.

For k_{1a}, Jacobs, Giedt, and Cohen (1967) used $10^{18.3}T^{-1}$, which is about twice as large as the current best estimate, as discussed earlier. Furthermore, since they scaled k_{1b} and k_{1c} relative to k_{1a} (they used $k_{1b} = 2.47\, k_{1a}$, $k_{1c} = 10k_{1a}$), these rate coefficients are also subject to revision. Current best estimates put k_{1b} at approximately 2.5 k_{1a} and $k_{1c} \cong 20\, k_{1a}$. Thus, their k_{1b} should be decreased by a factor of 2, but their k_{1c} is correct. When these revisions were made in the values for k_1 and k_4 and the computer profiles rerun, the agreement with the experimental profiles was not quite as good. Several variations in k_3 were tried, but none was found that gave as good agreement with the data throughout the temperature range as did the earlier set of rate coefficients. However, the best overall fit is obtained with $k_3^{HF} = 8 \times 10^{17} T^{-1} \exp(-111{,}000/RT)$ cc/mol-sec, which is about 30% larger than the previous value of k_3^{HF} at 4000 K and about 30% smaller at 5000 K. However, because of the larger deviations between this revised rate coefficient and the experimental data, there is some doubt that this expression is more useful than the previous one when extrapolated into the regime of lower temperatures, which is of greater interest. The large discrepancy between this revised apparent activation energy of 111 kcal/mol and the HF bond energy will lead to unreasonably large dissociation rates near room temperature. (This problem was discussed in connection with F_2 dissociation in Section I. B.) Therefore, for the present, the earlier value obtained by Jacobs, Giedt, and Cohen (1967) is recommended because of its greater use at low temperatures.

III. PUMPING REACTIONS

A. $F + H_2 \rightarrow HF + H$

1. OVERALL REACTION RATE

Until recently, there have been few reports of direct experimental measurements of F-atom reactions, partly because of the handling difficulties, and partly because of the complications resulting from the presence of molecular F_2 in most cases. Experimental studies of the $F + H_2$ reaction fall into three categories: (a) direct, absolute rate measurements; (b) relative, competitive fluorination measurements; and (c) complex systems in which the rate coefficient is inferred by detail modeling.

a. Direct, Absolute Measurements

Five separate studies fall into this category. In the earliest, Homann et al. (1970) produced F atoms in a flow system by the reaction $N + NF_2 \rightarrow N_2 + 2F$ and then introduced H_2 downstream. In some experiments, the disappearance of F atoms was monitored by titration with ClNO; in others, the appearance of HF was followed with mass spectrometry. From measurements at 400, 360, and 300 K, an Arrhenius expression of $k_4 = 1.6 \times 10^{14} \exp(-1600/RT)$ cc/mol-sec was obtained with a room-temperature value of 1.1×10^{13}. There are a few questionable aspects to this procedure. The possible disadvantages of the ClNO titration technique have been discussed by Clyne, McKenney, and Walker (1973). Another question concerns the effect of excess N atoms of NF_2 radicals if the titration reaction producing F atoms is not carried out under stoichiometric conditions. If NF_2 is present in excess, it is possible that H atoms produced in Reaction (4) could react with NF_2, increasing the yield of HF. Since this process is probably fast compared to Reaction (4), the calculated k_4 would then be too large by a factor of up to 2. (The possibility that $N + NF_2$ reacts to give 2NF, which, in turn, produce $N_2 + 2F$, should not be discounted, because it would lead to kinetic complications if the reaction between N and NF_2 is not carried out stoichiometrically.)

Dodonov et al. (1971) studied the reaction in a fast flow of He, with F atoms produced by a high-frequency discharge through F_2. H_2, diluted with He, was added downstream, and the reaction system was probed by a mass spectrometer. They observed nearly complete disappearance of F_2 when the discharge was turned on, with roughly comparable concentrations of F atoms and SiF_4 (from reaction with the glass walls) being formed. If the reaction rate of H atoms with SiF_4 is negligible at room temperature, which it probably is, then these experiments give a good measure of the value of k_4, for which Dodonov et al. (1971) obtained 1.8×10^{13} at 293 K, with an estimated uncertainty of 33%, largely resulting from uncertainty in the F atom concentration measurement.

Clyne, McKenney, and Walker (1973) produced F atoms in a microwave discharge through flowing CF_4 and He and reacted the mixture with H_2. The F-atom concentration was monitored by titration with Cl_2; the H_2 concentration was followed by mass spectrometry. The rate coefficient at 298 K was 1.5×10^{13} cc/mol-sec, with 50% uncertainty because of considerable experimental scatter. In the same system, they measured the rate of F + CH_4, which is of interest in connection with the competitive F + H_2 measurements to be discussed later, and obtained 3.6×10^{13}, with even larger scatter.

Kompa and Wanner (1972) produced F atoms by the flash photolysis of WF_6 at 298 K in the presence of H_2 in a stationary laser cavity. The reaction rate coefficient was deduced by monitoring the decay of chemiluminescence from vibrationally excited HF. This technique requires the minimization of the vibrational-relaxation process and of the secondary reaction of H or H_2 with WF_x, the decomposition products from WF_6. The first of these requirements can be met by operating at sufficiently low pressures; the limitation on pressure then becomes the sensitivity of the optical detection system. The rate coefficient obtained was 3.8×10^{13} cc/mol-sec. In the same system, the rate coefficient for F + CH_4 was measured to be 4.3×10^{13}. A second possible complication is not so easily disposed of. Kompa and Wanner (1972) operated at reactant pressures of 0.25 Torr each of WF_6 and H_2 (or CH_4).

With a 0.5% photolysis assumed, the H atoms produced in Reaction (4) would react with WF_6 rather than combine by a three-body process if $k_{H+WF_6} \cong 10^9$ cc/mol-sec, i.e., if the activation energy is less than approximately 7 kcal/mol. For reaction with WF_5, the rate coefficient would have to be approximately 100 times larger or more, since $[WF_5]/[WF_6] \leq 0.01$. If either of these processes is significant, then the calculated rate coefficient for the $F + H_2$ reaction could be too large by as much as a factor of 2, which is very possible although the reactions of H with WF_6 and WF_5 have not been studied. Also, Igoshin, Kulakov, and Nikitin (1974) have pointed out the possibility that some F atoms in the above work were translationally hot because of the low total pressures, also resulting in a spuriously high value for k_4. Information is not available to evaluate quantitatively the extent to which this might occur. However, a comparison of the average bond strength in WF_6 (121 kcal/mol) with the peak in the WF_6 absorption spectrum [near 1800 Å, according to Kompa and Wanner (1972)] suggests that the F atoms formed in the photolytic act could easily have 30 kcal/mol excess translational energy, which they cannot lose before collision with H_2 (since collision with WF_6 will not remove significant translational energy). This excess of translational energy could be the most serious flaw in the experiment.

Hon, Axworthy, and Schneider (1973) studied the reaction of F atoms with a variety of potential laser system fuels, including H_2 and CH_4. Rate coefficients were obtained in a flow system with F atoms produced by thermal dissociation of F_2 and monitored by esr. The rate of reaction of F with H_2 at 298 K was found to be 1×10^{13} cc/mol-sec; that with CH_4 was 2.6×10^{13}.

The five determinations, thus, range from 1 to 4.3×10^{13} cc/mol-sec and are listed in Table 2. At present, the value of Clyne (1973) seems to be most reliable, in spite of the large uncertainty the authors place on their result. Thus, a value of $k_4 = 1.5 \times 10^{13}$ cc/mol-sec is suggested by the four direct absolute measurements.

b. Competitive Studies

The first relative measurements were made by Mercer and Pritchard (1959). In a thermal reactor over the temperature range 298 to 423 K, they

Table 2. Absolute Measurements of $F + H_2 \xrightarrow{k_4} HF + H$

T, K	$k_4 = A \exp(-E/RT)$		log k_4 (300 K)	Technique		Reference
	A, cc/mol-sec	E, cal/mol		F Source	Detection	
300-400	1.6×10^{14}	1600	13.04	$N + NF_2$ Reaction	[HF] by mass spectroscopy or [F] by ClNO titration	Homann et al. (1970)
293	-	-	13.25	Discharge through F_2	Mass spectroscopy	Dodonov et al. (1971)
298?	-	-	13.58	Flash photolysis of WF_6	HF(v) chemiluminescence	Kompa and Wanner (1972)
298	-	-	13.0	Thermal dissociation of F_2	[F] by esr	Hon, Axworthy, and Schneider (1973)
298	-	-	13.18	Discharge through CF_4	[F] by ClNO titration; [H_2] by mass spectroscopy	Clyne, McKenney, and Walker (1973)

studied the competition between H_2 and CH_4 for F atoms initiated by the photolysis of F_2. The consumption of reactants was monitored by mass spectrometry. The results, together with the other competitive measurements, are shown in Table 3. The results of competitive studies in Fig. 4 were calculated with the value for F + CH_4 recommended by Fettis and Knox (1964) assumed.

Kapralova, Margolin, and Chaikin (1970) studied the competitive fluorination between CH_4 and D_2 and between H_2 and D_2 in spherical heated flasks, diluted with He; the products HF and DF were analyzed by esr. The studies were conducted at 77, 173, and 293 K for CH_4 and D_2 and 223, 253, 293, and 353 K for H_2 and D_2. The D_2/CH_4 data are reasonable, but the D_2/H_2 data deviate considerably from an Arrhenius plot at 77 K, at which temperature their deduced rate coefficients are about the same as at 173 K. Furthermore, their 173 K result differs from the same ratio measured by Persky (1973) by almost a factor of 2. Only the room-temperature measurement appears to be reliable. If this result is combined with their D_2/CH_4 expression, a value for the ratio of k_{F+H_2}/k_{F+CH_4} is obtained. In Fig. 4, both their deduced rate coefficient and the result of ignoring the low-temperature data are given.

Foon and Reid (1971) conducted an extensive series of competitive fluorination measurements with H_2 and a variety of hydrocarbons. They used a packed, heated vessel to measure the consumption of reactants by gas chromatography. They found that no photo-initiation was required, the F atoms being produced in sufficient quantities by the equilibrium dissociation of F_2. They measured the rate of reaction with H_2 relative to CH_4 and C_2H_6 in separate experiments. A third measurement of the relative rates with CH_4 and C_2H_6 provided an additional check on the internal consistency of the measurements. However, in spite of the internal agreement demonstrated, it is not obvious how the complication of chain reaction (H + F_2) is avoided.

Jonathan et al. (1971c) produced F atoms by a discharge through CF_4, then observed the infrared chemiluminescence from vibrationally excited HF

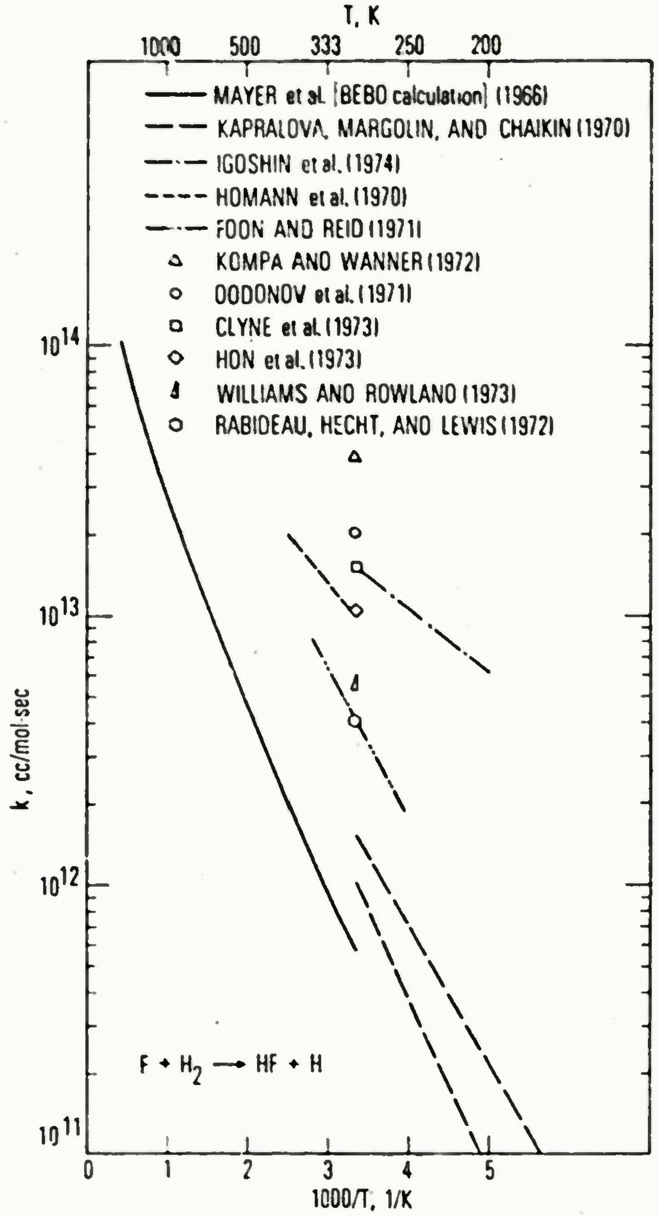

Fig. 4. Rate Coefficient k_7 for $F + H_2 \rightarrow HF + H$ Versus $10^3/T$

Table 3. Relative Measurements of $F + H_2 \xrightarrow{k_4} HF + H$

T, K	Relative to Reaction with X	$\frac{k_{H_2}}{k_{CH_4}}$	$\frac{k_{H_2}}{k_{CH_4}}$ at 300 K	Technique		Reference
				F Source	Detection	
298-423	CH_4	0.95 exp(-500/RT)	0.41	F_2 thermal reactor	$[H_2]$, $[CH_4]$ by mass spectroscopy	Mercer and Pritchard (1959)
173-293	D_2; D_2 relative to CH_4	0.7 exp(-1080/RT)[a]	0.146	No direct initiation	[HF], [DF] by esr	Kapralova, Margolin, and Chaikin (1970)
253-348 273-343	CH_4, C_2H_6	1.2 exp(-630/RT)	0.42	No direct initiation	$[H_2]$, $[CH_4]$ by mass spectroscopy	Foon and Reid (1971)
300	CH_4	-	0.74	Discharge through CF_4	HF chemi-luminescence	Jonathan et al. (1971c)
~300	C_2H_2, CH_4 relative to C_2H_2	-	0.34	Nuclear reaction	Products by gas chromatography; [HF] by loss of $[CH_2 CHF]$	Williams and Rowland (1971, 1973)

[a] Ignores data at 77 K.

produced by reaction with various reagents, including H_2 and CH_4. From the relative intensities, they deduced relative F-atom rate coefficients.

Williams and Rowland (1973) formed ^{18}F by nuclear reaction; the translationally hot atoms were moderated by collisional deactivation, then allowed to react with pairs of reactants, one of which was always C_2H_2. Products were analyzed by radio gas chromatography. However, concentrations were never measured directly, but only inferred from the diminution in CH_2CHF yield.

Results of the above competitive studies are listed in Table 3. From Tables 2 and 4 can be calculated k_{F+H_2}/k_{F+CH_4} from those studies in which the two reactions were studied separately. With the exception of the result of Kapralova, Margolin, and Chaikin (1970), the various values for k_{F+H_2}/k_{F+CH_4} fall between 0.34 and 0.88 at room temperature. A possible explanation for the high value obtained by Kompa and Wanner (1972) has already been discussed. The best value for the ratio is probably 0.6 ± 0.2.

Measurements of the $F + CH_4$ reaction rate coefficient are given in Table 4. The absolute studies of Kompa and Wanner (1972); Hon, Axworthy, and Schneider (1973); and Clyne, McKenney, and Walker (1973) have already been discussed, as has the relative measurement of Foon and Reid (1971). Foon and Reid studied relative fluorination rates for several pairs of hydrocarbons, ultimately relying on the assumed rate coefficient for the $F + C_4H_{10}$ reaction arrived at by Fettis and Knox (1969) after a careful review of all the data available at that time. Foon and Reid's (1971) CH_4 rate coefficient is about 60% smaller than the value recommended by Fettis and Knox (1969). However, both of these values depend on the assumption that the activation energy for F + higher hydrocarbons is 0, whereas the number actually may be slightly negative. If it is negative by a few hundred calories, then the calculated value for k_{F+CH_4} would be larger than is generally quoted, placing the results of Fettis and Knox (1969) and of Foon and Reid (1971) in better agreement with the other values in Table 4.

One other absolute measurement of $F + CH_4$ has been reported by Wagner, Warnatz, and Zetzsch (1971). They produced F atoms by the reaction

Table 4. Reaction Rate Coefficient for $F + CH_4 \rightarrow HF + CH_3$

T, K	k, cc/mol-sec	Source of F Atoms	Technique	Reference
298?	$\geq 6 \times 10^{13}$	$F_2 + NO$	Relative to $F + NO + M \rightarrow FNO^* + M$	Pollack and Jones (1973)
298	4.8×10^{13}	$N + NF_2$ (no F_2 present	Absolute measurement; mass spectroscopy, flow	Wagner, Warnatz, and Zetzsch (1971)
298?	4.3×10^{13}	Flash photolysis of WF_6	Absolute measurement; HF^* chemiluminescence monitored	Kompa and Wanner (1972)
298	1×10^{13}[a]	No direct initiation	Relative to CH_3Cl, relative to C_4H_{10}; gas chromatography of products	Foon and Reid (1971)
298	2.6×10^{13}[b]	Thermal dissociation of F_2	F atoms monitored by esr; absolute measurement	Hon, Axworthy, and Schneider (1973)
298	3.6×10^{13}	Discharge through CF_4	[F] by ClNO titration	Clyne, McKenney, and Walker (1973)

[a] This value is six times larger than Foon and Reid reported, because they inadvertently took the A factor for the standard reaction of $F + C_2H_6$ to be 1×10^{13} (the A factor per H atom) rather than 6×10^{13} cc/mole-sec. However, it has been suggested [see D. G. Truhlar, J. Chem. Phys. 56, 3189 (1972) and J. T. Muckerman and M. D. Newton, ibid., 3191] that the latter value is too large by a factor of 2 to 3.

