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A Review of Rate Coefficients in the D_2-F_2 Chemical Laser System

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Interim Report

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The literature pertaining to the chemical kinetics of the deuterium-fluorine chemical laser system is critically reviewed and data are evaluated. A set of "best values" of all rate coefficients is recommended for modeling and computer calculations. Where experimental data are lacking, estimates are made on the basis of current theoretical techniques or data for analogous kinetic processes.

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PREFACE

The assistance of Dr. J. F. Bott in the original compilation of some of the vibrational relaxation data and in review of the manuscript is greatly appreciated.

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I. INTRODUCTION

Continued interest on the part of the chemical laser community in the D_2-F_2 system and a considerable amount of new experimental data have justified an update of the chemical kinetics review prepared two years ago. In these reports, part of a series prepared by the Chemical Kinetics Department of the Aerophysics Laboratory during the past five years, the kinetics of hydrogen halide laser systems are reviewed [Cohen (1971, 1972, 1974); Kerber, Cohen, and Emanuel (1973); Cohen and Bott (1975, 1976a, 1976b)]. 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 have not been covered again; to this extent, the reports are not completely cumulative in content.

The scope of this survey includes all reactions of interest in the D_2-F_2 chemical laser system. In addition, some energy-transfer processes involving other molecules are included because of the great interest in transfer laser systems involving the DF molecule.

In this report, all rate coefficients are entered in the form $AT^n \exp(-E/RT)$, even when theory or data suggest a slightly different temperature dependence. JANAF (Joint Army, Navy, Air Force) data have been used for thermochemical quantities, with the notation $K_{a,b} = k_a/k_b$ 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 the fitting of data with analytic expressions, particular attention has been given to the 300 to 1000 K temperature range; higher temperatures are not of practical interest, and lower temperatures are largely devoid of data. Extrapolation of the recommended rate coefficients outside this range should be carried out with caution.

II. RECOMBINATION-DISSOCIATION REACTIONS

A. D_2

The recombination/dissociation of deuterium was studied by three groups under shock-tube conditions. Jacobs, Giedt, and Cohen (1968), who summarized the results of two earlier studies, obtained for

$$2D + M \rightarrow D_2 + M \tag{1}$$

$$k_1^{Ar} = 10^{18}T^{-1},\ k_1^{D} = 20\ k_1^{Ar},\ \text{and}\ k_1^{D2} = 1.75\ k_1^{Ar}$$

This value of k_1^{Ar} is 1.4 times larger than that of Rink (1962) and approximately 1.3 times larger than that of Sutton (1962). The value of k_1^{D2} is larger than the results of Rink and Sutton by factors of 1.75 and approximately 3, respectively, and k_1^{D} is almost 2.9 times larger than Rink's value. Sutton's value for k_1^{D} agreed with that of Jacobs et al. at about 3500 K but had a considerably larger temperature coefficient.

Both Sutton and Rink used densitometry to monitor the course of the reaction; Jacobs, Giedt, and Cohen used the infrared emission from DCl as a tracer. More recently, Appel and Appleton (1974) studied D_2 dissociation in the presence of Ar by the more direct technique of atomic resonance absorption spectrophotometry. Over the 1800 to 4000 K temperature range, they obtained a dissociation rate coefficient $k_{-1}^{Ar} = 1.45 \times 10^{14}\ \exp(-93,000/RT)\ \text{cm}^3/\text{mol-sec}$. From this value and the equilibrium constant, a value of $3 \times 10^{11}\ T^{0.53} \exp(15,000/RT)\ \text{cm}^6/\text{mol}^2\text{-sec}$ can be calculated for k_1^{Ar} over that temperature range. This is within 25% of the value of Jacobs, Giedt, and Cohen at 3000 K but is significantly larger at 1000 K. Because of the larger temperature dependence of the expression, it does not seem reasonable to extrapolate to temperatures below the range of experimental conditions.

The uncertainties in these high-temperature rate coefficients are probably on the order of 50% or more; on the other hand, in the single recent low-temperature study of $k_1^{D_2}$ by Trainor, Ham, and Kaufman (1973), the quoted experimental uncertainty is less than 10%. These latter workers obtained $k_1^{D_2} = 10^{17}T^{-0.67}$ from data at 77 and 298 K. This extrapolates to a value of 4.7×10^{14} at 3000 K, which is 0.8 times the shock-tube result of Jacobs et al. and within their experimental error. Therefore, the $k_1^{D_2}$ value of Trainor et al. seems reliable at both high and low temperatures. An early room-temperature value of $k_1^D = 10^{15.88}$ was obtained by Amdur (1935); this is an order of magnitude smaller than the extrapolated results of Jacobs, Giedt, and Cohen if the T^{-1} temperature dependence is assumed valid down to 300 K. However, Amdur's result for H + H + H recombination is smaller than more reliable recent results by a factor of more than 2; it is possible, therefore, that a remeasurement at room temperature would prove Amdur's result for the D + D + D rate to be on the low side as well. Nevertheless, it does seem possible that T^{-1} is too strong a temperature dependence for k_1^D at lower temperatures than the shock-tube results, and, since lower temperatures are of greater interest, the single room-temperature measurement should be taken into account. Therefore, we suggest a rate coefficient of $k_1^D = 3 \times 10^{17}T^{-1/2}$, which agrees with the shock-tube results of Jacobs, Giedt, and Cohen at the midpoint of their temperature range (4000 K) and is about three times larger than Amdur's room-temperature measurement. This evaluation is tentative, however, and it is clear that a better room-temperature measurement is needed. Other results for $k_1^{D_2}$ have been summarized by Baulch et al. (1972).

B. F_2

The dissociation-recombination of fluorine was reviewed in some detail in the most recent report in this series (Cohen and Bott, 1976b); therefore, we will not reopen the subject here but simply note the conclusion of that review, namely, that the best current value for the dissociation rate coefficient of fluorine in argon, k_2^{Ar}

$$F_2 + Ar = 2F + Ar \tag{2}$$

is $k_2^{Ar} = 10^{13.7} \exp(-35,100/RT)$. Efficiencies of other chaperones, none of which has been reliably measured experimentally, are assumed to be

$$k_2^{Ar}:k_2^{H2}:k_2^{HF}:k_2^{F2}:k_2^{H}:k_2^{F} = 1:1:1:2.7:3:10$$

C. DF

The dissociation rate coefficient of DF has not been reported. Shock-tube measurements were recently made in this laboratory by Bott, but the data have not yet been fully analyzed. It seems reasonable to assume the same rate as that for HF, except for a slight increased activation energy corresponding to the increased bond dissociation energy of DF relative to HF, i.e., $k_3^{Ar} = 10^{19.05} T^{-1} \exp(-D_o/RT)$, where reaction (3) is

$$DF + M \rightarrow D + F + M \tag{3}$$

and D_o is taken to be 137.13 kcal/mol. Following our arguments in the HF case, we assume $k_3^{DF} = k_3^{D} = k_3^{F} = 5\ k_3^{Ar}$ and that other species have the same efficiency as Ar.