[b] An alternative value of 3.2×10^{13}, depending on the method of analysis, was also reported.

of N + NF_2 in the same apparatus used by Homann et al. (1970) for the study of the F + H_2 reaction. Their result of 4.9 × 10^{13} cc/mol-sec is about 15% larger than that of Kompa and Wanner (1972).

The measurement of Pollack and Jones (1973), which is somewhat larger than any of the others (Table 5), was made relative to the rate of the reaction of $F + NO + M = FNO^* + M$, a reaction that does not seem to be sufficiently well understood at present to serve as a calibration standard for kinetics measurements. Thus, the best value for the F + CH_4 reaction rate coefficient at room temperature is probably 4 ± 1 × 10^{13} cc/mol-sec, making the best estimate of k_4 2.6 ± 1.4 × 10^{13}, slightly larger than the results of the direct study.

c. Complex Systems

Almost a decade ago, Levy and Copelend (1965) attempted to deduce the value of k_4 from the inhibiting effect of oxygen on the reaction of H_2 with F_2. They believed the inhibition was due to one of two reactions, either

$$H + O_2 + M \rightarrow HO_2 + M$$

in competition with the chain propagation step

$$H + F_2 \rightarrow HF + F \qquad (5)$$

or by the analogous

$$F + O_2 + M \rightarrow FO_2 + M$$

competing with Reaction (4). Assuming the oxygen reacted with H atoms, they deduced an activation energy for Reaction (4) of 5 to 7 kcal/mol. On the other hand, the assumption that inhibition occurred by the reaction with F atoms implied an activation energy for Reaction (5) of 5 to 7 kcal/mol. They concluded, on the basis of comparison with analogous reactions with known activation energies, that 5 to 7 kcal/mol was too large for Reaction (5), but reactions of other similar atoms and radicals, i.e., H, D, and CH, with H_2 had activation energies in the range of 5 to 10 kcal/mol. They concluded, therefore, that inhibition was by reaction with F atoms, and Reaction (4) had an activation energy of 7 kcal/mol with a pre-exponential factor of 10^{12} cc/mol-sec assumed. These calculations were made by taking the reaction rate coefficient for $H + O_2 + M$ to be $10^{14.1}$ cc^2/mol-sec, and that for $F + O_2 + M$ to be the same. However, since they performed their work, more recent experiments indicate that the rate coefficient for $H + O_2 + M$ is about 50 times larger than was accepted at the time of Levy and Copeland's (1965) work. Therefore, if the competition is for H or F atoms, the activation energy for Reaction (5) or (4) would be 1.8 to 3.7 kcal/mol. Since this is reasonable for the $H + F_2$ reaction, there is no need to postulate the otherwise unknown reaction of $F + O_2 + M$. Therefore, Levy and Copeland's (1965) work should not be taken as suggesting anything about the activation energy of Reaction (4). Later (Levy and Copeland, 1968), they rejected this conclusion on other grounds.

Rabideau, Hecht, and Lewis (1972) used a microwave discharge to dissociate H_2 in a teflon-coated flow system, obtaining about 66% dissociation. The $H + H_2$, in a He carrier, was mixed with a stream of F_2, and the reaction was monitored by measuring the H and F atoms by esr spectroscopy. Since it was recognized that both reactions, $F + H_2$ and $H + F_2$, were occurring, a computer program was used to simulate the observed atom profiles and thereby deduce reaction rate coefficients. At room temperature, best results were obtained by the assumption that $k_4 = 4$ [illegible] 1×10^{12} and $k_5 = 2.5 \pm 0.2 \times 10^{12}$ cc/mol-sec. This result for k_4 agrees well with those of Foon and Reid (1971) and of Williams and Rowland (1973) but is a factor of 2.5 to 10 lower than most of the other determinations. Rabideau, Hecht, and Lewis (1972) gave no indication of the sensitivity of their result for k_4 to changes in their result for k_5; obviously, a decrease in one of these rate coefficients would induce an increase in the calculated value for the other.

Igoshin, Kulakov, and Nikitin (1974) determined k_4 from the stimulated emission of HF molecules formed by the electric-discharge-initiated reaction between H_2 and NF_3 in a laser cavity at 195 and 293 K. A computer model, which took into account initiation, vibrational energy transfer, spontaneous and stimulated emission, and wall deactivation, was used to match the power output from the lasing medium. The accuracy of this technique must depend on the values assumed for the other reaction rate coefficients; however, Igoshin, Kulakov, and Nikitin (1974) do not give detailed values for individual rate processes, making it difficult to assess the validity of the calculations. From their two temperature determinations, they calculated an Arrhenius expression of $k_4 = 9.3 \times 10^{13} \exp[-(1080 \pm 170)/RT]$ cc/mol-sec. Their room-temperature rate is 2×10^{13} cc/mol-sec, almost a factor of 2 smaller than that of Kompa and Wanner (1972), the largest value reported. Igoshin, Kulakov, and Nikitin (1974) separately determined the rate coefficient for the $F + D_2$ reaction, which provides an independent check on the reliability of their method. They obtained, for k_{F+D_2}, $4.9 \times 10^{13} \exp[-(790 \pm 180)/RT]$ cc/mol-sec, giving $k_{H_2}/k_{D_2} = 1.88 \exp(-290/RT)$. Two recent direct experimental measurements of this ratio give values very close to $1.06 \exp(360/RT)$ or 1.94 at 300 K. The value deduced by Igoshin, Kulakov, and Nikitin (1974) disagrees with these more reliable results by approximately a factor of 2.

d. Theoretical Calculations

Wilkins (1971 and 1972); Jaffe and Anderson (1971); Jaffe, Henry, and Anderson (1973); and Muckerman (1971, 1972a, 1972b) have reported the results of high-speed, computer-generated trajectory calculations of the overall rate coefficient for Reaction (4); however, these results depend sensitively on the parameters of the potential energy surface used, and since there are as yet no precise a priori methods for generating such surfaces, the technique is of little value in generating independent Arrhenius factors for k_4. For determining rate coefficients for the production of individual vibrational-rotational energy states of product molecules or for examining the effect of excess reagent internal energy, however, such techniques do provide rough information that might not be available otherwise. Such work is discussed in more detail later in this review. Before the machine calculations were made, several estimates and calculations of k_4 were published. Only the BEBO calculations of Mayer, Schieler, and Johnston (1966) and Mayer and Schieler (1968) are of interest here. They predicted a room-temperature value for k_4 of about 6×10^{11}, over an order of magnitude smaller than the average experimental value.

Two other theoretical studies are of some interest. Tully (1974) studied the role of spin-orbit effects on Reaction (4). He found $F(^2P_{1/2})$ to react almost an order of magnitude slower with H_2 than the ground state $F(^2P_{3/2})$. Klein and Persky (1974) studied the reaction with para-enriched H_2 and concluded that the rotational excitation of the H_2 molecules slows the reaction, but the effect is small, and important only at very low temperatures.

e. Conclusions

The five direct, absolute measurements suggest a room temperature value for k_4 of $1.5 \pm 0.5 \times 10^{13}$ cc/mol-sec. Only one, that of Homann et al. (1970), was obtained for a range of temperatures, making it possible to calculate an activation energy for the reaction. The room-temperature value of Homann et al. (1970) is 1.0×10^{13}; the competitive studies, together with an evaluation of the $F + CH_4$ rate coefficient, suggests a slightly larger value of k_4, but with correspondingly larger uncertainty. A brief analysis of the technique of Homann et al. (1970) suggests only possible errors that would have led them to deduce too large and not too small a value of k_4.

2. VIBRATIONAL PRODUCT DISTRIBUTION

Three laboratories have studied the product distribution of Reaction (4). Pimentel and his coworkers [Kompa and Pimentel (1966), Parker and Pimentel (1969), Krogh and Pimentel (1972)] examined the reaction by measuring gains of appropriate spectral lines in a chemical laser. Polanyi and coworkers [Polanyi and Tardy (1969), Anlauf et al. (1970), Polanyi and Woodall (1972)] and Jonathan et al. (1971c) used a discharge flow system and made measurements in a nonlasing medium. The various results are given in

Table 5. The three groups have converged on the value $k_4(v = 1)/k_4(v = 2) = 0.3$. The two groups that have measured $k_4(v = 3)$ and $k_4(v = 2)$ now substantially agree as well with the probable value for the ratio of 0.48 to 0.5. There is one recent report on the experimentally measured temperature dependence of the relative pumping rates. Coombe and Pimentel (1973), using laser techniques, found $k_4(v = 2)/k_4(v = 1) = 2.14 \exp(254/RT)$ and $k_4(v = 3)/k_4(v = 2) = 0.39 \exp(117/RT)$.

Because HF concentrations are determined by emission measurements, the formation rate of HF($v = 0$) has not been ascertained in any of the experiments. Recent Monte Carlo computer calculations by Wilkins (1972)(Fig. 5) are of interest. His results suggest that $k_4(v = 0) = 0$ and that the activation energies for $v = 1$, 2, and 3, are, respectively, 1.5, 1.23, and 1.25 kcal/mol, implying a difference in activation energies between $k_4(2)$ and $k_4(1)$ of 270 cal/mol, which agrees with experiment. Since the differences in activation energies are rather slight, we prefer at this time to assume, for computational convenience, the same temperature dependence for each of the k so that each $k_4(v)$ can be expressed as $\underline{f}(v)k_{4(\mathrm{total})}$, where $\underline{f}$ is temperature independent. We accept Wilkins' (1972) result that negligible pumping into the zeroth vibrational level takes place.

Recently, Coombe and Pimentel (1973b) reported the effect of H_2 rotational energy on the vibrational energy distribution in reaction. They found a greater tendency to inversion, especially on the 2 → 1 transition when the H_2 was para-enriched (85% para).

Anderson (1970) published in brief the results of a classical trajectory study of the reaction between H and HF(v) for $v = 0 \ldots 5$, showing the threshold translational energy required for reaction. Wilkins (1973b), with a Monte Carlo computer technique, calculated the rates for reactions of the form $H + HF(v) \rightarrow F + H_2(v')$ for $v = 3$, 4, 5, 6 and $v' = 0$, 1, 2. His results suggest

Table 5. Relative Pumping Rates for $F + H_2 \xrightarrow{k_4(v)} HF(v) + H$

$k_4(v)$ (300 K)				Technique	Reference
v = 0	v = 1	v = 2	v = 3		
--	1.5	1	--	Laser experiment	Kompa and Pimentel (1968)
--	0.18	1	<1.33	Laser experiment (T = 539 K)	Parker and Pimentel (1969)
--	~0.3	1	--	Laser experiment	Krogh and Pimentel (1972)
--	$\lesssim$0.29	1	$\gtrsim$0.47	Discharge flow	Polanyi and Tardy (1969)
--	0.31	1	0.48	Discharge flow	Anlauf et al. (1970)
--	0.31	1	0.47	Discharge flow	Polanyi and Woodall (1972)
--	0.29	1	0.76	Discharge flow	Jonathan, Melliar-Smith, and Slater (1971)
--	0.30	1	0.5	Discharge flow	Jonathan et al. (1971c)
~0	0.15	1	0.49	Semi-empirical calculation/Monte Carlo	Wilkins (1972)
0	0.53	1	0.18	Semi-classical calculation/Monte Carlo	Jaffe and Anderson (1972)
0	1.28	1	0.0023	Variational theory/ Monte Carlo	Jaffe, Henry and Anderson (1973)

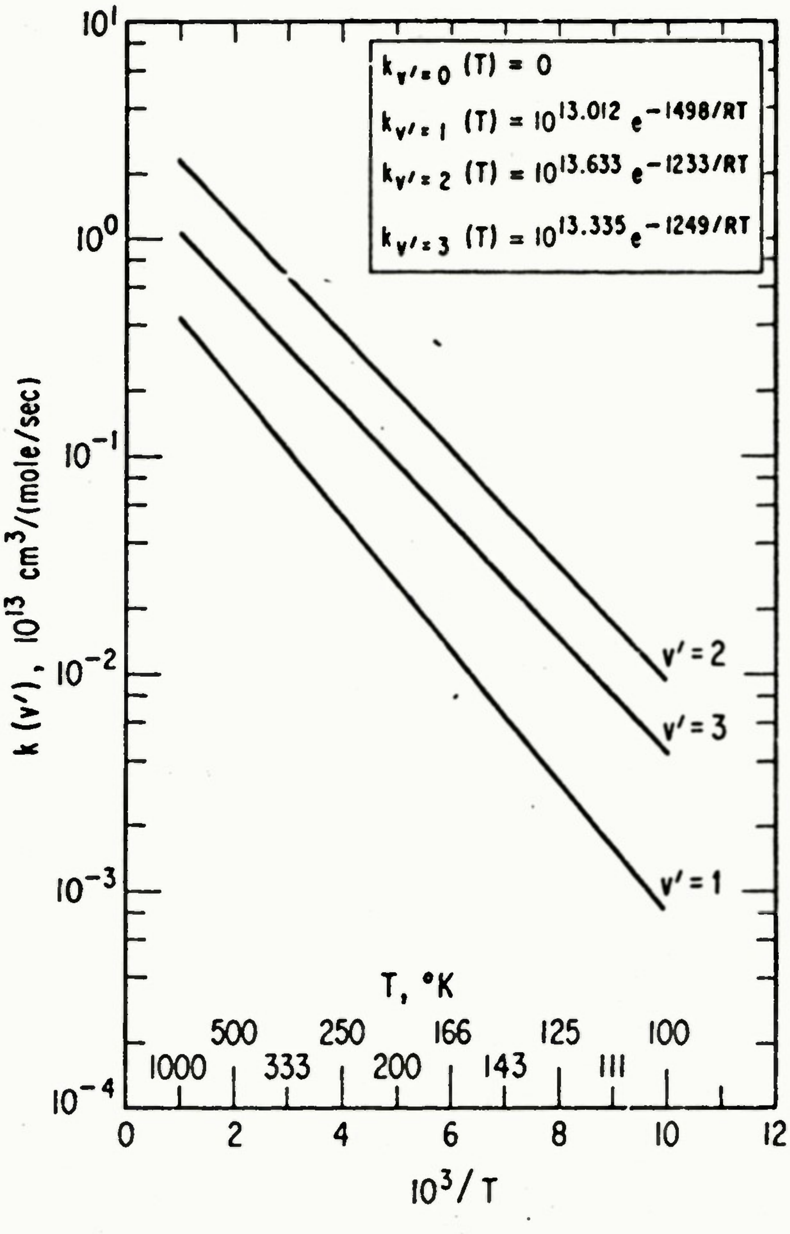

Fig. 5. Values of $k_4(v)$ Versus $10^3/T$ for $F + H_2 \rightarrow HF(v) + H$ for Various v as Computed by Wilkins

that all of these reactions proceed with activation energies of approximately 500 to 600 cal/mol and that at high temperatures total probability for reaction of a given v into all possible v' is about 0.1 to 0.2; the rate coefficients are tabulated in Table 6. The results can be simplified and summarized approximately (within 20 to 30%) by the following expressions for various $k_{-4}(v, v')$.

$$k_{-4}(6, v') = f_6(v')\,(1.9 \times 10^{13})\,\exp(-580/RT)$$

$$f_6(0) = 0.22,\ f_6(1) = 0.22,\ f_6(2) = 0.56$$

$$k_{-4}(5, v') = f_5(v')\,(1.1 \times 10^{13})\,\exp(-510/RT)$$

$$f_5(0) = 0.36,\ f_5(1) = 0.64,\ f_5(2) = 0$$

$$k_{-4}(4, v') = f_4(v')\,(7.4 \times 10^{12})\,\exp(-460/RT)$$

$$f_4(0) = 0.5,\ f_4(1) = 0.5,\ f_4(2) = 0$$

$$k_{-4}(3, v') = f_3(v')\,(1.62 \times 10^{13}\,T^{-0.01})\,\exp(-835/RT)$$

$$f_3(0) = 1$$

B. $H + F_2 \rightarrow HF + F$

In comparison with the previous reaction, experimental work on the reaction

$$H + F_2 \rightarrow HF + F \tag{5}$$

has been meager. The data for k_5, both experimental and theoretical, are tabulated in Table 7. There has been only one experimental determination of k_5 over a temperature range sufficient to permit calculation of Arrhenius rate parameters. Albright et al. (1969) obtained a value of $k_5 = 1.2 \times 10^{14}$

Table 6. Computed Rate Coefficients for $H + HF(v) \xrightarrow{k_{-f}(v, v')} H_2(v') + F$[a]

v	v'	$k = AT^n e^{-E/RT}$		
		log A	n	E, cal/mol
6	0	12.66	-0.03	570
	1	12.41	0.085	540
	2	13.02	0.01	565
5	0	12.54	0.015	510
	1	12.92	-0.005	575
4	0	12.82	-0.44	570
	1	12.10	0.13	380
3	0	13.21	-0.01	835

[a] From Wilkins (1973b)

Table 7. Rate Coefficients for $H + F_2 \xrightarrow{k_5} HF + F$

T, K	$k_5 = A \exp(-E/RT)$		k (300 K)	Technique	Reference
	A, cc/mol-sec	E, kcal/mol			
298-2500	$2.1 \times 10^{12} T^{0.67}$	1.5	7.7×10^{12}	BEBO theory	Mayer, Schieler, and Johnston (1967)
288		~ 1.5[a]	1.8×10^{12} (288 K)	Photochem reactor	Levy and Copeland (1968)
294-565	1.2×10^{14}	2.4	2.1×10^{12}	Flow/mass spectroscopy	Albright et al. (1969)
250-500	1.1×10^{14}	2.46	1.8×10^{12}	Monte Carlo trajectory calculations	Wilkins (1973a)[b]
300			2.5×10^{12}	Fast flow/esr	Rabideau, Hecht, and Lewis (1972)

[a] The value of k_5 was determined from an experimentally measured ratio of rates of reaction for $H + F_2$ to $H + O_2 + N_2$. Assuming a value of 9.2×10^{15} for the latter rate coefficient, Levy and Copeland (1968) calculated the value of k_5 given here. Then, assuming a pre-exponential value of log A = 9.1, they calculated the activation energy shown here.

[b] Wilkins reported a three-parameter expression for kg: $7.26 \times 10^{15} T^{-0.614} \exp(-2838/RT)$.

exp(-2400/RT) in a discharge flow system at temperatures of 294 to 565 K, using mass spectrometry to monitor species. However, their determination of the rate coefficient for H + Cl_2, obtained in the same apparatus at the same time, is larger than some other evaluations by an order of magnitude at 300 K; therefore, their value of k_5 is somewhat subject to "doubt by association." The measurement of Rabideau (1972) was made in an H_2-F_2 system in which both Reactions (4) and (5) were occurring. Observed F- and H-atom concentrations were matched by computer calculations; the best fit was obtained with their resultant values of k_4 and k_5, which, possibly, are subject to greater uncertainty than their quoted 25% (k_4) and 8% (k_5).

One earlier, indirect experimental measurement has also been reported. Levy and Copeland (1968) examined the kinetics of the H_2-F_2 photochemically initiated reaction at 288 K. In the presence of O_2, inhibition was noted, which was accounted for by the reaction H + O_2 + M, where in their system M = N_2, principally. The value of k_5 was determined from the ratio of rates of reaction for H + F_2 to H + O_2 + N_2. Assuming a value of 9.2×10^{15} cm^6-mol^{-2} sec^{-1} for the latter rate coefficient, Levy and Copeland (1968) calculated the value of k_5 at 288 K to be 1.8×10^{12}. Then, assuming a pre-exponential value of $10^{9.1}$, they calculated an activation energy of 1.5 kcal/mol. The rate coefficient for the competitive H + O_2 + N_2 reaction is not accurately known; at higher temperatures, N_2 seems to be slightly less efficient than Ar [Baulch (1972)], suggesting a value of approximately 5×10^{15} cm^6-mol^{-2} sec^{-1} for the three body process, so that k_5 would be approximately 0.5 times the value that they obtained and the activation energy would be slightly larger.

Two theoretical determinations are also listed in Table 7. The BEBO calculation by Mayer, Schieler, and Johnston (1967) predicts a room-temperature value for k_5 that is almost certainly too large by about an order of magnitude. Wilkins (1973a) obtained a value for k_5 of $10^{15.86}$ $T^{-0.614}$ exp(-2840/RT), or approximately $10^{14.04}$ exp(-2450/RT) between 200 and 500 K, by three-dimensional classical Monte Carlo trajectory calculations, yielding a room-temperature value about 25% smaller than that of Albright et al. (1969).

It is evident that another determination of k_5 is needed; such an experiment is under way in this laboratory. In its absence, however, the value of Albright et al. (1969) is recommended, with the cautionary note that it may be somewhat too large.

The energy distribution of Reaction (5) has been studied in two laboratories. Jonathan, Melliar-Smith, and Slater (1970, 1971a, 1972) have reported successively improved measurements of the pumping distribution in a discharge flow system. Polanyi and Sloan (1972), using a somewhat different discharge flow technique, have also published distribution numbers. Both studies report measurements of emission from v = 1 through 9; Jonathan's (1972) work includes data on the relative rate of formation of the v = 0 level monitored by absorption techniques. Jonathan (1972) used the measured-relaxation method, while Polanyi and Sloan (1972) used the arrested-relaxation technique. In principle, the latter should be the more direct technique, but, in practice, both procedures require great care. In both laboratories, the emission intensities were converted to population densities by means of Einstein coefficients calculated by the method of Cashion (1963). Herbelin and Emanuel (1974) have recalculated the Einstein coefficients and have adjusted the data of Jonathan, Melliar-Smith, and Slater (1970, 1971a, 1972) and of Polanyi and Sloan (1973) to produce revised sets of rate coefficients. The original and the corrected results are shown in Table 8. The g(v) shown are the relative k's normalized to sum to unity. Thus, $k_5(v) = g(v)k_5$ (total). In the original work, the k's were normalized by arbitrarily setting $k_{max} = 1$.

Wilkins' (1973a) classical Monte Carlo Trajectory calculations (Fig. 6) of the distribution of vibrationally excited HF product molecules in Reaction (5) indicate that no molecules are formed in the levels with $v \leq 2$ or ≥ 7. The g(v) obtained at 300 K from his calculations are g(3)...g(6) = 0.10:0.23:0.43:0.25, suggesting that the low vibrational levels observed in the experiments are formed by vibrational-vibrational (V-V) processes and from the "cold" Reaction (4) and the very high vibrational levels are populated by VV processes, which are expected to be very rapid for large v. It is, therefore, assumed that reaction takes place into levels v = 4 through 8 only and Polanyi and

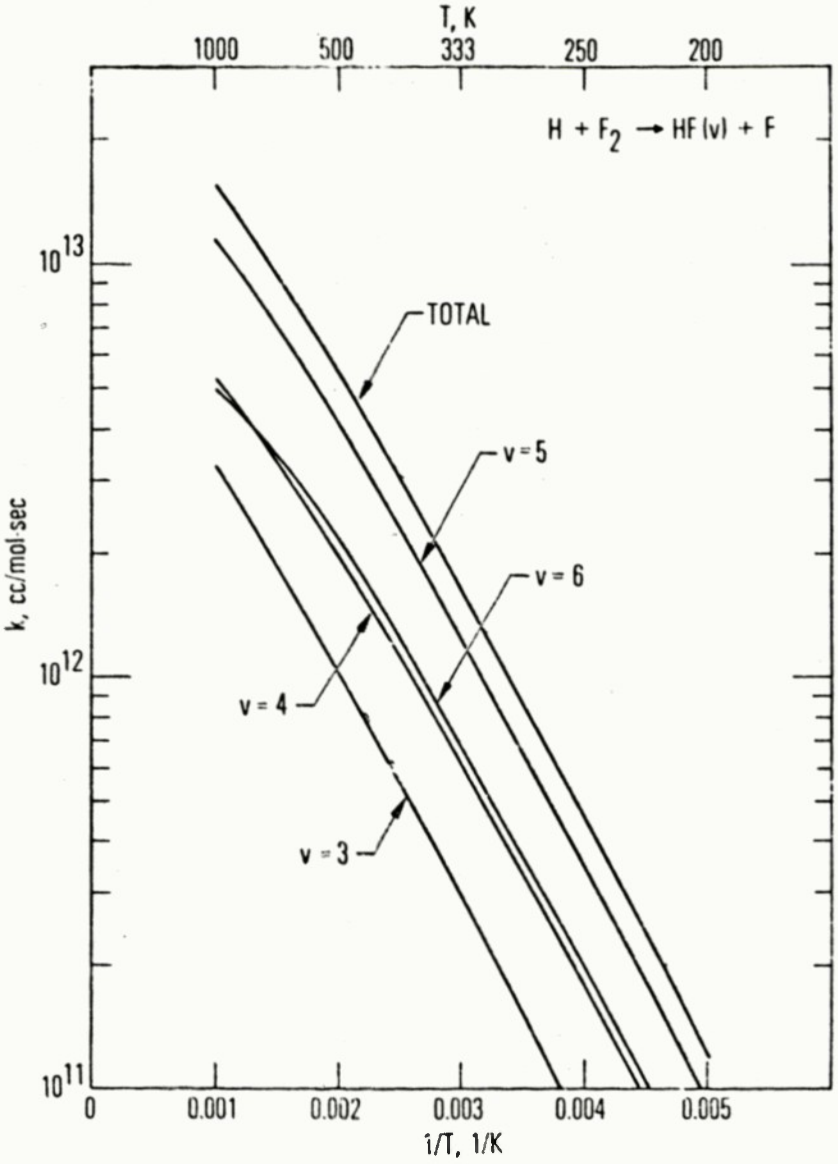

Fig. 6. Values of $k_5(v)$ Versus 1/T for $H + F_2 \rightarrow HF(v) + F$ for Various v as Computed by Wilkins (1973a)

Table 8. Relative Pumping Rates for $H + F_2 \xrightarrow{k_5(v)} HF(v) + F$

$k_5(v) = g_5(v)k_5(\text{total})$

$g_5(0)$	$g_5(1)$	$g_5(2)$	$g_5(3)$	$g_5(4)$	$g_5(5)$	$g_5(6)$	$g_5(7)$	$g_5(8)$	$g_5(9)$	$g_5(10)$	Reference
--	0.06	0.08	0.14	0.18	0.28	0.26	--	--	--	--	Jonathan, Melliar-Smith, and Slater (1970)
--	0.05	0.09	0.14	0.17	0.24	0.23	<0.07	--	--	--	Jonathan et al. (1971a)
0.012[a]	0.026	0.032	0.038	0.13	0.26	0.29	0.13	0.059	0.012	0.012	Jonathan, Okuda, and Timlin (1972)
0.009	0.021	0.029	0.030	0.134	0.30	0.40	0.046	0.02	0.004	0.004	Jonathan, Okuda, and Timlin (1972)[b]
≤0.03[a]	0.034	0.037	0.070	0.10	0.22	0.28	0.113	0.073	0.045	--	Polanyi and Sloan (1972)
0.025	0.03	0.038	0.062	0.11	0.28	0.36	0.044	0.028	0.017	--	Polanyi and Sloan (1972)[b]

[a] Obtained by extrapolation.

[b] Corrected with Einstein coefficients of Herbelin and Emanuel (1974).

Sloan's (1972) experimental results, computed with the Einstein coefficients of Herbelin and Emanuel (1974), are renormalized so that $\sum_{v=3}^{6} g_5(v) = 1$, then the values $g_5(3):g_5(4):g_5(5):g_5(6): = 0.07:0.14:0.35:0.44$ are obtained. These numbers are expected to be near the values that will be agreed upon eventually and are recommended for computational purposes.

IV. ENERGY-TRANSFER PROCESSES

A. VIBRATIONAL-TRANSLATIONAL (ROTATIONAL) ENERGY TRANSFER INVOLVING HF

Vibrational-translational (rotational) (VTR) energy-transfer processes drive the vibrational populations toward equilibrium with the translational degrees of freedom with a resulting loss of potential power in a laser system.

The relaxation processes for the hydrogen halides have posed a challenge to both experimentalists and theoreticians. These molecules provide a sensitive test of any theory of vibrational energy transfer because of their large rotational velocities, their strong intermolecular attractive forces, and the large effect of isotopic substitution. Theoretical predictions based on the Schwartz, Slawsky, and Herzfeld (1952) (SSH) vibrational-translational (VT) theory, the vibrational-rotational (VR) theory of Moore (1963), or Millikan and White's (1963) semi-empirical correlation do not reproduce the experimental data for the hydrogen halides. A VR model, developed by Shin (1971b, 1973), predicts results in reasonable agreement with the hydrogen halide self-relaxation data. In this model, based on a collision between a rotation-averaged oscillator and a rigid rotor, the two H atoms interact strongly in close-in collisions to transfer vibrational and rotational energies. Classical trajectory calculations, as discussed by Wilkins (1974), have been performed in only a few cases. Because of the difficulties of the theoretical calculations, only experimental data exist for most of the relaxation processes. For some of the processes, there are neither experimental data nor theoretical calculations.

The VTR deactivation of the HF can be described by

$$\mathrm{HF}(v) + M_i \overset{k_{6(v,\, v-\Delta v)}^{M_i}}{\rightleftharpoons} \mathrm{HF}(v - \Delta v) + M_i$$

where $k^{M_i}_{6(v, v-\Delta v)}$ is the rate coefficient of the reaction, v represents the initial vibrational level of HF, and Δv *is* the number *of* quanta *transferred* to rotational-translational energy. Relaxation rate coefficients have been measured for the self-deactivation of HF and for its deactivation by other hydrogen halides, other diatomic molecules, and some atoms and polyatomic molecules. Most of the experimental measurements have been made for $v = \Delta v = 1$; only a few studies have reported rates for the higher vibrational levels.

The complexity of Shin's (1971b, 1973) theory and the specific nature of the classical trajectory calculations preclude any general conclusions on the v and Δv dependence of the reaction rates. Since the deactivations of the upper vibrational levels affect the power of a laser, kinetic models of the laser medium must include these upper levels. The harmonic oscillator (HO) model predicts the rate coefficients for the higher vibrational levels to be given by $k_{(v, v-1)} = vk_{(1,0)}$ for $\Delta v = 1$ and the multiquantum transitions, $\Delta v > 1$, to be negligible compared to single quantum transitions. HF is, however, far from an ideal harmonic oscillator, and the HO model cannot be expected to give a precise description of the relaxation processes. The extent to which anharmonicity changes the v dependence of the HO predicted rates depends on the collision model assumed. It is not clear whether the v dependence of k increases or decreases as a result of anharmonicity. The use of the Landau-Teller approximation for the calculation of the relaxation rates in the harmonic oscillator model results in a negligible probability for multiquantum exchanges. This approximation is based on a consideration of only the strong repulsive intermolecular forces and may break down completely where the collision partners exert strong attractive forces. Trajectory calculations have been performed for a few deactivation processes, and these results are used as a guide for estimating the higher level rate coefficients of those few processes. In this review, most extrapolations of experimental data for the deactivation rates to higher vibrational levels will be based on the HO model for lack of any other information. The v dependence as well as the multiquantum transitions remain the largest uncertainties in kinetic models of chemical lasers and certainly will need revision when critical experiments can be devised to measure them.

Most experimental investigations result in the measurement of a relaxation time τ at a given pressure p and temperature T. To convert this relaxation time to a rate coefficient k in units of cc/mol-sec, certain assumptions concerning the nature of the relaxation process must be made. According to the HO model,

$$p\tau = \frac{RT}{k_{(1,0)} - k_{(0,1)}} = \frac{RT}{k_{(1,0)}[1 - \exp(-\Delta E/RT)]}$$

where $k_{(1,0)}$ is the rate coefficient for the deactivation of the v = 1 level to v = 0, $k_{(0,1)}$ is the rate coefficient for the backward reaction, ΔE is the exothermicity of the reaction, and R is the universal gas constant.

In the following paragraphs, different chaperones are treated. An analytical expression has been fitted to the results of each experimental study in which the deactivation reactions were studied over a range of temperatures. These expressions fit the data with an accuracy of 10 to 15%. Most of the results are summarized in Tables 9 through 12.

1. M = HF

Self-relaxation of HF has been studied at the higher temperatures (above 1350 K) in shock tubes and at lower temperatures by laser-induced fluorescence studies. The laser-induced fluorescence technique has been used mostly at room temperature, although some studies in heated or cooled cells or behind reflected shock waves have yielded data over a wide range of temperatures. The relaxation of HF has been studied more extensively than any of the other hydrogen halides, with rates reported between 295 and 5000 K.

Shock-tube studies of Solomon et al. (1971), Bott and Cohen (1971a), Just and Rimpel (1972), and Vasil'ev et al. (1973) gave values of $p\tau$ for HF-HF relaxation at 1400 K between 0.19 and 0.25 μsec/atm, or k between 4.7 and 6.2×10^{11} cc/mol-sec. At 4000 K, Solomon et al. (1971) measured somewhat faster rates and Just and Rimpel (1972) measured somewhat slower rates than those found by Bott and Cohen (1971a) and by Vasil'ev et al. (1973).

Table 9. Experimental Rates for VTR Relaxation of HF(v = 1) by Various Collision Partners

$$HF(v = 1) + M \xrightleftharpoons{k, (P\tau)^{-1}} HF(v = 0) + M$$

M	T, K	log A	E, cal/mol	F_2, %	Reference
Ar	1330-1580	12.85	29,800	5, 10, 20	Johnson and Britton (1964)[a]
Ar	900-1900	10.24	14,000	3, 6, 15	Cglukian (1964)[b]
Ar	1300-1700	12.49	27,300	5	Seery and Britton (1966)[c]
Ne	1650-2700	12.18	23,900	0.5, 1	Diesen (1966)
Ne	1400-2000	13.30	35,000	0.5	Diesen (1968)
Ar	1200-1500	13.57	31,700	10	Just and Rimpel (1970)[d]
Ar	1400-2600	13.55	34,700	10, 20	Breshears and Bird (1973)
F_2	1400-2600	13.99	34,800	10, 20	Breshears and Bird (1973)
Ar	1575-2540	13.10	32,700	0.5	Mastromonico (1974)
Ar	--	12.66	28,500	(review of data)	Lloyd (1971)

[a] The tabulated results are for the six runs with 5% F_2. In a series of nine runs in 10% F_2 in Ar mixtures, Johnson and Britton (1964) obtained log A = 11.54 and E = 20,680 cal/mol; in a series of five runs in 20% F_2 in Ar, they obtained log A = 9.61 and E = 11,025 cal/mol. They considered their 5% results to be the most reliable.

[b] The results are based primarily on the twelve 6% runs. The 3% runs yielded a considerably smaller value for E. The scatter in the 15% runs was too large to permit a reliable assignment of E.

[c] Results are based on data of Johnson and Britton (1964) and Seery and Britton (1966). In mixtures of 5% F_2, 20% Kr, and 75% Ar, Seery and Britton obtained log A = 13.15 and E = 21,100; in 10:20:70 mixtures, they obtained log A = 11.57 and E = 19,600 cal/mol.

[d] Just and Rimpel (1970) also expressed results in the form $k_2 = AT^n \exp(-D/RT)$, obtaining log A = 11.54, n = -1.9, and D = 36,700 cal/mol.