III. METATHESIS REACTIONS

A. $F + D_2$

Several studies of the metathesis reaction have been reported in the past five years. In all cases, the reaction rate was determined relative to some other fluorine atom reaction – either the isotopic reaction with H_2 or fluorination of a hydrocarbon or fluorocarbon. Because of the emphasis on the H_2/D_2 relative rates, a final determination of the best value for k_4

$$F + D_2 \rightleftharpoons DF + D \tag{4}$$

depends on the value for the $F + H_2$ rate coefficient, which, as suggested by Cohen and Bott (1976b), is itself still subject to some uncertainty.

Kapralova, Margolin, and Chaikin (1970) studied the competitive fluorination of H_2 and D_2 in spherical flasks at 77, 173, and 293 K. The HF and DF formed were analyzed by subjecting the mixture to a high-frequency discharge, then using EPR to assay the relative H and D atom concentrations. The rate coefficient ratio for $F + H_2/F + D_2$ was quoted as (1.48 ± 0.22) $\exp(-45 \pm 30)/RT$. However, when the data of Kapralova et al. are examined, it is seen that the calculated rate coefficient ratio for the three temperatures does not lie on a straight line on a log k versus 1/T plot. The data at 293 and 77 K give an Arrhenius activation energy difference of -45 cal/mol, rather than the quoted value of +45. The data at 293 and 173 K, however, give a relative activation energy of -146 cal/mol, and the results at 173 and 77 K are nearly the same within the experimental scatter. This negative relative activation energy is contrary to all of the other findings. Therefore, both sets of low-temperature data are suspect and should perhaps be ignored in an overall assessment of the best value for k_4.

Berry (1973) has reported relative rate coefficients for pairs of reactions, $F + HD/H_2$, $F + HD \rightarrow HF/DF$, and $F + HD/D_2$, obtained by measuring the relative gain coefficients of individual transitions in HF/DF lasers. From the three rate coefficient ratios for the above sets of reactions, one can calculate the ratio of k_{F+H_2}/k_{F+D_2} at room temperature to be 1.84. In order to deduce the various ratios, however, Berry must make use of the relative vibrational distributions of the various metathesis reactions involved. These numbers are determined as part of the same study. In the case of $F + H_2$ and $F + D_2$, Berry's results can be compared to the distribution numbers obtained by others [see Cohen and Bott (1976b) for a discussion of $F + H_2$; see below for $F + D_2$ distribution numbers], and the numbers are found to be slightly different. In the case of F + HD → DF/HF, however, there are no other data. If the available corrections are made, then the calculated ratio of 1.84 becomes 1.6. All of Berry's experiments were conducted at room temperature.

In two independent experiments, radiofluorine formed in the nuclear reaction $^{19}F(n, 2n)^{18}F$ was moderated to thermal velocities by buffer gas, then allowed to react with various hydrogenous compounds in pairs — the relative formation rates being determined by radioassay of the product molecules. In the experiments of Williams and Rowland (1973), the $F + D_2$ and $F + H_2$ reactions were studied in competition with the $F + C_2H_2$ reaction. HF and DF yields were inferred from the diminution in the CH_2CHF yield, which was determined by radiogas chromatography. From the ratio of the H_2/C_2H_2 and the D_2/C_2H_2 results, one can calculate the rate coefficient ratio for $F + H_2/F + D_2$ to be approximately 1.8 ± 0.6 at room temperature. Grant and Root (1974) studied the competition in D_2/C_3F_6 and H_2/C_3F_6 mixtures over the 303 to 475 K temperature range. From their results, they calculated the Arrhenius expression for the ratio of the H_2/D_2 fluorination reactions to be $(1.11 \pm 0.05) \exp[(356 \pm 26)/RT]$, which yields a room temperature ratio of 2.0.

Igoshin, Kulakov, and Nikitin (1974) used computer modeling of the shape of a chemical laser output pulse to determine the best values for the $F + H_2$ and $F + D_2$ rate coefficients in an HF and a DF laser, respectively.

For the two rate coefficients, they obtained $9.3 \times 10^{13} \exp(-1080/RT)$ and $5.9 \times 10^{13} \exp(-790/RT)$, respectively, the ratio of which is $1.6 \exp(-290 \pm 350/RT)$ or 0.98 at 300 K. Their measurements were made at 195 and 294 K. The accuracy of these results must depend, to some extent, on the reliability of the other rate coefficients used, and these are not amenable to comment because the paper provided insufficient detail.

Persky (1973) studied the competition between H_2 and D_2 for F atoms directly in a flow tube in which the F atoms were generated by passing SF_6 or CF_4 through a microwave discharge. HF and DF yields were measured by a quadrupole mass spectrometer. In the presence of large excesses of H_2 and D_2, the kinetics can be described simply by the competition between the two processes of interest, and all that is required for the analysis is a knowledge of the relative flow rates of H_2 and D_2 and of the relative peak heights of $m/e = 20$ and $m/e = 21$. Over the 163 to 417 K temperature range, Persky found that the rate coefficient ratio $k_{F+H_2}/k_{F+D_2} = (1.04 \pm 0.02) \exp(370 \pm 10/RT)$. The room temperature ratio is 1.91 ± 0.08.

Foon, Reid, and Tait (1972), as part of an extended series of studies of fluorination reactions, measured the relative rate coefficients k_{F+CH_4}/k_{F+D_2} and $k_{F+C_2H_6}/k_{F+D_2}$ at 183 to 358 K and 273 to 356 K, respectively. The rate coefficients for reaction of the ethane and methane had previously been determined by similar competitive techniques relative to higher hydrocarbons. Absolute values were assigned on the assumption of zero activation energy for reaction with C_3H_8 or n-C_4H_{10} and a value of 1×10^{13} cm^3/mol-sec for the Arrhenius A factor for C_2H_6. This latter value, however, was originally meant to be the assumed A factor per H atom; therefore, a better value for the A factor would be 6×10^{13}. [More recently, Truhlar (1972) and Muckerman and Newton (1972) advanced theoretical arguments that 6×10^{13} is too large by a factor of 2 to 3.] From this latter value, k_{F+D_2} is calculated to be $2 \times 10^{14} \exp(-2600/RT)$. From the value for k_{F+H_2} previously determined by Foon and Reid (1971), one obtains a rate coefficient ratio $k_{F+H_2}/k_{F+D_2} = (1.5 \pm 0.4) \exp(130/RT)$, or 1.87 at 300 K.