Table 10. Calculated Vibrational Relaxation Rate Coefficients of HF(v) by F Atoms

$$\mathrm{HF}(v) + \mathrm{F} \xrightarrow{k_6^{\mathrm{F}}(v,\ v')} \mathrm{HF}(v') + \mathrm{F}$$[a]

v	v'	$k_{v,v'} = AT^n \exp(-E/RT)$		
		log A	n	E, cal/mol
1	0	14.85	-0.766	3100
2	1, 0	14.79	-0.708	3075
3	2	14.99	-0.724	3645
3	1	14.80	-0.757	3720
6	5	15.71	-0.712	3645
6	4	15.56	-0.741	3640
6	3	15.15	-0.70	3590
6	2	14.89	-0.658	3810

[a] From Wilkins (1973c). Calculated values for $k_{3,v'}$ and $k_{6,v'}$ include comparable contributions from both reactive, i.e., H-atom transfer, and nonreactive processes.

Table 11. Experimental Deactivation Rate Coefficients of HF(v) by H Atoms

$$HF(v) + H \xrightarrow{k_{6(v,v')}^{H}} HF(v') + H, \; v' < v$$

v	v'	10^{-11} k(300 K), cc/mol-sec	Reference
1	0	1.4 ± 0.4	Heidner and Bott[a]
1	0	<0.1	Quigley and Wolga (1974)
1	0	19	Kwok and Wilkins (1974)
2	1, 0	110	Kwok and Wilkins (1974)
3	2, 1, 0	180	Kwok and Wilkins (1974)
1	0	4	Kwok and Wilkins[b, c]
2	1, 0	40	Kwok and Wilkins[b, c]
3	2, 1, 0	80	Kwok and Wilkins[b, c]

[a] R. F. Heidner and J. F. Bott, J. Chem. Phys. 63, 1810 (1975).

[b] Recalculation of data based on assumption that HF-HF VT deactivation scales as v^2.

[c] M. A. Kwok and R. L. Wilkins, The Aerospace Corporation, private communication.

Table 12. Computed Rate Coefficients for Deactivation of HF(v) by H Atoms[a]

$$HF(v) + H \xrightarrow{k^{H}_{6(v,v')}} HF(v') + H$$

v	v'	$k^{H}_{6,v,v'} = AT^{n}\exp(-E/RT)$		
		log A, cc/mol-sec	n	E, cal/mol
1	0	13.96	-0.28	1170
2	0	13.63	-0.08	900
2	1	12.64	0.20	720
3	0	13.59	-0.06	760
3	1	13.45	-0.08	680
3	2	13.57	-0.09	890
4	0	14.17	-0.32	810
4	1	12.82	0.09	640
4	2	13.10	0.03	670
4	3	13.21	0.0	520
5	0	13.98	-0.23	640
5	1	13.60	-0.15	610
5	2	13.30	-0.04	710
5	3	13.50	-0.06	670
5	4	13.34	-0.05	530
6	0	13.88	-0.19	620
6	1	13.60	0.16	570
6	2	13.61	-0.15	750
6	3	13.23	-0.01	670
6	4	13.82	-0.21	600
6	5	13.96	-0.22	630

[a] From Wilkins (1973b). Values for n have been rounded off to two significant figures; those for E to the nearest 10 cal.

The laser-induced fluorescence technique has been used to measure HF relaxation times between 295 and 2400 K. We have fitted the results of these various determinations with functions describing the temperature dependencies and listed them in Table 9. They are also plotted in Fig. (7). The results of Lucht and Cool (1974), Stephens and Cool (1972), Hancock and Green (1972a), Airey and Fried (1971), and Ahl and Cool (1973) have been adjusted for the gasdynamic correction discussed by Bott (1974a). The measured relaxation times agree within a factor of 1.6 at any temperature between 295 and 1000 K, with the exception of the early measurement of Airey and Fried (1971) at 350 K, which is somewhat faster. The room-temperature value for k is 1×10^{12} cc/mol-sec, within about 20%. The high-temperature data combined with those at low temperature show that the HF-HF VTR relaxation times must have a maximum near 1200 K [Lucht and Cool (1974), Bott (1972), Osgood, Javan, and Sackett (1972), Fried, Wilson, and Taylor (1973), Hinchen (1973a, 1973b), and Bott and Cohen (1973b)]. This maximum was confirmed by Blair, Breshears, Schott (1973) in an experimental study covering the range between 600 and 2400 K. However, their numerical results for k, in the neighborhood of 1500 K, are too large by a factor of approximately 1.5. The phenomenon of a relaxation time maximum has been observed or predicted for other diatomic molecules [Donovan, Husain, and Stevenson (1970b)] but at much lower temperatures. The increase in deactivation rate at low temperatures, of course, is due to the effects of an intermolecular attractive force, but the origin of that force is not understood.

Shin's (1970, 1971b) model predicted relaxation rates for HCl, HBr, and HI that substantially agree with experimental data above 700 K. Applying the same theory to HF-HF and DF-DF VR energy transfer, Shin (1971a, 1973) found it necessary to include strong dipole-dipole attraction to reproduce the experimental data between 300 and 4000 K.

The trajectory calculations by Berend and Thommarson* for HF-HF and DF-DF deactivation gave good agreement with the experimental data when a

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*G. C. Berend and R. L. Thommarson, McDonnell-Douglas Corporation, private communication.

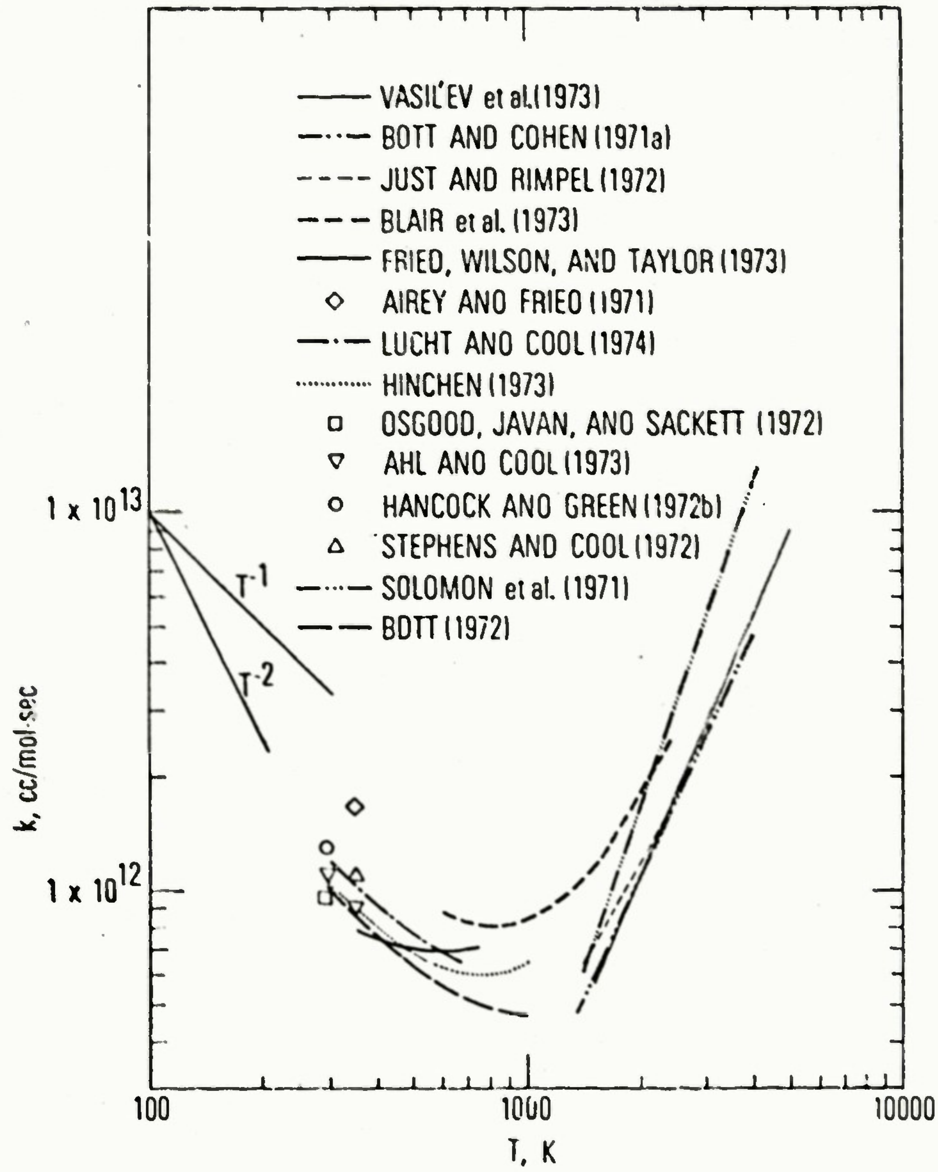

Fig. 7. Experimental Values of Rate Coefficient $k^{HF}_{6(1,0)}$
HF(1) + HF → HF(0) + HF (VT Deactivation) Versus T

sufficient number of J levels were considered. Berend and Thommarson's (1973a) initial calculations were based on fewer J levels than were necessary to describe adequately the relaxation at low temperatures. They observed that below 1000 K the deactivation resulted from the collision of HF($v = 1$) with HF($v = 0$) and the formation of internally excited $(HF)_2$ dimers. The excited dimer lives long enough to allow a redistribution of energy so that neither of the HF molecules is vibrationally excited when the dimer dissociates.

Both HF and DF self-relaxation rates have been described by two-term expressions by Bott and Cohen (1973b) that fit the experimental data over the temperature range of 295 to 4000 K. At temperatures below about 1000 K, the low-temperature term dominates the high-temperature term and $P\tau$ is proportional to T^2. The probability p of HF self-deactivation is 0.01 at 300 K and extrapolates to about 0.02 at 200 K. Low-temperature relaxation rates for HF as yet have not been published; however, studies by Lucht and Cool* suggest a $T^{-1.3}$ temperature dependence for p below 300 K, which means $k \propto T^{-0.8}$ and $p\tau \propto T^{1.8}$. The experimental data from 295 to 4000 K can be fitted by the expression $k = 3 \times 10^{14} T^{-1} + 3.5 \times 10^4 T^{2.26}$ cc/mol-sec, where the high-temperature term has been chosen for computational ease to be of the form T^n instead of the usual Landau-Teller $\exp(B/T)^{1/3}$ dependence. However, to approximate more accurately the expected $T^{-0.8}$ dependence at low temperatures, the expression $k = 1 \times 10^{14} T^{-0.8}$ should be used. This expression is valid for temperatures between about 1000 and 200 K.

The question of how to scale the VT self-relaxation rate with v remains. In past reviews, the harmonic oscillator rule $k_{(v, v-1)} = v k_{(1,0)}$ has been recommended [Cohen (1971, 1972, 1974)]. However, recent efforts to fit pulsed-laser data as well as flow-tube-kinetics experiments suggest a strong v dependence,** with $k_{(2,1)} \approx 7k_{(1,0)}$. The uncertainty in the higher $k_{(v,v-1)}$ is large, but there

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*R. A. Lucht and T. A. Cool, Cornell University, private communication.

**M. Kwok, The Aerospace Corporation, private communication, and N. Cohen, The Aerospace Corporation, unpublished work.

is some indication that the k's increase to a maximum around v = 4. There is no direct evidence for multiquantum transitions, partly because, to a good approximation, any multiquantum transition scheme can be closely matched by a single-quantum scheme. For example, allowing all multiquantum transitions and setting $k_{(v, v')} = k_{(1, 0)}$ gives almost the same deactivation rate for a given v level as the harmonic oscillator rule, even though the total vibrational energy of the system would be removed at a faster rate. These problems are discussed further in Section III. B.

2. M = Ar, He

Bott and Cohen (1971a) and Vasil'ev et al. (1973) have reported relaxation times for HF-Ar relaxation between 1500 and 5000 K that substantially agree with each other. Blair, Breshears, and Schott (1973) measured somewhat faster HF-Ar relaxation times between 800 and 2400 K than the overlapping and extrapolated data of Bott and Cohen (1971a) and Vasil'ev et al. (1973). Their data also show some curvature on the Landau-Teller plot, whereas those of Bott and Cohen (1971a) and Vasil'ev et al. (1973) do not. The curvature could be real or the result of the effects of impurities such as H_2O or residual HF, which become more important at low temperatures. Bott and Cohen (1971a) found He to be only a factor of two more efficient than Ar for deactivating HF. Room-temperature measurements by Airey and Fried (1971), Hancock and Green (1972b), and Hinchen (1973a) led only to upper limits on the relaxation rate coefficient of 300 sec^{-1} $Torr^{-1}$ at 350 K [Airey and Fried (1971)] and 60 sec^{-1} Torr at 295 K [Hancock and Green (1972b) and Hinchen (1973a)]. These results are consistent with extrapolations from the shock-tube data.

The SSH VT calculations do not adequately predict the data for the rare-gas deactivations of the hydrogen halides of Bott and Cohen (1973) and Zittel and Moore (1973). The trajectory calculations of Berend and Tommarson (1973b) for the relaxation of HF by Ar agree within a factor of three with the shock-tube data but do not have as steep a temperature dependence. They concluded that a reduction of the range parameter σ_{Ar-H} by 20 to 30% would lead to much better agreement with the shock-tube data. Such a variation is well within the range of uncertainty of α. Variation of 20 to 30% in the range parameter does not substantially improve the SSH predictions. Steele and Moore (1974) made approximate calculations for the relaxation of HCl (DCl) by Ar and He and concluded from the qualitative fit to their data that both rotational and translational degrees of freedom play important roles. Experimental data and theoretical calculations for HF-Ar vibrational relaxation are shown in Fig. 8. HF-He data [Bott and Cohen (1971a), Smith (1974)] are somewhat more sparse; they are plotted in Fig. 8 also. He is about 2 to 3 times more efficient than Ar throughout the temperature range of the measurements.

3. M = F

Bott and Cohen (1971b) and Solomon et al. (1971) observed the formation of HF(v = 1) in the presence of F atoms produced by dissociating F_2 in one case [Solomon et al. (1971)] and SF_6 in the other case [Bott and Cohen (1971b)] at temperatures between 1900 and 3500 K in shock tubes. Solomon et al. (1971) reported rate coefficients for $k^{F}_{6(1,0)}$ of 5×10^{13} cc/mol-sec and Bott and Cohen (1971b), 3×10^{13} cc/mol-sec at 2500 K. Blauer and Solomon (1973) also measured, by means of a different technique, the rate for HF(v = 1) and HF(v = 2) relaxation by F atoms at 2545 K. They monitored the formation and decay of HF(v = 1) and HF(v = 2) in the reaction of F with HCl behind an incident shock wave. Their estimate of 8×10^{12} cc/mol-sec for the deactivation of HF(v = 1) is slower by a factor of 6 than both their previously measured value [Solomon et al. (1971)] and their estimate for HF(V = 2) deactivation by F. This slow rate coefficient agrees with the value obtained by Blair, Breshears, and Schott (1973), with laser-induced fluorescence behind a reflected shock wave in mixtures of HF and F_2. In these experiments, F_2 was completely dissociated before the vibrational relaxation process was initiated by laser pulse, so that the F-atom concentration was well characterized, in contrast to the previous experiments in which the rate of F_2 or SF_6 dissociation was required. Note that Blair, Breshears, and Schott (1973) require the HF-HF relaxation rate in order to extract an HF-F rate. Their HF-HF rate is, as was noted previously, faster by a factor of 1.5 to 2 than other measurements over the same

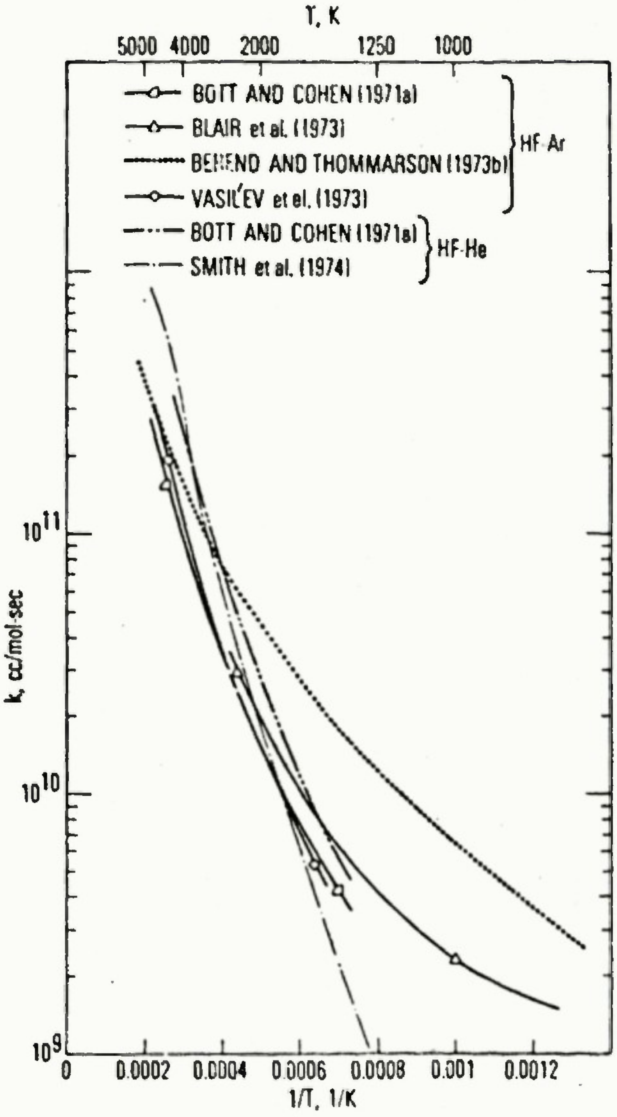

Fig. 8a. Experimental and Theoretical Values of $k_{6(1,0)}^{M}$ for M = Ar, He Versus 1/T

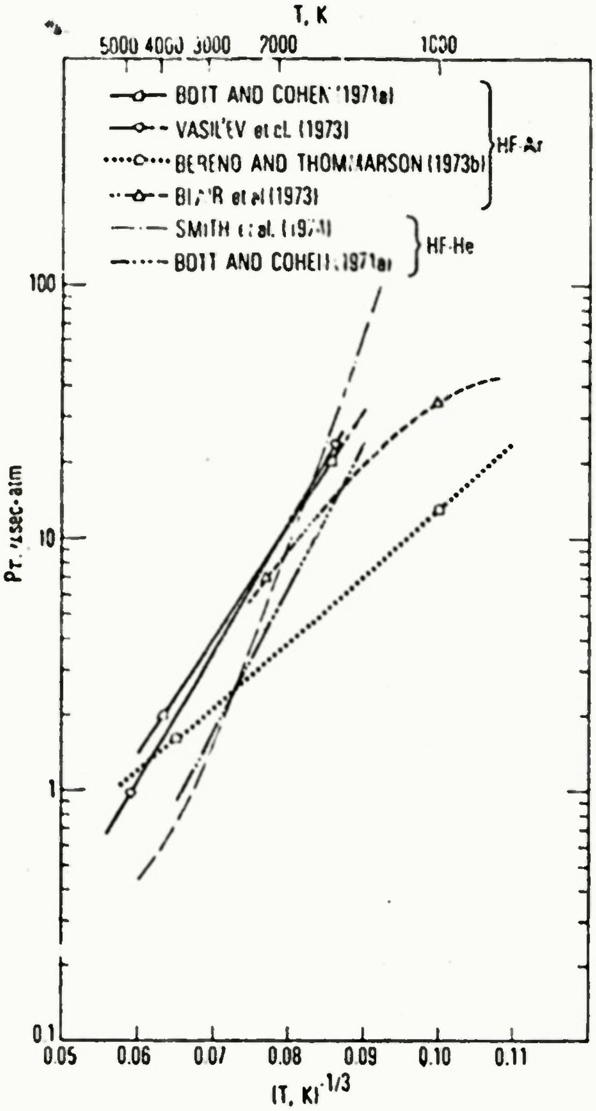

Fig. 8b. Experimental and Theoretical Values of Pτ for $HF(1) + M \rightarrow HF(0) + M$, $M = Ar$, He Versus $T^{-1/3}$

temperature range, probably making their calculated HF-F rate a little too slow, but the effect would not account for all of the discrepancy between the different workers. Of the four measurements, the faster two were obtained under conditions for which the underpopulated, first-vibrational level was relaxing toward an equilibrium concentration, whereas the slower rates were measured for an overpopulated, HF(1) concentration relaxing toward a lower equilibrium concentration. Quigley and Wolga (1974) examined the deactivation of HF(1) by F, O, and H atoms at room temperature using laser-induced fluorescence to produce the HF(1) and esr to measure the concentration of atomic species, which were generated by discharge through the parent diatomic molecule. They reported a rate coefficient of 1.7×10^{11} cc/mol-sec for HF-F deactivation; O atoms were over an order of magnitude more efficient at relaxing HF(1). Their data require a small correction from O atoms in the F experiments because their purification of the F_2 was limited to cold trapping, which would not remove the approximately 1% O_2. If the traces of O atoms react with F_2 to produce FO, the effects on relaxation are difficult to predict. Several theoretical studies of the effects of F atoms on vibrationally excited HF have been carried out. Thompson (1972a) performed trajectory calculations and obtained rates that extrapolate to 8×10^{12} cc/mol-sec at 2500 K, agreeing with the lower of the two sets of experimental numbers; however, the laser-induced fluorescence data between 1500 and 2500 K have a much steeper temperature dependence. Wilkins (1973c) calculated a lower value of 2×10^{12} at 2500 K with a different potential energy surface. Thommarson and Berend (1974) tried to take into account the effects of multiple-potential energy surfaces. However, they concluded that their nonreactive surface, FHF $^2\Pi$, was too repulsive, leading to an overestimation of the contribution to total vibrational relaxation rate coefficient. Shin (1972) assumed an inverse-power potential and calculated analytically the transition probability for the deexcitation of HF($v = 1$) by F. His calculations extrapolate to 9×10^{11} cc/mol-sec at 2500 K; however, his rate coefficient increases below 800 K to about 2×10^{13} cc/mol-sec at 300 K. Neither Wilkins (1973a), Thompson (1972a), nor Thommarson and Berend (1974) calculated such an increase. For laser modeling purposes, we have chosen $k_{(1,0)} = 10^{13.2} \exp(-2,700/RT)$ for deactivation of HF by F atoms, which has the temperature dependence obtained by Wilkins (1973a) between 300 and 1000 K but has a value of 9×10^{12} cc/mol-sec at 2500 K, a compromise between theoretical and experimental results (Figs. 9 and 10).

Wilkins' (1973c) theoretical calculations show that multiquantum transitions contribute significantly to the deactivation of the vibrational levels higher than 2. Both Wilkins (1973c) and Thompson (1972a) found the rate coefficients for single-quantum deactivation HF(v) to be between v and v^2 times as fast as the deactivation of HF(v = 1). Rate coefficients listed in Appendix 1 are proportional to v. In most cases, HF deactivation by F atoms will have a minimal effect on laser performance compared to other mechanisms. The rate coefficient for HF(v = 1) deactivation has a steep temperature dependence and decreases to approximately $10^{11.2}$ cc/mol-sec at room temperature. Both HF and H atoms are usually more important deactivators. If F atoms are found to contribute significantly to the deactivation in specific lasers, it may be desirable to include reactions involving multiquantum transitions.

4. M = F_2

Solomon et al. (1971) tried to measure the relative efficiencies of Ar and F_2 in their shock-tube experiments, but they were unable to measure either since both molecules were found to be much less efficient than HF. However, Bott and Cohen (1971b) were able to obtain results for M = Ar. In this study, their value is adopted, and arbitrarily it is recommended that $k^{F_2}_{(1,0)} = k^{Ar}_{(1,0)}$. Fried, Wilson, and Taylor (1973) obtained an upper limit at 350 K of 2×10^9 cc/mol-sec, which is consistent with the foregoing assumption.

5. M = H

The deactivation of HF(DF) by H ~~atoms~~ has been studied by means of classical trajectory calculations by Wilkins (1973b) and Thompson (1972b) as well as in the laboratory. The deactivation can occur by: (1) the loss of vibrational energy to translation or rotation (nonreactive), (2) an exchange reaction in which the incident H atom abstracts the F-atom from the excited HF, thereby converting the vibrational energy to kinetic energy in the liberated H atom

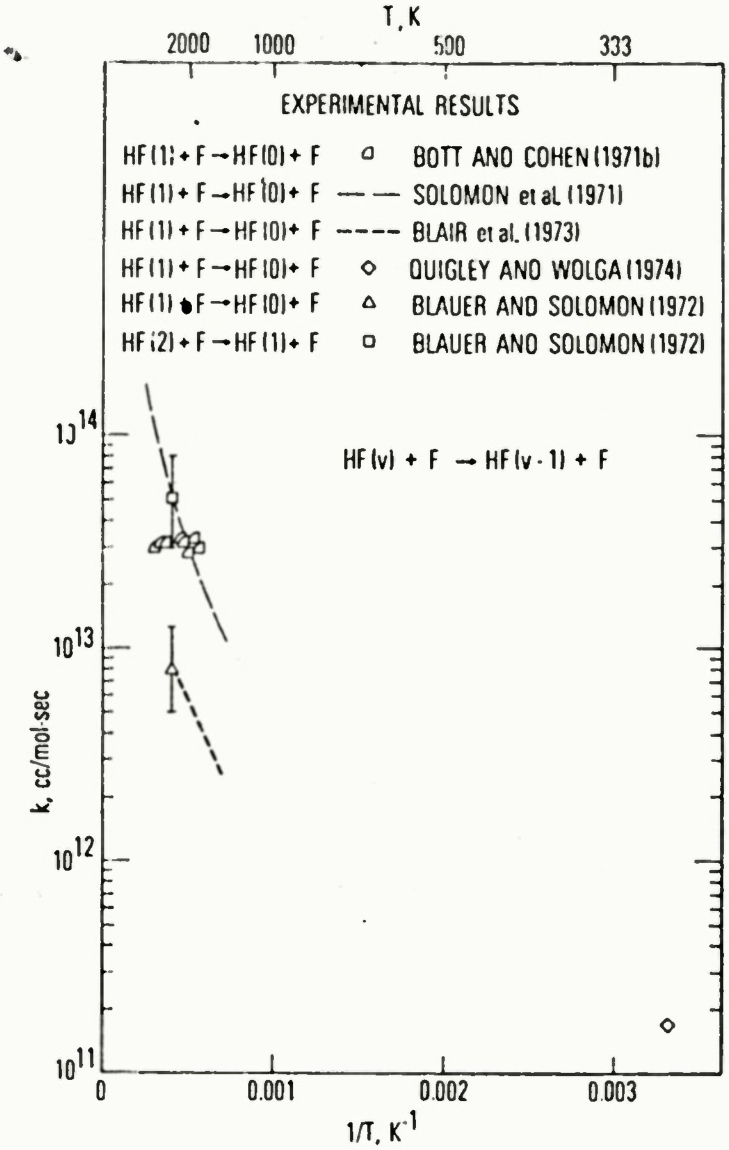

Fig. 9. Experimental Results for $k^F_{6(v, v')}$ for HF(v) + F → HF(v') + F Versus 1/T

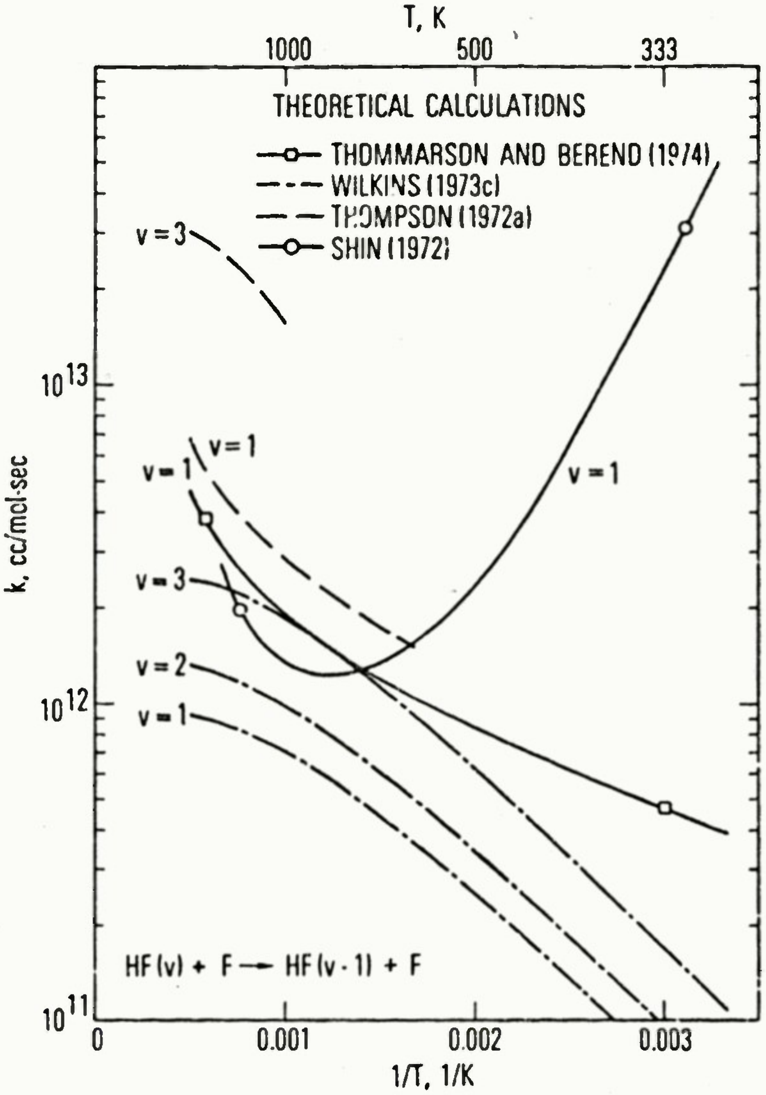

Fig. 10. Theoretical Calculations for $k_{\epsilon(v, v-1)}$ for $HF(v) + F \rightarrow HF(v-1) + F$ Versus 1/T

(reaction), and (3) for levels of ≥ 3, the reaction of the incident H atom with HF(v), forming H_2 and F. Wilkins (1973) calculated the deactivation rates for the third case, $H + HF(v) \rightarrow H_2(v') + F$, $v \geq 3$, with the same London-Eyring-Polanyi-Sato (LEPS) surface used for the pumping reaction, $F + H_2$. The deactivation results have been presented in Section II.A.2. Laboratory experiments cannot distinguish between (1) and (2).

Three independent experimental studies have been reported, all at room temperature. Kwok and Wilkins (1974) worked in a large-diameter, medium-pressure flow tube at room temperature. An rf discharge through SF_6 generated F atoms. Downstream of the discharge, H_2 was added to the flow and reacted with the F atoms to produce excited HF. Vibrational relaxation of HF occurred by the concurrent processes of collisional deactivation by HF, H_2, and H. Spontaneous emission also contributed to the de-excitation. The observed decay of the various vibrational levels of HF was simulated by computer with the various individual rate coefficients being adjusted to give a good fit to the observed data. Experiments were performed for a variety of reagent concentrations to separate the collisional deactivation of HF and H from that of H_2. Kwok and Wilkins (1974) first reported that HF(v = 1) is deactivated by H atoms at a rate of less than 1.9×10^{12} cm^3/mol-sec, which can be compared with 10^{12} cm^3/mol-sec for the self-deactivation by HF, which is made in equal quantities as the H atoms. Much faster rates of 1.1 and 1.8×10^3 cm^3/mol-sec were deduced for the H atom deactivation of HF(v = 2) and HF(v = 3), respectively, with the HF self-deactivation rates assumed to be linear in v. A more recent analysis of the system* suggests values of 0.4, 6, and 14×10^{12} cc/mol-sec for the three vibrational levels if the HF-HF VT rates are linear in v, and 0.4, 4, and 8×10^{12} if they are quadratic. As will be shown later, we believe the latter assumption is probably the more accurate.

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

A second experimental study was carried out by Heidner and Bott* in a very slow flow tube in which H atoms were generated upstream of the observation port by a microwave discharge through H_2. The atom concentration was measured by isothermal calorimetry. HF was mixed into the flow, and a small amount was excited to the first vibrational level by a laser pulse from a TEA HF chemical laser. Deactivation rates were calculated from the decay times of the infrared fluorescence with and without H atoms. The results of this study indicated a rate for $H + HF(1) \rightarrow H + HF(0)$ of $(1.4 \pm 0.4) \times 10^{11}$ $cm^3/mol\text{-}sec$. A similar experiment was performed by Quigley and Wolga (1974) in which the H atoms were measured by esr. They reported a rate coefficient of $< 1 \times 10^{10}$ cc/mol-sec. However, Heidner and Bott* argued that their data analysis was faulty. The experimental results are summarized in Table 11.

Wilkins (1973b) calculated the deactivation rates of several vibrational levels of HF by H atoms by Monte Carlo-selected, three-dimensional classical trajectories on a semi-empirical LEPS potential energy surface. Rate coefficients over a broad temperature range could be deduced. The initial trajectory calculations were performed with a 1.5 kcal/mol barrier height in the potential energy surface; the results are given in Table 12 (selected results are shown in Fig. 11). Because they yielded H-atom deactivation rates that were considerably faster than the experiments suggested, the effects of the barrier height were examined in a series of trajectory calculations performed with heights of 2.5 and 3.5 kcal/mol. The trajectory calculations for the three sets of energy surfaces all predict that chemical exchange provides an efficient mechanism for relaxing vibrationally excited HF by H atoms and that multiquantum transitions are important deactivation processes. The calculation with the 1.5 kcal/mol barrier gave a value of 2.5×10^{12} $cm^3/mol\text{-}sec$ for the room-temperature relaxation rate of HF(1) by H atoms, whereas that with the 3.5kcal/mol for the surface of Polanyi and Schreiber as quoted by Bender, Garrison, and Schaefer (1975) gave a value of 3.1×10^{10}. An intermediate value of 3.1×10^{11}

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*R. F. Heidner and J. F. Bott, The Aerospace Corporation, to be published in J. Chem. Phys.