Several theoretical investigations of the $F + D_2$ reactions have been published; the most extensive is that of Wilkins (1973a, 1974a). Using three-dimensional Monte Carlo-selected trajectory calculations over an assumed LEPS potential energy surface, Wilkins determined not only the overall rate coefficient for the metathesis reaction but also the vibrational level distribution of the product DF molecules. From Wilkins' tabulated data, one calculates an expression of $1.57 \times 10^{16} T^{-0.86} \exp(-2026/RT)$ for k_{F+D_2} over the 300 to 800 K temperature range. Combining this with the expression Wilkins (1972) previously calculated for k_{F+H_2}, one obtains, for the rate coefficient ratio k_{F+H_2}/k_{F+D_2}, a value of 2.4 ± 0.3 at $T = 300$ to 800 K, with a room-temperature value of 2.3. Muckerman (1971) found the room-temperature ratio to be 1.2 ± 0.2; Jaffe and Anderson (1971, 1972) calculated $k_{F+D_2} = 10^{13.8} \exp(-2160/RT)$.

The various results are tabulated in Table 1. In the 300 to 400 K temperature range, good agreement is found in the results of Foon, Reid, and Tate, Williams and Rowland, Persky, and Grant and Root. At 200 K, the results of Foon, Reid, and Tate give a considerably smaller value for the rate coefficient ratio (2.08) than do the results of Persky (2.64) or Grant and Root (2.72); however, there is an experimental uncertainty of at least ±15% in the value of k_{CH_4}/k_{D_2}. The number of Foon, Reid, and Tate, therefore, could easily be as large as 2.4. Thus, when all the data are considered and weighed, the close agreement between Persky and Grant and Root strongly suggests a rate coefficient ratio of $k_{F+H_2}/k_{F+D_2} = [(1.1 \pm 0.05) \exp(360 \pm 20)/RT]$. Cohen and Bott (1976b) argued that the best room-temperature value for k_{F+H_2} is $1.5 \pm 0.5 \times 10^{13}$ cm^3/mol-sec. Only one study (Homann et al., 1970) was performed over a sufficient temperature range to make possible a determination of the activation energy, and that study yielded a value of 1.6 kcal/mol and a value at 300 K of 1×10^{13}. Therefore, to be consistent with the recommendation of Cohen and Bott (1976b) for the results of Homann et al. (1970) for k_{F+H_2}, one should choose $1.5 \times 10^{14} \exp(-1960/RT)$ cm^3/mol-sec for the expression for k_{F+D_2}.

Table 1. k_{F+H_2}/k_{F+D_2}

k_{H_2}/k_{D_2}	Temperature, K	Ref.
$(1.11 \pm 0.05) \exp[(356 \pm 26)/RT]$	303-475	Grant and Root (1974)
$(1.04 \pm 0.02) \exp[(370 \pm 10)/RT]$	163-417	Persky (1973)
1.75 ± 0.4	300 ?	Williams and Rowland (1973)
$(2.1 \pm 0.4) \exp[(-45 \pm 50)/RT]$[a]	77-293	Kapralova, Margolin, and Chaikin (1970)
$(1.5 \pm 0.4) \exp[(130 \pm 300)/RT]$	210-350	Foon, Reid, and Tait (1972)
$1.6 \exp[(-290 \pm 350)/RT]$	195-294	Igoshin, Kulakov, and Nikitin (1974)

[a] The expression given is the best fit for the data and differs from the expression the authors quote, which is $(1.48 \pm 0.22) \exp[(45 \pm 30)/RT]$.

In Table 2 are shown the results of studies (six experimental and one theoretical) of the product distribution of the vibrationally excited DF formed in the F + D_2 reaction. The molecular beam experimental measurements of Schafer et al. (1970) are for backscattering only (at 547 K) and are inconsistent with the other data (unless the relative rate coefficients have very different temperature dependencies). The four remaining measurements are in approximate agreement, although it is apparent that a more careful remeasurement would be of some value. The most recent results of Perry and Polanyi (1976) seem to be the most reliable at this time, and we recommend them here. These data should be corrected for the revision in Einstein coefficients discussed by Herbelin and Emanuel (1974), but the numerical change is very slight (within experimental uncertainty), and the results tabulated in Table 2 are uncorrected. According to the results of Perry and Polanyi, at room temperature, 75% of the available energy goes into vibrational and rotational energy of the product molecules. This is almost identical to the corresponding value for the F + H_2 reaction.

Table 2. Relative Pumping Rates for $F + D_2 \xrightarrow{k_{11}(v)} DF(v) + D$ at T = 300 K

$$k_{11}(v) = g_{11}(v)\, k_{11}(\text{total})$$

$g_{11}(0)$	$g_{11}(1)$	$g_{11}(2)$	$g_{11}(3)$	$g_{11}(4)$	Ref.	Technique
		>0.22	>0.36	0.42	Parker and Pimentel (1969)	Equal-gain chemical laser
0.009	0.014	0.037	0.21	<0.73	Schafer et al. (1970)	Crossed molecular beam (T = 547 K)
		0.29	0.41	0.3	Anlauf et al. (1970)	Discharge flow
	0.11	0.25	0.38	0.27	Polanyi and Woodall (1972)	Discharge flow
0.043	0.10	0.24	0.44	0.17	Berry (1973)	Relative-gain chemical laser
	0.04	0.14	0.50	0.32	Wilkins (1974a)	Theoretical Monte Carlo trajectory calculations
0.02	0.07	0.23	0.43	0.26	Perry and Polanyi (1976)	Discharge flow

Only recently has the question of the temperature dependence of the relative distribution numbers been satisfactorily answered by experimental data. The Monte Carlo calculations of Wilkins (1974) indicated that the ratios of pumping rates of v = 2, 3, and 4 were only slightly temperature-dependent, as can be calculated from Wilkins' three-parameter rate coefficients. These were derived from a least-squares fit through Wilkins' data derived from classical trajectory analysis:

$$k_{4(v=4)} = 10^{15.03} T^{-0.66} \exp(-1690/RT)$$

$$k_{4(v=3)} = 10^{15.5} T^{-0.76} \exp(-1730/RT)$$

$$k_{4(v=2)} = 10^{16.33} T^{-1.17} \exp(-2250/RT)$$

The latter two expressions yield a ratio of $k_{4(v=3)}/k_{4(v=2)}$ of approximately 4 at 500 K, increasing to about 10 at 200 K.