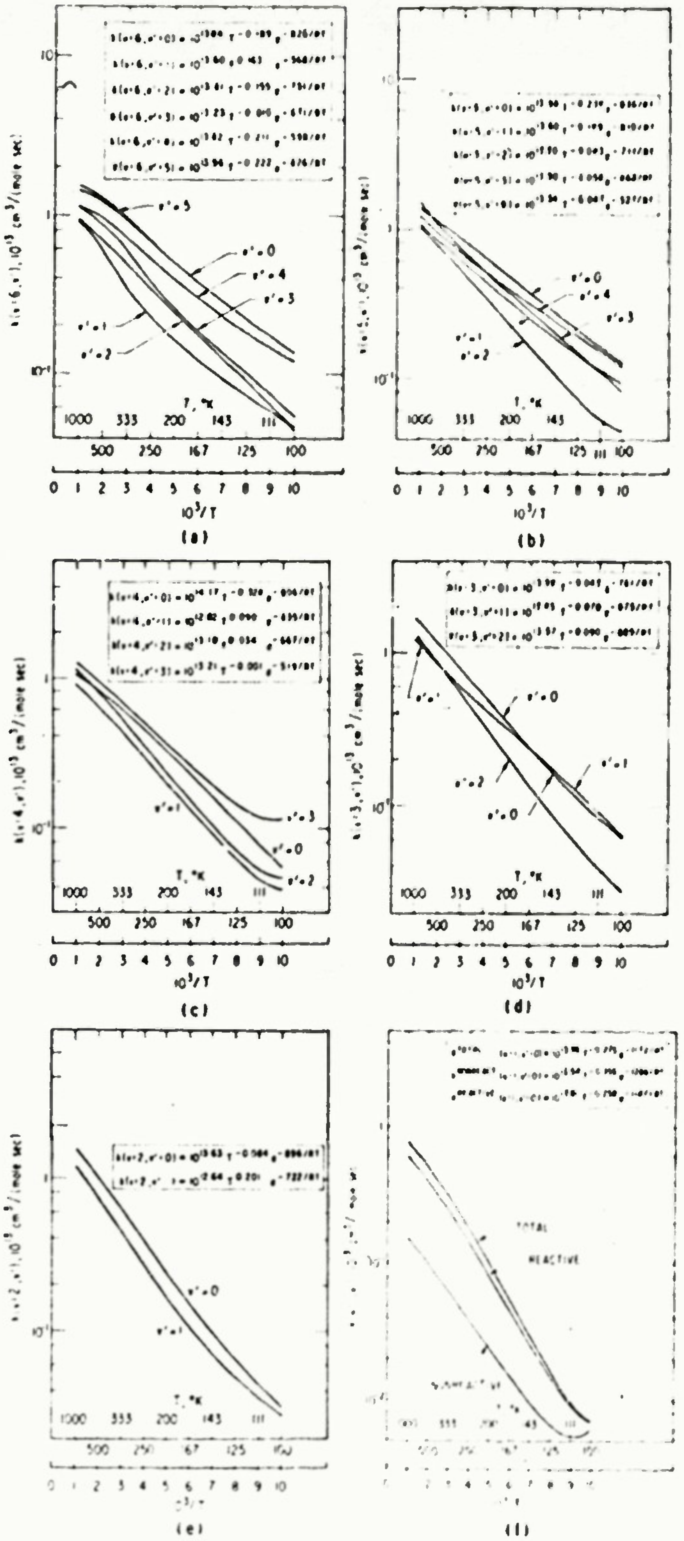

Fig. 11. Rate Coefficients for $k^{H}_{6(v,v')}$ for HF(v) + H → HF(v') + H Versus $10^3/T$ as Computed by Wilkins.
(a) v = 6; (b) v = 5;
(c) v = 4; (d) v = 3;
(e) v = 2; (f) v = 1

cm^3/mol-sec was obtained with a potential energy surface with a 2.5-kcal/mol barrier height and agrees reasonably well with the experiments. For each barrier height, the trajectory calculations predict that the overall rate coefficient for the deactivation of HF(v = 2) by H atoms is approximately five times larger than the value obtained for the deactivation rate of HF(v = 1) by H atoms, which is somewhat consistent with the flow-tube experiments in which a much faster rate is required for the HF(2) deactivation than for HF(1) deactivation.

Recently, it was suggested by Bender, Garrison, and Schaefer (1975) that the H + FH potential surface energy barrier is no less than 40 kcal/mol, which, if true, would rule out the possibility of F-atom exchange as a significant contributor to the vibrational relaxation of HF by H atoms, leaving only nonreactive processes as the responsible mechanism. This conclusion is consistent with experimental results in this laboratory on the rate of the exchange reaction*

$$D + HF(0) \rightarrow H + DF(0)$$

6. M = H_2

The vibrational relaxation of HF in the presence of H_2 was studied by Bott and Cohen (1972, 1973c, 1974b) behind incident shock waves in the temperature range 1350 to 4000 K and by the combined shock-tube laser-induced-fluorescence (STLIF) technique from 298 to 611 K. Because of the near resonance in vibrational frequencies between HF and H_2 (Table 15), VV energy exchange takes place readily; the effect is to couple the two VT processes: HF deactivation by H_2 and H_2 deactivation by HF.

$$HF(1) + H_2(0) \xrightarrow{k_{6(1,0)}^{H_2}} HF(0) + H_2(0)$$

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*R. F. Heidner, III, and J. F. Bott, The Aerospace Corporation, to be published.

$$H_2(1) + HF(0) \xrightarrow{k^{HF}_{7(1,0)}} H_2(0) + HF(0) \qquad (7)$$

The experimental data cannot, therefore, readily be treated analytically. The high-temperature shock-tube results were simulated by computer experiments; reasonable matches between experimental and computed profiles were obtained when the efficiency of H_2 as the collision partner was taken to be 0.3 to 0.5 times that of HF itself. However, this result was considered an upper limit; the actual value could have been smaller since the calculated profiles are relatively insensitive to the H_2 efficiency if it is very small.

From the lower temperature STLIF data, Bott (1974b) was able to extract a value for $k^{HF}_{7(1,0)} + 2.66k^{H_2}_{6(1,0)}$ of $(1 \pm 0.3) \times 10^3$ sec^{-1} $Torr^{-1}$, or approximately 6.2×10 T cc/mol-sec, where the two k's are, respectively, for H_2 deactivation by HF and HF deactivation by H_2. It is impossible to isolate the contributions of the two separate terms to the overall expression. Therefore, all that can be said is that $k^{H_2}_{6(1,0)}$ is no greater than approximately 390 sec^{-1} $Torr^{-1}$ or 2.3×10^7T cc/mol-sec. On a $P\tau$ versus $T^{-1/3}$ plot, this expression is consistent with the one derived from the high-temperature data. The contribution of $k^{HF}_{7(1,0)}$ is expected to be small. For example, Bott's (1974b) overall relaxation rate coefficient at 500 K is 3.1×10^{10} cc/mol-sec, whereas the H_2-H_2 VT rate coefficient (discussed below) at this temperature is about 4×10^8 cc/mol-sec. HF would not be expected to be much more efficient at chaperoning H_2 vibrational relaxation than H_2 itself. Therefore, at temperatures below about 1000 K, it is reasonable to assume that $k^{H_2}_{6(1,0)}$ is described by the expression 6×10^7T cc/mol-sec. At higher temperatures, this expression may no longer be valid. For example, at 2000 K, the latter expression gives 1.2×10^{11} cc/mol-sec for the overall relaxation rate coefficient, whereas the H_2-H_2 self-relaxation rate coefficient is about 1.6×10^{11}. Therefore, in this temperature regime, the contributions from Reactions (6) and (7) may be comparable.

Bott's (1974) room-temperature value is in favorable agreement with the limiting values obtained by Hancock and Green (1972b) and by Osgood;[*] however, Hinchen (1973a) has deduced a much faster rate coefficient from his data.

7. $M = DF, D_2$

Because of the frequent presence of D_2 in combustion-driven HF-laser systems (and, therefore, of DF in the lasing region), there is interest in the deactivation rate coefficients of HF in the presence of these two deuterated species.

In shock-tube laser-induced-fluorescence experiments, Bott and Cohen (1973c) studied HF relaxation in the presence of DF in the temperature range of 295 to 1000 K. HF relaxation occurs simultaneously by VV and VT processes with DF as chaperone. Therefore, their results yield a sum of two rate coefficients, for the two processes

$$HF(1) + DF(0) \xrightarrow{k_{6(1,0)}^{DF}} HF(0) + DF(0)$$

and

$$HF(1) + DF(0) \xrightarrow{k_{8(1,0;0,1)}} HF(0) + DF(1) \qquad (8)$$

The value of $k_{6(1,0)}^{DF} + k_{8(1,0;0,1)}$ was about 1.4×10^{12} cc/mol-sec at 300 K, decreasing slightly to $(7 \pm 1) \times 10^{11}$ between 550 and 1000 K. The room-temperature value is about 15% larger than that previously obtained by Hinchen (1973a).

The experimental data can be described by a two-term expression, $k_{6(1,0)}^{DF} + k_{8(1,0;0,1)} = 10^{17.03}T^{-2} + 10^{8.8}T$. To separate the VV, Reaction (8), and VT, Reaction (6) contributions, the VT deactivation of HF(1) by DF can be assumed to compare in rate to that of the deactivation of

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[*] R. M. Osgood, MIT, private communication.

of DF(1) by HF. The latter has been measured; in this case, the experimental rate is a direct measure of the VT process because the VV process is too endothermic to be significant. The VT rate would then be $k^{DF}_{6(1,0)} = 10^{14.28}T^{-1} + 10^{2.13}T^{3}$, making a VV rate coefficient $k_{8(1,0;0,1)}$ that varied between 3 and 8×10^{11} cc/mol-sec in the temperature range of 300 to 1000 K, or approximately 6×10^{11} cc/mol-sec throughout that range, within 50% (Fig. 12).

Bott and Cohen (1973c) also studied HF relaxation in the presence of D_2 at the same time by the same technique. Again, their results yield a sum of rate coefficients for VV and VT processes. D_2 is a considerably less efficient deactivator than is DF, the total deactivation rate coefficient at room temperature being $(6 \pm 2) \times 10^{10}$ cc/mol-sec and increasing with temperature to approximately 1.3×10^{11} at 1000 K. The temperature-dependent rate coefficient is described, within 10% by the expression $k = 1.38 \times 10^{9}T^{0.65}$ cc/mol-sec, where both VV and VT contributions are included.

B. VIBRATIONAL-VIBRATIONAL ENERGY TRANSFER INVOLVING HF

Because, in general, the rates of energy transfer increase as the magnitude of vibrational energy converted to translational energy decreases, VV transfer in which only a small surplus of energy is transformed into translational energy is very fast (much faster than VT transfer). HF is unusual since the VT, room-temperature relaxation rate coefficient is only about an order of magnitude smaller than that in VV. No experimental data for HF-HF transfer were available until very recently. Because theoretical calculations indicate that VV transitions in which the quantum numbers of the colliding molecules change by $\Delta v > 1$ are one or more orders of magnitude slower than those in which $\Delta v = 1$ [Rapp and Kassal (1969)], it has been customary to consider only VV energy transfer reactions of the type shown in Reaction (9)

$$\mathrm{HF}(v) + \mathrm{HF}(v') \xrightleftharpoons{k_{9(v,\,v+1;v',\,v'-1)}} \mathrm{HF}(v+1) + \mathrm{HF}(v'-1) \qquad (9)$$

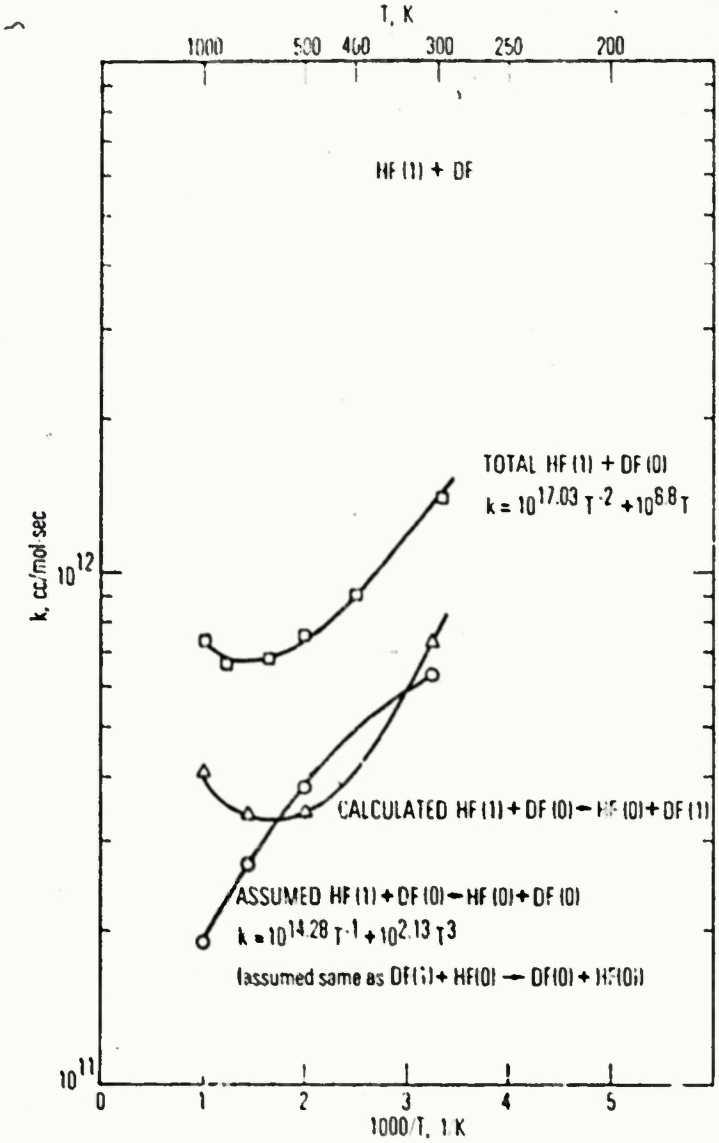

Fig. 12. Vibrational Relaxation Rate Coefficients, $k^{DF}_{6(1,0)}$ and $k_{8(1,0;0,1)}$, Estimated From Experimental Overall Relaxation Rate Coefficient for HF(1) + DF(0) Versus $10^3/T$

If the molecule losing energy is an harmonic oscillator and the perturbing force linear with distance, the rate coefficients are related by the simple relationship

$$k_{9(v,v+1;v',v'-1)} = (v+1)v'k_{(0,1;1,0)} \qquad (a)$$

Because HF is very anharmonic, the actual relationship among the various k's may be considerably different, and, in fact, k_9 may decrease rather than increase with v.

Another effect of anharmonicity on the value of k has been the subject of much experimental and theoretical investigation. In an anharmonic oscillator, the VV energy transfer is not a resonant process; some internal energy must be converted to translational energy during the reaction. The energy converted to the translational energy is given by

$$\Delta E = (E_{v+1} - E_v) + (E_{v'-1} - E_{v'})$$

For an anharmonic oscillator in the lowest rotational state, the energy levels to the first approximation, i.e., for a Morse oscillator, are given by

$$E_v = hc\omega_e\left(v + \frac{1}{2}\right) - hc\omega_e x_e\left(v + \frac{1}{2}\right)^2 \qquad (b)$$

Thus, the energy to be transferred to translation in the above VV reaction is

$$\Delta E' = 2hc\omega_e x_e(v' - v - 1) \qquad (c)$$

The reaction will be resonant only for the trivial condition that $v' = v + 1$, in which case no reaction is physically distinguishable. For greater accuracy (seldom warranted because of the current state of energy transfer theory), expression (c) for ΔE can be extended to include the second-order anharmonicity term contribution

$$\Delta E'' = 3hc\omega_e y_e(v^2 - v'^2 + 2v + 1) \qquad \text{(d)}$$

Because $\omega_e y_e = 0.011\ \omega_e x_e$ for HF, $\Delta E''/\Delta E' = -0.0165\ (v + v' + 1)$. For $v = 9$ and $v' = 8$, the correction amounts to about 30%. In most cases of interest, it is considerably less.

In the preceding discussion, it was assumed that $\Delta J = 0$ for the energy transfer process. When J is allowed to change during the collision, the amount of internal energy that must be converted to translational energy can be decreased considerably. For example, near 300 K, more than 20% of the HF molecules are in the $J = 3$ level. For the reaction

$$HF(v = 1,\ J = 3) + HF(v = 1,\ J = 3) \rightleftharpoons HF(v = 0,\ J = 2) + HF(v = 2,\ J = 4)$$

ΔE is only 85 cm^{-1}. The large possible effect of ΔJ on the magnitude of ΔE and, therefore, on the rate of an HF-HF VV energy-transfer process may result in a very weak dependence of the rate coefficients on the values of v and v', i.e., on the value of ΔE as computed by Eqs. (6; and (7).

As is true for VT transfer, further corrections to account more accurately for the effects of anharmonicity vary from theory to theory, not only in magnitude but in the direction of the effect.

1. HF-HF

Several groups have reported experimental results for the deactivation of HF by VV energy transfer [Bott (1972), Osgood, Sackett, and Javan (1972, 1973, 1974), Airey and Smith (1972)]. In all the studies reported, it is necessary to know rate of the competing VT process in order to extract a VV rate coefficient. In general, the competition is between

$$HF(v) + HF(0) \overset{k_{-9}(v,\, v',\, 0,\, 1)}{\rightleftharpoons} HF(v') + HF(1) \qquad \text{(VV)}$$

and

$$\mathrm{HF}(v) + \mathrm{HF}(0) \xrightleftharpoons{k_{6(v,\,v')}^{HF}} \mathrm{HF}(v') + \mathrm{HF}(0) \qquad \mathrm{(VT)}$$

Usually, it is assumed that $v' = v - 1$. For even the simplest case, i.e., $v = 2$, the competing VT process has not been measured directly. Therefore, its rate coefficient must be assumed, and, in the studies published to date, it has always been assumed that $k_{6(v,\,v-1)}^{HF} = vk_{6(1,\,0)}^{HF}$.

In a laser-induced fluorescence, room-temperature study, Bott (1972) obtained an overall rate coefficient for the disappearance of HF(2). By assuming $k_{6(2,\,1)}^{HF} = 2k_{6(1,\,0)}^{HF} = 2.48 \times 10^{12}$ cc/mol-sec, he obtained 0.95×10^{13} for $k_{9(2,\,1;\,0,\,1)}$, i.e., $2 \rightarrow 1$; $0 \rightarrow 1$, or, for the exothermic rate coefficient, $k_{9(1,\,2;1,\,0)} = 2.2 \times 10^{13}$ cc/mol-sec. If k_{6}^{HF} scales faster than linearly with v, then the VV rate coefficient will be proportionately smaller. In particular, if $k_{6(2,\,1)}^{HF} = 6k_{6(1,\,0)}^{HF} = 7.5 \times 10^{12}$, then $k_{9(1,\,2;1,\,0)} = 1.05 \times 10^{13}$. Note that the largest $k_{6(2,\,1)}^{HF}$ can be 1.2×10^{13} cc/mol-sec, according to Bott. It is apparent that $k_{9(1,\,2;1,\,0)}$ is only weakly dependent on $k_{6(2,\,1)}^{HF}$.

Osgood, Sackett, and Javan (1974) obtained measurements for the VV exchange of HF(v) with HF(0) for $2 \leq v \leq 4$ in experiments in which one to three vibrational levels were simultaneously pumped in fixed ratios by the absorption of laser radiation. The exchange rates were deduced from the rise times of the fluorescence from the vibrational level above the highest level being pumped. The results are given in Table 13. For the harmonic oscillator type of dependence previously defined, the last column in Table 13 should read 1, 1.5, and 2. Note that the exothermic rate coefficients for $v = 3$ and $v = 4$ (Column 4) exceed the gas kinetic collision frequency.