Coombe and Pimentel (1973), using chemical laser equal gain measurements, found a value of approximately 2.7 for $k_{4(v=3)}/k_{4(v=2)}$ at 567 K, which decreased to slightly more than unity at 153 K. More recently, Perry and Polanyi (1976), using what should be a more reliable technique, measured the relative distribution of product vibrational states over the 280 to 1130 K temperature range. They found the relative distribution to be even less temperature-sensitive than predicted by Wilkins' theoretical calculations, with $k_{4(v=3)}/k_{4(v=2)}$ decreasing from 2.0 at 300 K to 1.7 at 1130 K. Their ratio of $k_{4(v=4)}/k_{4(v=3)}$ was nearly constant at 1.7, in good agreement with Wilkins' calculations. The reason for the discrepancy between theory and experiment in the case of $k_{4(v=3)}/k_{4(v=2)}$ is not obvious, but at present we prefer the experimental results. If we utilize the results of Perry and Polanyi at 300 and 1130 K, and assume that the temperature dependence of the relative product distribution numbers can be expressed in the form of T^n, we can calculate values of n = 0, 0, -0.01, and -0.01 for v = 1, 2, 3, and 4, respectively. These, combined with the assumed value of 1.5×10^{14} $\exp(-1960/RT)$ for the overall value of k_4 given above, yield the following expressions for $k_{4(v)}$:

$$k_{4(v=1)} = 0.10 \times 10^{14} T^{0} \exp(-1960/RT) \text{ cm}^3/\text{mol-sec}$$

$$k_{4(v=2)} = 0.35 \times 10^{14} T^{0} \exp(-1960/RT) \text{ cm}^3/\text{mol-sec}$$

$$k_{4(v=3)} = 1.2 \times 10^{14} T^{-0.1} \exp(-1960/RT) \text{ cm}^3/\text{mol-sec}$$

$$k_{4(v=4)} = 0.7 \times 10^{14} T^{-0.1} \exp(-1960/RT) \text{ cm}^3/\text{mol-sec}$$

It is assumed that no DF product molecules are formed directly in the 0th vibrational level, although Perry and Polanyi did report a value for 0th-level production based on an extrapolation of their data for the higher vibrational levels. In any case, the fraction of DF formed in $v = 0$ is very small, if not zero; any errors arising from this assumption, therefore, are sure to be negligible.

B. $\underline{D + F_2}$

There have been no experimental studies of the overall rate coefficient for the pumping reaction

$$D + F_2 \rightarrow DF + F \tag{5}$$

In a Monte Carlo trajectory study, Wilkins (1973b) reported a value of $k_5 = 10^{15.46} T^{-0.55} \exp(-2840/RT)$ between 200 and 1000 K or approximately $10^{13.83} \exp(-2460/RT)$ between 200 and 500 K. A comparison of other pairs of reactions of H and D atoms with the same reagent leads one to expect the activation energy for k_5 to be a few hundred calories smaller than that for k_{H+F_2}. However, Wilkins' calculated $H + F_2$ rate coefficient in the same paper is in excellent agreement with the best available experimental results for that reaction, so the calculated $D + F_2$ rate will be accepted until direct experimental data are available.

No experimental data on the pumping distribution of reaction 5 are available. Kerber, Cohen, and Emanuel (1973) arrived at a set of distribution numbers by comparison with the analogous $H + F_2$ reaction. This is a reasonable approach in the absence of experimental data. Using such a comparison to the above $H + F_2$ pumping distribution measured by Polanyi and Sloan (1972) and recomputed with the Einstein coefficients of Herbelin and Emanuel (1974), we obtain values for $g_5(5)....g_5(9)$ of 0.10:0.19:0.29:0.38:0.04. Wilkins' theoretical trajectory calculations indicate that only v = 5....9 in the product DF molecules are formed. His temperature-dependent rate coefficients evaluated over the 200 to 1000 K temperature range are

$$k_5(5) = 10^{14.4} T^{-0.43} \exp(-2830/RT)$$

$$k_5(6) = 10^{14.1} T^{-0.37} \exp(-2770/RT)$$

$$k_5(7) = 10^{15.0} T^{-0.54} \exp(-3160/RT)$$

$$k_5(8) = 10^{15.4} T^{-0.74} \exp(-2750/RT)$$

$$k_5(9) = 10^{17.0} T^{-1.32} \exp(-4570/RT)$$

These results give room-temperature distribution values of approximately $k_5(5)....k_5(9)$ = 0.2:0.15:0.23:0.39:0.02, which are in reasonable agreement with the values derived from the comparison with the $H + F_2$ distributions. It is possible to fit all of the theoretical values obtained by Wilkins with reasonable accuracy (within a factor of 2) by the same temperature dependence, namely, $k_5(v) = 6.2 \times 10^{13}\, g(v) \exp(-2500/RT)\ \mathrm{cm^3/mol\text{-}sec}$, where $g(5) = 0.2$, $g(6) = 0.16$, $g(7) = 0.22$, $g(8) = 0.4$, and $g(9) = 0.02$. For ease of computation, these latter values are recommended in the Appendix.

IV. ENERGY TRANSFER PROCESSES

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

Vibrational energy transfer studies involving DF, though extensive, have lagged behind HF studies to some extent. Therefore, although we discuss here only results directly involving DF, additional insights can sometimes be gained by examination of the relevant HF data. We have not attempted a critical evaluation of the theoretical calculations that have been published. In the cases where experimental evidence seems so firm as to leave little room for doubt, theoretical predictions have been ignored. Theoretical results are discussed only where experimental data are insufficient or completely lacking.

Most experimental investigations result in the measurement of a relaxation time τ at a given pressure p and temperature T. In order to convert this relaxation time to a rate coefficient k in units of cm^3/mol-sec, certain assumptions concerning the nature of the relaxation process must be made. According to the harmonic oscillator 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 $v = 0$, $k_{(0,1)}$ the rate coefficient for the backward reaction, ΔE the exothermicity of the reaction, and R the universal gas constant.

In the following paragraphs, different chaperones are treated, and an analytical expression has been fitted to the results of each experimental study where the deactivation reactions were studied over a range of temperatures. Generally, these expressions fit the data with an accuracy of 10% to 15%. Most of the results are summarized in Table 3 and Figs. 1 through 9.

Table 3. Comparison of HF(v = 1) and DF(v = 1) Deactivation by Several Polyatomic Molecules at Room Temperature