In an earlier experiment, Airey and Smith (1972) measured the relaxation of upper vibrational levels $v = 2$, 3, 4, and 5 in a steady-state fluorescence quenching experiment and deduced values for $k_{9(v-1,\,v;\,1,\,0)}$ that increased as 1:2.4:13.5:44. Again, results for the upper rate coefficients exceeded the

Table 13. HF-HF VV Exchange Rates From Osgood, Sackett and Javan (1974)

$$\mathrm{HF}(v) + \mathrm{HF}(0) \xrightleftharpoons{k_{-9(v,\,v-1;0,\,1)}} \mathrm{HF}(v-1) + \mathrm{HF}(1)$$

v	k_{exp} (VV + VT Deactivation)	$k_{-9(v,\,v-1;1,\,0)}$ $\left[k^{HF}_{6(v,\,v-1)} = vk^{HF}_{6(1,\,0)}\ \text{assumed}\right]$	$k_{9(v-1,\,v;1,\,0)}$ (Exothermic Direction)	$\frac{k_{9(v-1,\,v;1,\,0)}}{k_{9(1,\,2;1,\,0)}}$
2	15	12, 6	30	1
3	30	26	135	4.6
4	26	22	260	8.75

Note: All k's in units of 10^{12} cc/mol-sec.

gas kinetic collision frequency. This experiment is somewhat more complicated than that of Osgood, Sackett, and Javan (1974), requiring computer modeling as well as the usual assumptions concerning the scaling of the VT rate coefficients.

The large VV rates deduced from the data of Osgood, Sackett, and Javan (1972) with the assumption of VT rate coefficients linear with v (Table 13) are inconsistent with observations in HF lasing systems, both pulsed and continuous. Modeling studies undertaken in this laboratory* to match any of the pulsed HF laser studies of Suchard (1973), Chen et al. (1974), and Nichols, Wrolstad, and McClure (1974) show that when the fast VV rate coefficients are introduced into the rate package, the proportion of energy that comes from the upper vibrational levels is far too high. That is, the effect of fast VV rates is to pump-up upper levels more than would be expected on the basis of the initial pumping distribution. Similar effects have been observed in the case of continuous HF lasers.** The conclusion is that the VT rate coefficients must scale-up faster than linearly with v, and the VV rate coefficients are not as large as suggested by Osgood et al. (1974).

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*N. Cohen and J. F. Bott, The Aerospace Corporation, to be published in Appl. Opt.

**G. Emanuel, TRW Systems, private communication.

In order to match the relative energy output of the two lowest vibrational bands, i.e., $P_{2,1}/P_{1,0}$, from all three of the pulsed-laser experiments, it is necessary to have $k^{HF}_{6(2,1)} = 7k^{HF}_{6(1,0)}$. The behavior of the VT rate coefficients for higher v levels is not obvious because of disagreement among the experimental results. At present, the best assumption is that the VV rate coefficients are constant ($\approx 10^{13}$) with v for the series $k_{9(v,v-1;0,1)}$, which leads to k^{HF}_6 that scale as 1:8:28:25. Experimental results are less sensitive to other VV coefficients, i.e., those of the form $k_{9(v,v-1;v',v'+1)}$ for $v' > 0$. Therefore, in this report all these rate coefficients are assumed equal to those for which $v' = 0$.

Flow-tube studies in a nonlasing HF medium conducted in this laboratory, although not yet completely analyzed, seem to point to the same conclusion.[*] Kwok and Wilkins[*] studied the vibrational relaxation of upper HF levels in a medium-pressure (1 Torr) large-diameter (10 cm) flow tube in which HF(v) was generated by the reaction of F (obtained by passing SF_6 through a discharge) with H_2. Deactivation processes were followed by monitoring the vibrational chemiluminescence. They obtained overall rate coefficients in units of 10^{12} cc/mol-sec for the disappearance of the indicated vibrational level: $k(v = 1 \ldots 5) = 1.0:9.9 \pm 3.0:15.7 \pm 6.0:16.3 \pm 6.0:5.2 \pm 3.0$. These results agree within a factor of 2 with those of Osgood, Sackett, and Javan (1974) for v = 4. Kwok and Wilkins' additional result for v = 5 suggests that $k^{HF}_{6(5,4)}$ is considerably smaller than $k^{HF}_{6(4,3)}$. If the VV rate coefficients are constant, the VT rate coefficients would now scale as 1:8:28:25:5.

2. HF-H_2

Processes of the type shown in Reaction (10) are expected to be fast because of the accidental occurrence of near-resonance between the two molecules

$$HF(v) + H_2(v') \xrightleftharpoons{k_{10(v,v+n;v',v'-n)}} HF(v+n) + H_2(v'-n) \tag{10}$$

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[*] Kwok and R. L. Wilkins, The Aerospace Corporation, private communication.

In Table 14, the amounts of internal energy to be converted to translational energy in the above process are listed with all species assumed to be in the J = 0 rotational level or all species assumed to be J = 2 level.

Recently, Bott and Cohen (1973c), using the STLIF technique, obtained VV transfer rates for HF with several diatomic partners, including H_2 (Fig. 13). They found, for v = 0, v' = 1, that the transfer rate is nearly temperature independent

Table 14. Resonance Defect for VV Energy Transfer From H_2 to HF[a]

HF	H_2	Δv, cm^{-1}		K_{eq}[b]
0 → 1	1 → 0	199	(187)	0.38
1 → 2	1 → 0	372	(359)	0.17
2 → 3	1 → 0	539	(525)	0.075
3 → 4	1 → 0	702	(688)	0.034
0 → 1	2 → 1	-36	(-23)	1.19
1 → 2	2 → 1	136	(120)	0.52
0 → 2	2 → 0	336	(305)	0.20
0 → 3	3 → 0	409	(367)	0.14
1 → 3	2 → 0	675	(646)	0.038

[a] Calculated with all molecules assumed in the J = 0 rotational level. Values in parentheses calculated with all molecules assumed in the J = 2 level (the most heavily populated at T = 300 K). Data from Mann (1961) and Herzberg (1950). Positive Δv means an exothermic process.

[b] For all molecules in J = 0 rotational levels.

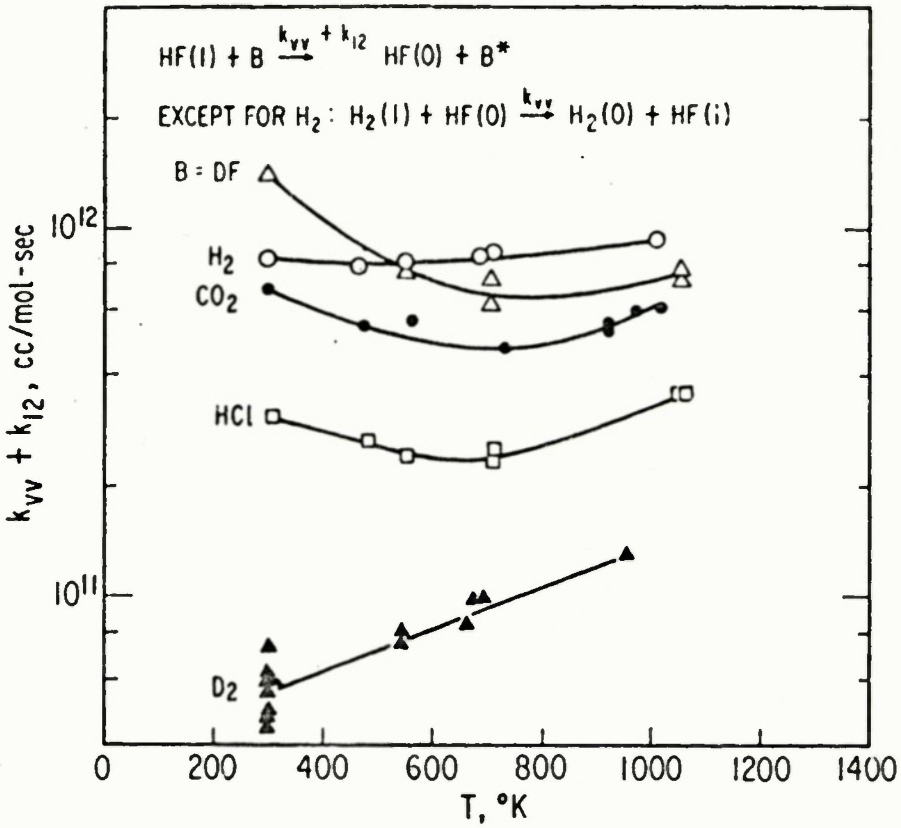

Fig. 13. Values of $k_{vv} + k_6$ Obtained for the Relaxation of HF by Several Molecules Versus T. (The data for H_2 were multiplied by exp(288/T) to obtain k_{-vv} for comparison with the other exothermic rates.)

over the range 300 to 1000 K, with a value of 8.3×10^{11} cc/mol-sec, or about a factor of 20 slower than HF-HF VV transfer. As the two processes transfer approximately the same amount of vibrational energy into translational modes, it is apparent that the rate of transfer does not depend solely on the degree of energy mismatch.

Kwok and Wilkins,* in a large-diameter flow tube, studied the energy transfer in an $HF-H_2$ system and attempted, by computer modeling, to extract numbers for the rate coefficients for processes of the type shown in Reaction (10). An important qualitative conclusion of their work was the convincing evidence attesting to the occurence of multiquantum process, i.e., $\Delta n > 1$. Quantitatively, their work suggests that the rate coefficients for the processes written in the exothermic direction increase slightly with increasing v. They considered only processes with $v' = 0$, since, in their studies, the concentration of vibrationally excited H_2 was too low to contribute measurably to the kinetics. Their results are summarized in Table 15. The experimental observation is the disappearance of a given HF(v) level, which is a measure of the rate coefficient sum given in the penultimate column. The breakdown of this sum into the individual contributions indicated by varying n is a refined perturbation on the total disappearance rate; therefore, the values for $k_{10(v, v-n; v', v'+n)}$ are subject to considerable uncertainly, e.g., on the order of 50%. Because of this uncertainty, it is sufficiently accurate to represent the data by the simplified relationships $k_{10(v-n, v; v'+n, v')} = vk_{10(0, 1; 1, 0)} = v \times 0.8 \times 10^{12}$. The temperature dependence is assumed to be negligible.

3. $HF-N_2$

Shock-tube studies of the relaxation of HF in the presence of N_2 were conducted both by Bott and Cohen (1971a) and by Blauer, Solomon, and Owens (1972). The former observed a slight degree of non-Landau-Teller-type behavior; $P\tau$ increased from about 1 μsec/atm at 3000 K to about 3μsec/atm at 1500 K. Blauer, Solomon, and Owens (1972) found a temperature-independent rate of

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

Table 15. Rate Coefficients for $HF(v) + H_2(v') \overset{k_{10}}{\rightleftharpoons} HF(v - n) + HF(v' + n)$[a]

v	v'	n	$k_{10(v,v-n;v',v'+n)}$	$\sum_n k_{10(v,v-m;v',v'+n)}$	$k_{10(v-n,v;v'+n,v')}$ (Exothermic Process)
1	0	1	0.31	0.31	0.8
2	0	1	0.20	0.44	1.2
2	0	2	0.24		1.2
3	0	1	0.18	0.63	2.4
3	0	2	0.12		3.2
3	0	3	0.33		2.4

[a] All k's in units of 10^{12} cc/mol-sec.

1.9 ± 0.5 μsec/atm throughout the same temperature range, which agrees with the results of Bott and Cohen (1971a) at 2400 K and is within a factor of 1.5 of their results at other temperatures. Room-temperature studies in two laboratories by Hancock and Green (1972a, 1972b) and Bott and Cohen (1973c) yield a value of Pτ of approximately 9 to 10 μsec-atm, indicating that there probably is some temperature dependence in Pτ at higher temperatures.

Initially, these results had been interpreted as a simple VT energy transfer from N_2 to HF. Later, however, Sentman and Solomon (1973) re-examined the data and concluded that while deactivation of N_2 by HF is probably very fast, deactivation of HF by N_2 by VT processes should be negligible at temperatures from 1500 to 3000 K. They concluded that the above experimental studies really measured the rate of VV transfer for the reaction:

$$HF(0) + N_2(1) \rightleftharpoons HF(1) + N_2(0) \qquad (-11)$$

The reported relaxation rates are ascribed, therefore, to VV transfer at this time; the VT contribution is assumed to be slight. When the experimental data are converted to units of cc/mol-sec, they are fitted throughout the temperature range by the expression $k_{11(1,0;0,1)} = 11T^3 + 2.3 \times 10^9$. In the absence of any experimental evidence, it is assumed that k_{11} is linear with the vibrational level of HF.

C. H_2 VIBRATIONAL RELAXATION

Occurrence of HF-H_2 VV energy-transfer reactions can permit the buildup of energy in vibrationally excited H_2 molecules. These species can relax by VT transfer from H_2 to various chaperone molecules.

$$H_2(1) + M \rightarrow H_2(0) + M \tag{7}$$

Kiefer and Lutz (1966) measured the vibrational relaxation of H_2 in a shock tube at temperatures from 1100 to 2700 K and obtained a Napier time of $3.9 \times 10^{-4} \exp(100/T^{1/3})$ µsec-atm. Their H_2-Ar VT rate was about 4.1 times slower; their H_2-H_2 rate, when extrapolated to room temperature, agrees with a Napier time of 1.06×10^3 µsec-atm obtained by DeMartini and Ducuing (1966). When converted to a rate constant expressed in the form AT^n, this becomes $k_7^{H2} = 10^{-3}T^{4.3}$; the value of k_7^{Ar} is 1/4 of this. Recently, Audibert, Joffrin, and Ducuing (1974) extended the temperature range down to 40 K; the rate coefficient below approximately 100 K is nearly temperature-independent, but to 40 K, the above expression fits the data within a factor of approximately 2.

Heidner and Kasper (1972) studied the room-temperature deactivation of H_2 by H atoms and obtained $k_7^H = 10^{11.25}$ cc/mol-sec, making H atoms about 1000 times more efficient than H_2 itself. Kapralova et al. (1963), in experiments designed to elucidate the chain-branching character of H_2-F_2 mixtures (discussed below), obtained deactivation rates for k_7^M with M = Ar, He, H_2, N_2, and CF_4. Their k_7^{H2}/k^{Ar} ratio is 1.9, somewhat smaller than the more direct determination of DeMartini and Ducuing (1966). The other species efficiencies were all within a factor of 2 of that of H_2. In this review, all other species are assumed to have the same efficiency as Ar. The HO type of dependence on the vibrational level of the excited H_2, i.e., $k \propto v$, is also assumed.

V. CHAIN BRANCHING

The possibility of the occurrence of energy chains in the H_2F_2 explosion requires brief discussion. Because the reaction between H atoms and F_2 can produce HF in highly excited vibrational states, it is possible, in principle, that Reaction (12) might occur.

$$HF(v \geq 4) + F_2 = HF(v') + 2F \qquad (12)$$

Such a reaction would be exothermic if the excited HF molecule can transfer four or more vibrational quanta during the encounter. In 1963, Vedeneev, Chaikin, and Shilov (1963) suggested the possiblity of the occurrence of such reactions to explain the observed upper explosion limit in H_2-F_2-O_2 mixtures. Shortly thereafter, Kapralova et al. (1963) claimed to have obtained proof of chain branching in the H_2-F_2 system as well as in other F_2 systems.

The idea of energy chains is quite old in kinetics. Such processes often have been used to explain CO oxidation, H_2 oxidation sensitized by NO_2 or ClNO, O_3 decomposition, and H_2-Cl_2 reaction. As pointed out by Dainton (1956), in no case has the evidence for the existence of such chains been unequivocal. (On the other hand, ordinary chain-branching processes are well-accepted and occur in a wide variety of systems.)

Later, Kapralova, Margolina, and Chaikin (1969) favored a more elaborate branching scheme, i.e.,

$$HF^* + H_2 = HF + H_2^* \qquad (12a)$$

$$H_2^* + F_2 = HF + H + F \qquad (12b)$$

because their experimental results did not support the one-step energy chain shown in Reaction (12). For the branching step, they obtained an approximate activation energy of 2 to 3 kcal/mol. Alternative explanations for the effects of inert gases that did not require postulating energy chains were offered by Pavlov (1965) and by Levy and Copeland (1968). However, Kapralova and Chaikin (1969) presented evidence that ruled out the latter explanations. Later, Kapralova, Margolina, and Chaikin (1971) attempted to answer the question of which of the two processes, Reaction (12) or Reactions (12a) and (12b), was occurring. They argued that the effect of pressure on the upper explosion limit could be interpreted in two ways, depending upon which of the two mechanisms was responsible. If HF* is the chain carrier, then deactivation is due mostly to radiative decay; however, if H_2^* is the carrier, the fastest deactivation process would be at the walls. The effect of varying vessel diameter suggested the latter possibility. As a second check of their argument, they added a small amount of HF to a mixture and found that it lowered the pressure at the upper limit considerably. This, they claimed, would happen only if H_2^* were the chain carrier, not HF^*. It appears, to us, however, that the effect of HF could be the same regardless which species was the chain carrier. Furthermore, since it is likely that HF^* and H_2^*, if both are present, will be in rapid equilibrium, then a process that removes either of these will, in effect, remove both. Therefore, wall effects could hardly be used with confidence to distinguish between two mechanisms.

More recent work of Vedeneev, Propoi, and Sarkisov (1970) on the D_2-F_2 reaction is relevant here. By the use of arguments similar to these of Margolina et al. (1971), they concluded that, in this system, D_2^* is the important chain carrier, and, thus, they favored the analog of Reactions (12a) and (12b) over the analog of Reaction (12). However, they continued their discussion by pointing out experimental observations inconsistent with Reactions (12a) and (12b) and concluded that the branching step had to be Reaction (12d')

$$D_2(v = 3) + F_2 = F + DF + D \qquad (12'd)$$

where the $D_2(v = 3)$ is presumably formed by a sequence of steps such as

$$DF(v \geq 1) + D_2 \rightleftharpoons DF + D_2(v = 1) \qquad (12a')$$

$$D_2(v = 1) + D_2(v = 1) \rightleftharpoons D_2(v = 2) + D_2(v = 0) \qquad (12b')$$

$$D_2(v = 2) + D_2(v = 1) \rightleftharpoons \qquad 3) + D_2(v = 0) \qquad (12c')$$

As the schemes necessary to account for the data become increasingly involved, as with the above succession of mechanisms, it seems that the probability of their being correct decreases. Almost as an afterthought, Vedeneev, Propoi, and Sarkisov (1970) suggested that perhaps there is a low-lying, electronically excited state of F_2 that is responsible for the behavior that is so different from the other halogens. The implications of such a process are not yet clear, but the suggestion is worth examination.