Deactivating Molecule	HF(v = 1), k(μsec Torr)$^{-1}$	Ref.	DF(v = 1), k(μsec Torr)$^{-1}$	Ref.	$\frac{k_{DF}}{k_{HF}}$
CH_4	5.3×10^{-2}	Hancock and Green (1973)	$(2.2 \pm 0.1) \times 10^{-1}$	Bott (1976)	0.3-1
	6.4×10^{-2}	Anlauf, Dawson, and Herman (1973)			
	2.1×10^{-2}	Kwok and Cohen (1974)			
	$(2.6 \pm 0.3) \times 10^{-2}$	Bott (1976)			
C_2H_6	11.0×10^{-2}	Hancock and Green (1973)	$(6.1 \pm 1.0) \times 10^{-1}$	Bott (1976)	0.55-1
	5.6×10^{-2}	Anlauf, Dawson, and Herman (1973)			
	$(5.9 \pm 0.6) \times 10^{-2}$	Bott (1976)			
C_4H_{10}	17.0×10^{-2}	Hancock and Green (1973)	$(12.6 \pm 1.5) \times 10^{-1}$	Bott (1976)	7.4-9.8
	$(12.8 \pm 1.3) \times 10^{-2}$	Bott (1976)			
C_2H_2	5.9×10^{-2}	Anlauf, Dawson, and Herman (1973)	$(4.0 \pm 0.6) \times 10^{-2}$	Bott (1976)	0.7-4
			$(2.34 \pm 0.03) \times 10^{-1}$	Wendelken and Stout (1975)	
C_2H_4	5×10^{-2}	Anlauf, Dawson, and Herman (1973)	$(1.75 \pm 0.2) \times 10^{-1}$	Bott (1976)	3.5
C_6H_6			$(3.9 \pm 0.02) \times 10^{-1}$	Wendelken and Stout (1975)	
CS_2			$(4.6 \pm 0.07) \times 10^{-2}$	Wendelken and Stout (1975)	
COF_2	$(5.74 \pm 0.5) \times 10^{-2}$	Bott and Cohen (1974)	$(3.81 \pm 0.05) \times 10^{-2}$	Wendelken and Stout (1975)	0.7
SO_2	$(2.4 \pm 0.3) \times 10^{-2}$	Bott and Cohen (1974)	$(1.27 \pm 0.15) \times 10^{-2}$	Bott (1976)	0.5
BF_3	$(1.53 \pm 0.15) \times 10^{-3}$	Bott and Cohen (1974)	$(7.0 \pm 1.0) \times 10^{-3}$	Bott (1976)	4.6
CF_4	$\leq(4.2 \pm 0.6) \times 10^{-4}$	Bott and Cohen (1974), Kwok and Cohen (1974)	$\leq(1.0 \pm 0.1) \times 10^{-3}$	Bott (1976)	
			1.1×10^{-4}	Wendelken, Wilson, and Clendening (1974)	
$CBrF_3$	$\leq(3.9 \pm 0.6) \times 10^{-4}$	Bott and Cohen (1974)	$\leq(5.8 \pm 0.6) \times 10^{-4}$	Bott (1976)	
NF_3	$<3 \times 10^{-4}$	Bott and Cohen (1974)	$\leq 5 \times 10^{-4}$	Bott (1976)	
		Wendelken, Wilson, and Clendening (1974)	4.9×10^{-4}	Wendelken, Wilson, and Clendening (1974)	
SF_6	$<5 \times 10^{-5}$	Bott and Cohen (1974)	$(2.58 \pm 0.05) \times 10^{-4}$	Wendelken and Stout (1975)	
NO		Blauer et al, (1972)		Blauer et al. (1972)	0.44[a]

[a] Rates calculated at 1200 K.

1. SELF-DEACTIVATION OF DF

Data on DF self-relaxation have been accumulated by several independent workers, permitting considerable reliance to be placed on the rate coefficient for the process

$$DF(1) + DF \rightleftharpoons DF(0) + DF \qquad (6)$$

over the temperature range of 200 to almost 5000 K. The data are shown in Fig. 1; the rate coefficient k_6 reaches a minimum at approximately 800 K, with a temperature dependence of $T^{-1.3}$ at low temperatures and $T^{2.37}$ at high temperatures. Throughout the temperature range, the data are fitted reasonably well by the expression $k = 10^{14.9}T^{-1.3} + 10^{4.05}T^{2.37}$ cm^3/mol-sec.

The behavior of the higher vibrational levels are of some interest, but no direct data, either experimental or theoretical, have been reported for any other processes of the form

$$DF(v) + DF(v') \rightleftharpoons DF(v-\Delta v) + DF(v')$$

Therefore, estimates for the variation of $k_{6(v,v')}$ with v, v', and Δv are best made by comparison with the HF system. However, this recourse is far from ideal, since there is still considerable uncertainty over the HF self-deactivation rate coefficients [Cohen and Bott (1976a, 1976b)]. One fact seems clear at present: early estimates of V-T, R rate coefficients based on the assumption of the harmonic-oscillator-like behavior of HF (and, therefore, presumably, DF) are almost certainly unrealistic, leading to the expectation of a smaller v-dependence of the rate coefficients for V-T deactivation than now seems to be the case. Part of the problem stems from the difficulty of separating V-V from V-T, R effects in the relaxation of vibrational levels above v = 1. Currently, the best estimate for the V-T, R rate coefficients for HF self-deactivation indicates that they scale with v as 1:6:12:20:35:60 for

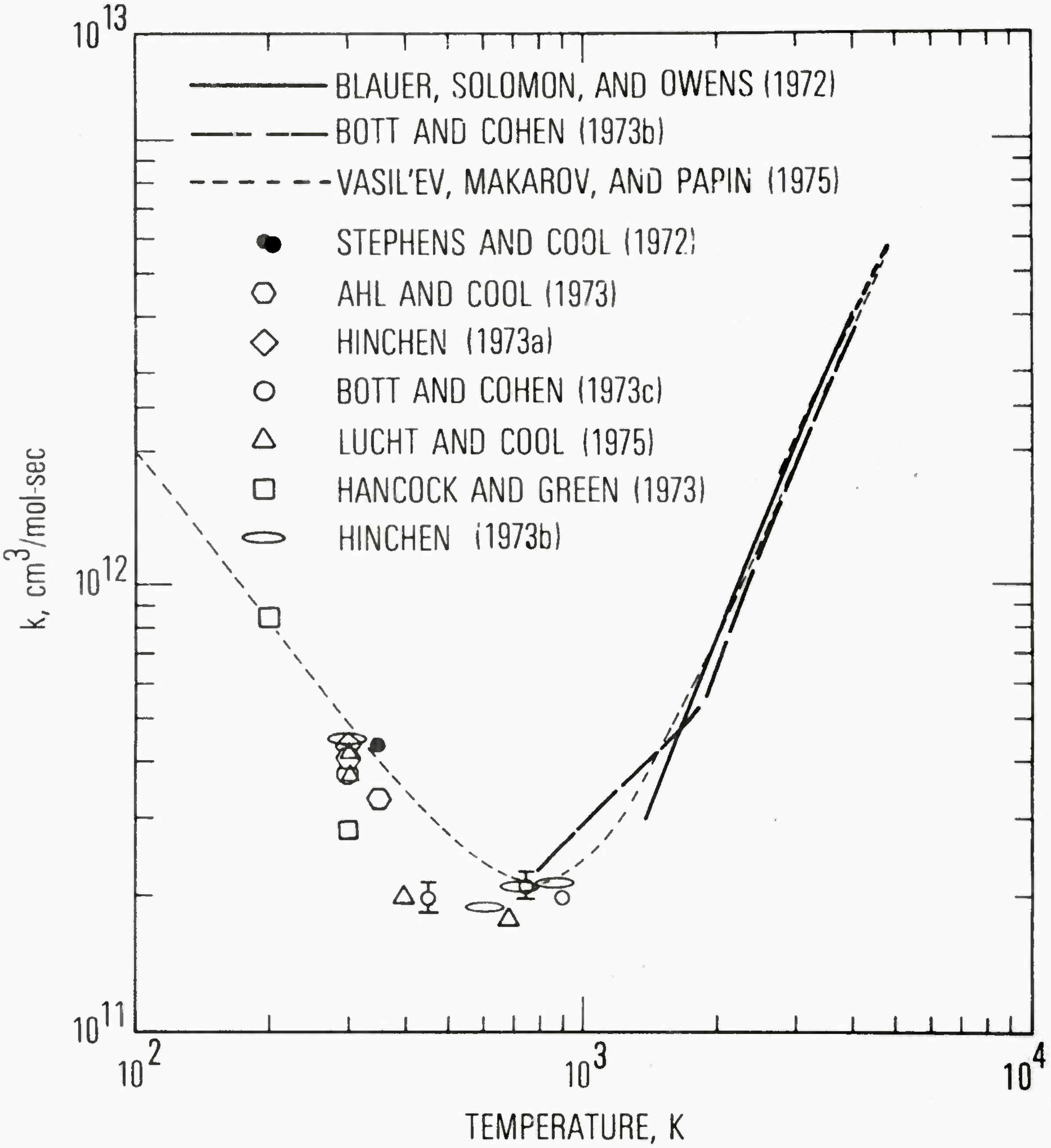

Fig. 1. Experimental Rate Coefficients and Vibrational Relaxation of DF(1) by DF(0): DF(1) + DF(0) → DF(0). (Solid curve is four-parameter fit through data, $k = 10^{14.9}\ T^{-1.3} + 10^{4.05}\ T^{2.37}$ cm^3/mol-sec.)

$v = 1, 2, 3, 4, 5, 6$. These numbers were estimated indirectly from experimental data, with the assumption that only single-quantum transitions take place. However, this assumption may also be violated, in which case, the above numbers would represent the total relative deactivation rates from each indicated vibrational level, with the product HF molecules distributed over all the vibrational levels below the initial level. In the case of DF, it seems best to assume single quantum transitions only and to scale the rate coefficients with v in the same manner as is done in the HF case. It should be recalled, however, that there is considerable uncertainty in this area at present. We also assume, for the present, that the temperature dependence of the relaxation rate coefficients for all the levels is the same as for the $v = 1$ level. Although this may be reasonable at high temperatures, it is likely to be incorrect at low temperatures, at which the vibrational energy can significantly perturb the intermolecular attractive forces (including hydrogen bonding) that are responsible for the collision and energy transfer mechanisms.

Theoretical calculations have been reported by Berend and Thommarson (1973) and are currently under way by Wilkins (private communication).

2. Ar AND He

The vibrational relaxation of DF in the presence of Ar was examined in three separate laboratories. The work covering the widest temperature range (1000 to 4600 K) was performed in a shock tube by Bott (1975); his work agrees well with, but expands upon, the earlier study of Bott and Cohen (1973a). Bott's results can be expressed within 10% below 3000 K by the simple expression $k_6^{Ar} = 7 \times 10^{-5} T^{4.3}$ cm^3/mol-sec. Hinchen (1973a) attempted a room-temperature measurement of the relaxation process but could obtain only an upper limit of 6×10^8 cm^3/mol-sec. This lies above the extrapolated values of Bott. Blauer, Solomon, and Owens (1972) were unable to detect any measurable contribution to DF relaxation in DF-Ar mixtures attributable to the Ar. Bott also reported values for DF relaxation by

He in the 1000 to 4000 K temperature range. His results are expressed by $k_6^{He} = 4 \times 10^{-6} T^{4.75}$ cm^3/mol-sec, which is slightly higher than k_6^{Ar} at the lower temperatures. A similar shock-tube study was reported by Vasil'ev, Makarov, and Papin (1975). They obtained a relaxation time described by $P\tau = 0.0019 \exp(101.5/T^{1/3})$ μsec-atm, which corresponds closely to an expression for the relaxation rate coefficient of $k = 17.2\ T^{2.75}$. Results are shown in Fig. 2.

3. D AND H ATOMS

Heidner and Bott (1975) studied the vibrational relaxation of HF and DF in the first vibrational level by H and D atoms (four combinations in all) at room temperature. Atoms were generated by passing He-H_2 or He-D_2 through a 2450-MHz microwave discharge in a low-velocity (300 cm/sec) flow system. An HF(DF) laser was used to excite the HF(DF) into the first vibrational level, and the rate of relaxation in the presence and absence of atomic species was monitored by observing the decay of the laser-induced fluorescence.

With the microwave turned off, the decay was due to the $H_2(D_2)$; with the discharge turned on, the altered decay rate was due to the presence of atomic species (increased decay rate) and smaller molecular species (decreased decay rate). In principle, then, one can observe either a faster or a slower decay when the microwave is turned on, depending on the relative concentration ratio of D_2:D and the relative relaxation rates. In the case of DF in the presence of D atoms, the best value for the relaxation rate coefficient k_6^D for the process

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

was $(-1 \pm 9) \times 10^{10}$ cm^3/mol-sec, where the above process includes both reactive (i.e., F-atom transfer) and nonreactive deactivation. This value, although possibly as large as 1×10^{11}, indicates that the DF + D rate coefficient is somewhat smaller than the HF + H rate coefficient, measured in the