An alternative to the mechanism Reactions (12a') through (12d') would be a sequence in which several quanta were transferred concertedly from HF^* to H_2, but there is no evidence, either experimental or theoretical, that such a process is likely. Trajectory calculations that could provide a better assessment of the probabilities of Reactions (12), (12a), and (12a') are under way in this laboratory.*

Kapralova, Margolina, and Chaikin (1972) subjected some of their explosion data to quantitative analysis in order to extract a numerical value for the supposed branching coefficient k_{12b}. When some of the rate coefficients values used in their calculations are updated, their conclusions lead to a value of $k_{12b} = 1.2 \times 10^7 \exp(-4100/RT)$ cc/mol-sec. Because of the simplifications in their kinetic scheme, necessitated by the simplicity of the analysis, this value is at best an approximate one. This expression yields a value of 1.2×10^4 cc/mol-sec at room temperature, whereas the deactivation rate of $H_2(1)$ by H_2, discussed previously, is about 4.4×10^7 at room temperature. Thus, in a stoichiometric mixture, less than 1/3000 of the excited H_2 would be expected

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*R. L. Wilkins, The Aerospace Corporation, private communication.

to undergo branching. However, there are serious difficulties with this entire analysis. For example, Kapralova, Margolina, and Chaikin (1972) deduced a value for $k_{10(0,1;1,0)}$ that is 60 times smaller than that obtained by more direct means.

A more extensive computer simulation analysis of the data given by Kapralova, Margolina, and Chaikin (1969) was carried out by Sullivan, Feber, and Starner (1975). They concluded that both Reactions (12) and (12b) were necessary to explain all the data. They deduced limits of the values of the corresponding rate coefficients of $0.6 - 2 \times 10^5$ for k_{12b} and $2 - 7 \times 10^6$ for k_{12}. The latter is about a factor of 200 to 700 times larger than that deduced by Kapralova, Margolina, and Chaikin (1972). Even if these larger values are correct, they are unlikely to have any influence on most chemical laser systems. Computer experiments carried out in this laboratory indicate that the occurrence of these two reactions with rate coefficients larger than the upper limits determined by Sullivan, Feber, and Starner (1975) has a negligible effect on H_2-F_2 pulsed-laser experiments *

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*N. Cohen, The Aerospace Corporation, unpublished studies.

VI. HYDROGEN FLUORIDE POLYMERS

Because of the great strength of the hydrogen bond formed between two HF molecules, there is a strong tendency for HF to form not only dimers but also polymers of higher order in the gas phase. The significance of these facts for chemical lasers is twofold: (1) The attractive force that results from the HF-HF hydrogen bond is probably responsible (at least in part) for the increasing rate of VT deactivation of HF by itself as the temperature decreases: and (2) The presence of the various polymers and their possible influence as chaperones promoting vibrational deactivation must be taken into account.

The first of these two issues has already been dealt with indirectly; the empirical expressions for HF VT self-deactivation include the contributions from attractive forces, including the hydrogen bond. The second matter has yet to be treated.

In order to determine the contributions of HF polymers to any relaxation processes, it is necessary to know their equilibrium concentrations. If the calculations published by the National Bureau of Standards in Report No. 10-904, Interim Report on the Thermodynamics of Chemical Species Important in Aerospace Technology (1972) are accepted as reliable, it can easily be shown that under most conditions of interest, dimers and hexamers are the polymeric species of greatest concentrations. The extent of dimerization and hexamerization as functions of HF pressure and temperature are shown in Figs. 14 and 15. For example, in Fig. 14, it is shown that at 300 K and an HF pressure of 60 Torr, the fraction of H_2F_2 is 1%. The same fraction of H_6F_6 is not reached, according to Fig. 15, until [HF] = 300 Torr at 300 K, but, at 200 K, both H_2F_2 and H_6F_6 are 1% of the HF pressure at 0.3 Torr.

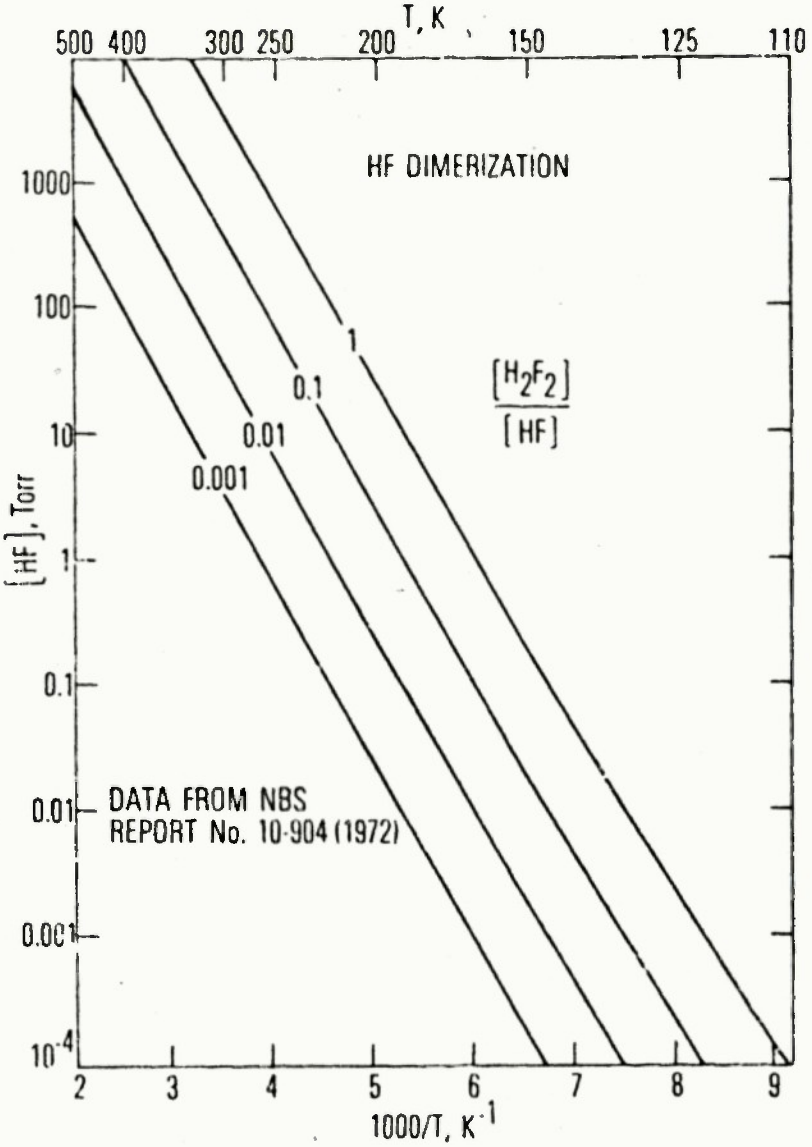

Fig. 14. HF Dimerization Calculated Values for $[H_2F_2]$/[HF] at Various Values of [HF] and $10^3/T$

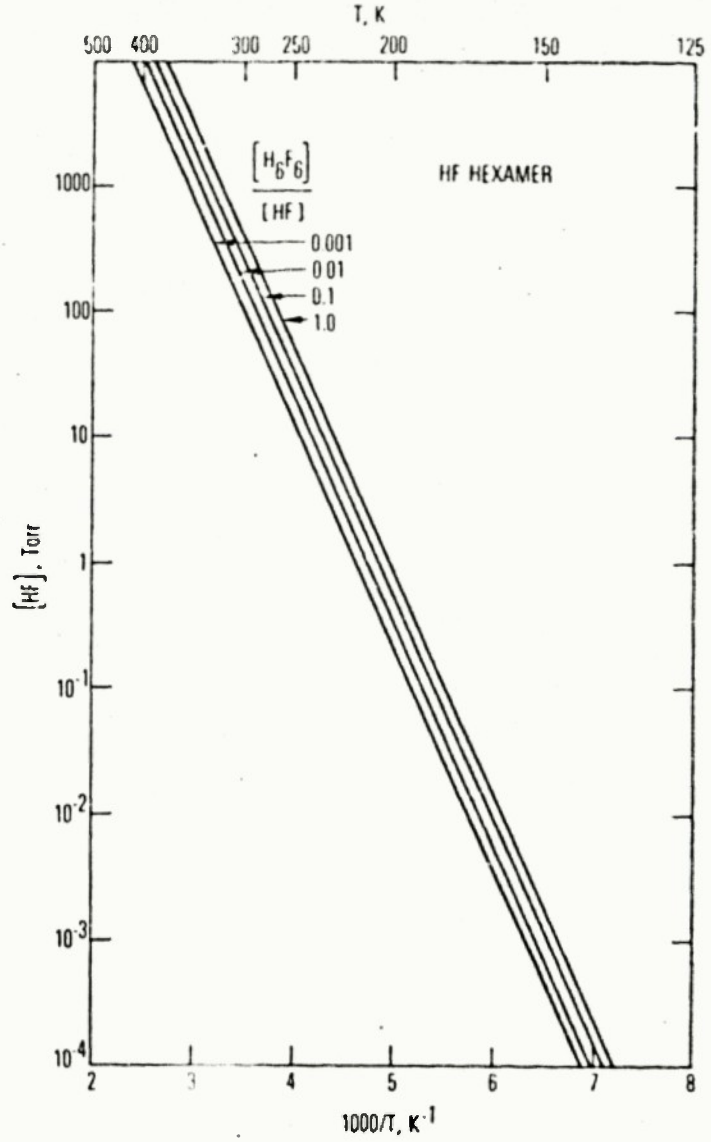

Fig. 15. Hexamerization Calculated Values for $[H_6F_6]/[HF]$ at Various Values of $[HF]$ and $10^3/T$

If the contribution of polymers to vibrational relaxation is significant, then the apparent value of $k^{HF}_{6(1,0)}$ should increase with HF total pressure. This effect has been observed at low temperatures by Hancock[*] and by Lucht and Cool.[**] In Hancock's study, the experiments were performed with DF rather than HF, but since the thermochemistry (including the hydrogen bond strength) of DF is nearly the same as that of HF, conclusions deduced in one case should apply reasonably well to the other. Hancock's relaxation data included a series at 197 K with DF in the pressure range of 0.08 to 0.5 Torr, at 210 K, 0 to 0.8 Torr, and, at 300 K, up to 18 Torr of DF. In each case, he observed an apparent increase in k as the pressure of DF increased. Calculations in this laboratory[***] indicate that the data could be explained reasonably well if it is assumed that the dimer has a probability of deactivation of 1/6 at all temperatures under consideration and the hexamer, 1/2. It then follows that the principal contribution at 300 K is from dimer (and monomer); at 200 K, the dimer is unimportant and the hexamer (and monomer) are responsible for the observed behavior.

It is, perhaps, still too early to try to fold these effects into HF chemical laser modeling. The uncertainties in the kinetic data and, more important, in the thermochemical data, are large, and refined measurements need to be made. Another important question, especially in cw lasers with gasdynamic effects, is whether the gas has time to reach equilibrium conditions with respect to polymer formation after nozzle expansion and freezing. The rate of polymer formation is, therefore, another important factor that should be studied.

Our recommended rate package at this time does not include values for HF deactivation by HF polymers; however, we feel that in the near future these processes will have to be taken into account if accurate laser modeling is desired.

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[*] J. K. Hancock, Naval Research Laboratory, private communication.

[**] R. Lucht, Cornell University, private communication.

[***] N. Cohen, unpublished studies.

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APPENDIX I

RECOMMENDED RATE COEFFICIENTS FOR H_2-F_2 SYSTEM

Reaction Number (as it appears in text)	Reaction	Rate Coefficient, cc, mol, sec, cal	M, A, g(v)
1a	$H_2(0) + M_1 \rightleftarrows 2H + M_1$	$k_{-1a} = 6.2 \times 10^{17} T^{-0.45}$	M_1 = all species except H and H_2
1b	$H_2(0) + H_2 \rightleftarrows 2H + H_2$	$k_{-1b} = 9.4 \times 10^{16} T^{-0.61}$	
1c	$H_2(0) + H \rightleftarrows 2H + H$	$k_{-1c} = 1.2 \times 10^{14} T^{0.5}$	
2	$F_2 + M_2 \rightleftarrows 2F + M_2$	$k_2^M = 5 \times 10^{11} A_M \exp(-35,100/RT)$	$A_F = 10, A_{F_2} = 2.7, A_M = 1$ all others
3	$HF(v) + M_3 \rightleftarrows H + F + M_3$	$k_{3(v)} = \frac{2A_M}{(n+1)} \times 10^{19} T^{-1} \exp[(-135100 + E_v - E_0)/RT]$	$A_F = A_H = A_{HF} = 5, A_M = 1$ for all others, n = 0 …
4	$F + H_2(0) \rightleftarrows HF(v) + H$	$k_4 = g(v) \times 1.6 \times 10^{14} \exp(-1600/RT)$	v = 1, 2, 3, g(1) = 0.17, g(2) = 0.55, g(3) = 0.28
4b-1	$HF(4) + H \rightleftarrows H_2(v) + F$	$k_{4b} = g(v) \times 7.4 \times 10^{12} \exp(-460/RT)$	g(0) = g(1) = 0.5, v = 0, 1
4b-2	$HF(5) + H \rightleftarrows H_2(v) + F$	$k_{4b} = g(v) \times 1.1 \times 10^{11} \exp(-510/RT)$	g(0) = 0.36, g(1) = 0.64, v = 0, 1
4b-3	$HF(6) + H \rightleftarrows H_2(v) + F$	$k_{4b} = g(v) \times 1.9 \times 10^{13} \exp(-580/RT)$	g(0) = g(1) = 0.22, g(2) = 0.56, v = 0, 1, 2
5	$H + F_2 \rightleftarrows HF(v) + F$	$k_5 = g(v) \times 1.2 \times 10^{14} \exp(-2400/RT)$	g(v) = 0, v = 0, 1, 2, g(3) = 0.06, g(4) = 0.13, g(5) = 0.35, g(6) = 0.44
6a	$HF(v) + HF \rightleftarrows HF(v-1) + HF$	$k_{6v}^{HF} = g(v)[1 \times 10^{14} T^{-1} + 3.5 \times 10^{4} T^{2.26}]$	g(1) = 1, g(2) = 8, g(3) = 28, g(4) = 25, g(v) = 5 for v ≥ 5, v = 1, …
6b	$HF(v) + H_2 \rightleftarrows HF(v-1) + H_2$	$k_6^{H_2} = 6 \times 10^{7} T v$	v = 1, …
6c	$HF(v) + M_4 \rightleftarrows HF(v-1) + M_4$	$k_6^{M_4} = 7.7 \times 10^{-7} A_M T^{3}$	$A_{Ar} = A_{F_2} = 1, A_{He} = 2$
6d	$HF(v) + H \rightleftarrows HF(v') + H$	$k_6^{H} = A(v) \times 4.5 \times 10^{12} \exp(-700/RT)$	0 ≤ v' ≤ v, v = 1, …, A(1) = 0.1, A(v ≥ 2) = 1. See Table 12 for detailed values for specific v, v'

APPENDIX I

RECOMMENDED RATE COEFFICIENTS FOR H_2-F_2 SYSTEM (Continued)

Reaction Number (as it appears in text)		Rate Coefficient, cc, mol, sec, cal	M, v, A, g(v)
6e	$HF(v) + F \rightleftarrows HF(v - 1) + F$	$k_6^F = 1.6 \times 10^{13}\ v\ \exp(-2700/RT)$	$v = 1, . . .$
7a	$H_2(v) + M_5 \rightleftarrows H_2(v - 1) + M_5$	$k_7^{M_5} = 2.5 \times 10^{-4} T^{4.3} A_{M_5}\ v$	$A_{H_2} = 4,\ A_{Ar} = 1$
7b	$H_2(v) + H \rightleftarrows H_2(v - 1) + H$	$k_7^H = 2 \times 10^{13} \exp(-2720/RT)$	$v = 1, . . .$
6f	$HF(v) + DF \rightleftarrows HF(v - 1) + DF$	$k_6^{DF} = 1.9 \times 10^{14} T^{-1} + 1.3 \times 10^2 T^3$	$DF = \sum_v DF(v)$
8	$HF(v) + DF(v') \rightleftarrows HF(v - 1) + DF(v' + 1)$	$k_8 = 6 \times 10^{11}\ v$	$v = 1, . . . ;\ v' = 0, . . . 6$
9	$HF(v) + HF(v') \rightleftarrows HF(v + 1) + HF(v' - 1)$	$k_9 = 3.3 \times 10^{15} T^{-1}$	$6 \geq v' \geq v + 2$
10	$HF(v - n) + H_2(v' + n) \rightleftarrows HF(v) + H_2(v')$	$k_{10} = v(8 \times 10^{11})$	$v = 1, . . . 6;\ n = 1, . . . v$
11	$HF(v) + N_2(0) \rightleftarrows HF(v - 1) + N_2(1)$	$k_{11} = v(11T^3 + 2.4 \times 10^9)$	$v = 1, ...$

APPENDIX II

VIBRATIONAL ENERGY LEVELS FOR HF AND H_2

Vibrational Level v	$E_v - E_o$, cal/mol	
	HF	H_2
1	11,327	11,897
2	22,161	23,121
3	32,517	33,687
4	42,406	43,607
5	51,839	52,900
6	60,824	61,570
7	69,369	69,640
8	77,477	77,120
9	85,149	84,020
10	92,878	90,360