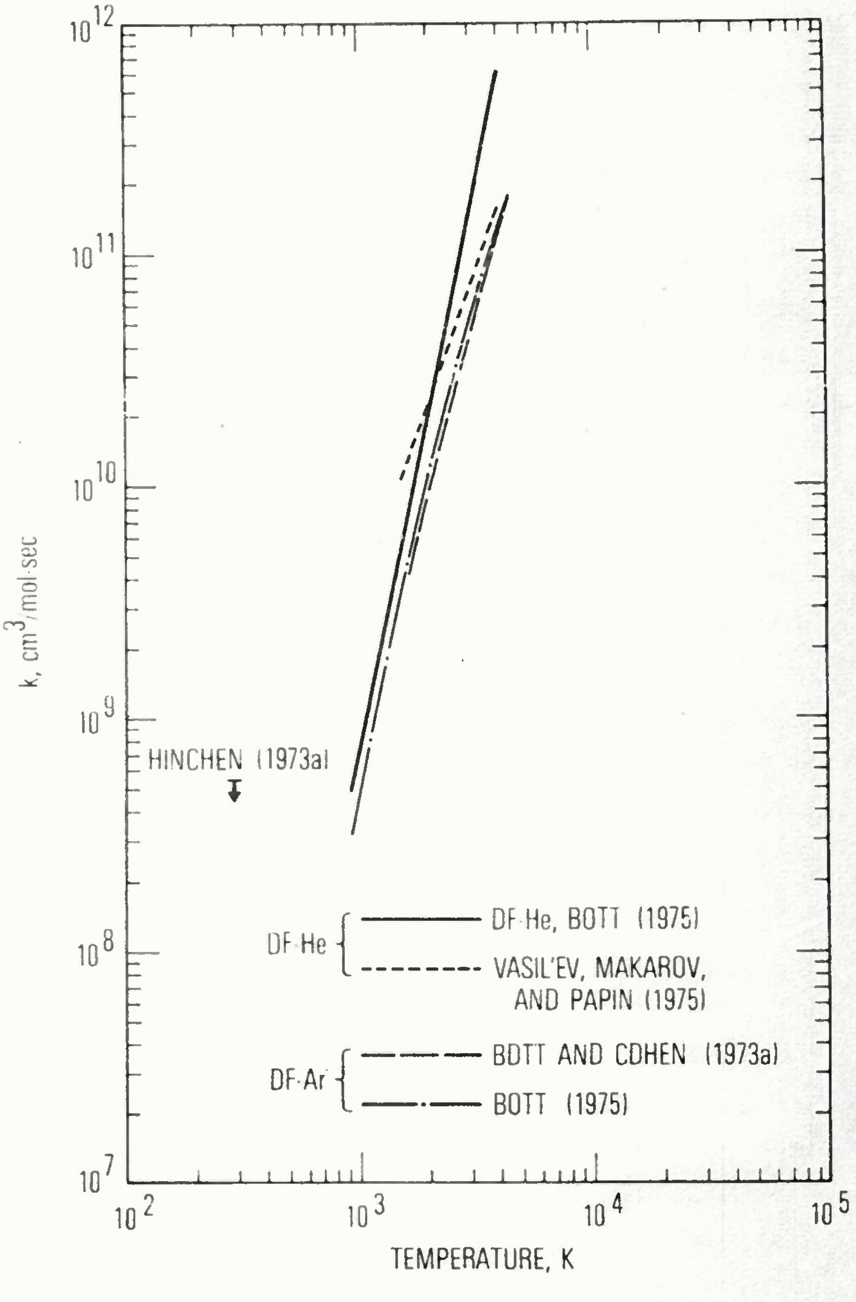

Fig. 2. Experimental Rate Coefficients for Vibrational Relaxation of DF(1) in the Presence of Ar or He

same apparatus to be $(1.4 \pm 0.04) \times 10^{11}$ cm^3/mol-sec. This pronounced isotope effect was anticipated, to some extent, by trajectory calculations by Wilkins (1975), who found that, at room temperature, $k_{HF+H}/k_{DF+D} = 3.8$. On the other hand, Thompson (1972) found k_{DF+D} to be slightly larger than k_{HF+H} at 1000 K, with temperature profiles indicating the same relationship at 300 K. The experimental results indicate that D atoms are considerably less significant as a deactivating species in a DF laser than H atoms are in an HF laser. The important questions of how the rates scale with v or T have not yet been addressed experimentally. Until they are, we use the theoretical results of Wilkins (1974c) to scale the rate coefficients. Wilkins' results indicate that all $k^{D}_{6(v,v')}$ can be fitted within a factor of 2 by $k_{v,v'} = 10^{13}$ exp(-2000/RT) cm^3/mol-sec. We reduce his value for v = 1, v' = 0 by a factor of 20 to give agreement with the experimental value of Heidner and Bott for $k^{D}_{6(1,0)}$.

In the same paper, Heidner and Bott reported the relaxation rate coefficient k^{H}_{6} of DF by H atoms to be $(6.7 \pm 1.8) \times 10^{10}$ cm^3/mol-sec, or about 0.5 times the HF+H rate coefficient. Wilkins calculated the ratio of k_{DF+H}/k_{HF+H} to be approximately 0.3 at room temperature.

4. F AND F_2

Quigley and Wolga (1975) studied the deactivation of both HF(1) and DF(1) by F atoms at 300 K by the laser-induced fluorescence method. They found k^{F}_{6} to be $(4 \pm 0.7) \times 10^{11}$ cm^3/mol-sec, which was approximately 2.3 times larger than the relaxation rate of HF(1) by F atoms. In these experiments, the complication of correcting for the effects of the parent homonuclear diatomic is minimal, since the deactivation rate of DF by F_2 is negligible. Quigley and Wolga measured $k^{F_2}_{6}$ to be $<5 \times 10^{8}$ cm^3/mol-sec. An even smaller upper limit has been reported for the deactivation of HF(1) by F_2 [Fried, Wilson, and Taylor (1973)].

Two high-temperature shock-tube studies have also been reported. Blauer and Solomon (1973) studied the reaction over the 1564 to 3385 K temperature range by shock heating mixtures of 3.6% DF and either 0.8% or 1.9% F_2. The F_2 dissociation rate is rapid compared with DF vibrational relaxation at these temperatures; thus, F atoms are the principal chaperone once corrections have been made for the DF itself and the inert diluent, Ar. They found $k_{6_{13}}^{F}$ to increase with temperature, from approximately 6×10^{12} at 1500 K to 4×10^{13} at 3400 K. Bott and Cohen (1973a) shock heated mixtures of 2% DF, 1% SF_6, and 97% Ar to temperatures between 1890 and 3000 K. From the known dissociation rate of SF_6, they could calculate the time-dependent values of [F] and obtained values of k_6^F of approximately $(1.5 \pm 0.5) \times 10^{13}$ cm^3/mol-sec throughout their temperature range. Comparison with HF-F data indicates that the DF(1)-F relaxation rate is slower than the HF(1)-F rate by a factor of approximately 2 at 2500 K.

Trajectory calculations on the DF(v) + F system were performed both Thompson and Wilkins, who presented and compared their results in a series of papers [Thompson (1972, 1974); Wilkins (1973c, 1974b)]. These calculations indicate that the DF(1)-F deactivation rate is comparable to the HF(1)-F rate at 2500 K and slower by a factor of 2 at 300 K. Thus, with respect to the isotopic rate coefficient ratio, the agreement between theory and experiment could be improved somewhat.

Wilkins' results indicate that the $k_{o(v,v')}^{F}$ can be fitted approximately by $k_{6(v,v')}^{F} = 4 \times 10^{12} v \exp(-3200/RT)$ cm^3/mol-sec. Until more experimental data are available, we recommend his results, scaled up by a factor of 10 to give near agreement with experimental data.

5. HF

The vibrational relaxation of DF(v) in the presence of HF(0) (or higher vibrational levels of HF) is of practical significance in combustion-driven devices that produce HF in the plenum. Several measurements of k_6^{HF} have been made, spanning the temperature range of 210 to 750 K and 1700 to 3800 K. All results, with the exception of those of Ahl and Cool (1973) and the uncorrected data of Lucht and Cool (1974a), are shown in Fig. 3; the latter two papers have been superseded by the more recent publication of Lucht and Cool (1975). Bott (1974), Lucht and Cool (1975), and Hinchen (1973b) all produced vibrationally excited DF by laser radiation and monitored the fluorescence decay in a stationary cell, heated or cooled to the desired temperature. Kwok and Wilkins (1975) and Airey and Smith (1972) used a chemical reaction to produce DF(v) and monitored higher vibrational levels as well. Airey and Smith used a microwave discharge to dissociate some D_2 in the presence of Ar, then mixed these species with F_2 in a spherical vessel. They were able to observe DF(1) and DF(2) decay. Kwok and Wilkins produced F atoms by passing a mixture of SF_6 and Ar through an 8-MHz rf discharge; these were admitted to a 10-cm-diameter flow tube operated at 1-Torr pressure and allowed to mix with D_2. The fluorescence of DF(v) was monitored for v = 1 through 4.

The results of Bott, Lucht and Cool, and Hinchen are in good agreement, as Fig. 3 shows. All the data below 750 K can be fitted, within 25%, by the expression $k_6^{HF} = 5.2 \times 10^{14} T^{-1.18}$ cm^3/mol-sec. The data of Lucht and Cool above 300 K lie somewhat below those of Bott and of Hinchen. However, in view of the experimental uncertainties, it does not seem fruitful at this time to select one set of data to the exclusion of the others; therefore, the recommended rate coefficient falls impartially between the different sets of data. Comparison with Fig. 1 shows that HF is a slightly less efficient chaperone than DF itself above 1500 K; in the low-temperature portion of the V-shaped curve, however, the efficiencies are very similar.

Although the results of both Kwok and Wilkins and of Airey and Smith at 300 K for DF(1) lie considerably above the others, we can still use their relative results to conclude something about the behavior of DF(v) relaxation in the presence of HF as a function of v. Airey and Smith found DF(2) to

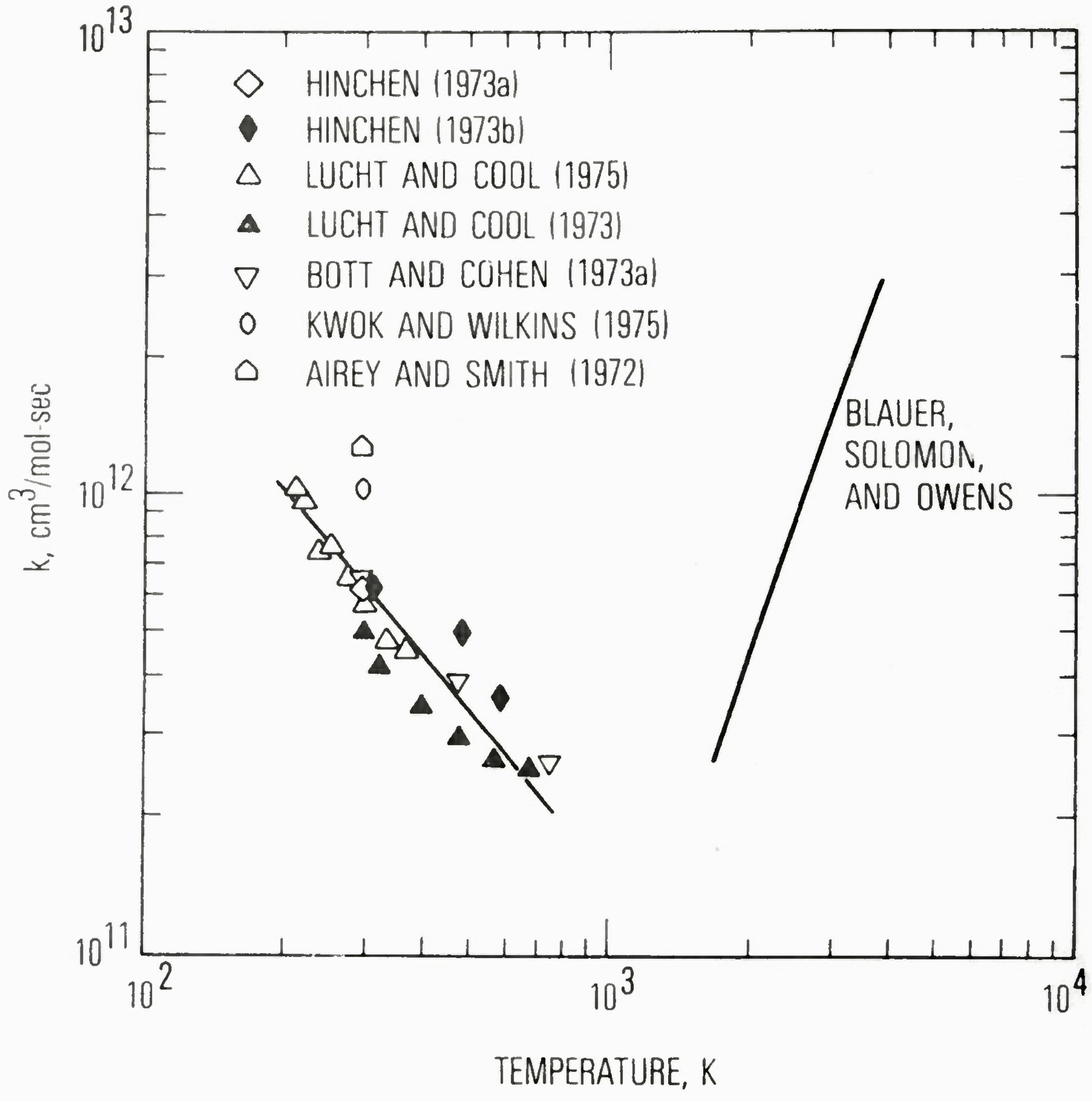

Fig. 3. Experimental Rate Coefficients for Vibrational Relaxation of DF(1) by HF(0): DF(1) + HF(0) → DF(0) + HF(0). (Solid line through data below 1000 K is best two-parameter fit.)

relax about 30% faster than DF(1). Kwok and Wilkins found the relaxation rate coefficients to vary as 1:2.8:5:1.6 for v = 1, 2, 3, 4. Kwok plans to refine these results and extend them to still higher v levels at a later date. The latter results indicate considerable deviation from the simple harmonic oscillator law of $k(v) \propto vk(1)$. This observation has been made in the case of HF(v) relaxation by HF but with greater precision. Until the DF results are confirmed and refined, we recommend application of the conclusions in the HF case to DF: namely, that k(v) varies as v_n where $2 < n < 3$. At present, a value of 2.2 ± 0.2 seems to be the best choice for n.

6. D_2

Because of the near resonance between DF and D_2, it is difficult to separate V-V effects from V-T(R) effects. (The same difficulty is encountered in the case of DF-DF interactions,as discussed earlier.) Under certain conditions, the separation can be made. When DF molecules are excited to the first vibrational level in the presence of D_2, there is an initial fast decay of the DF(1) population as energy is transferred to D_2 vibrational energy (V-V process). At longer times, the coupled populations of DF(1) and $D_2(1)$ decay together by V-T(R) processes. If the two time constants for the V-V and the V-T(R) processes are sufficiently different, meaningful conclusions can be drawn about the rates of the individual steps. The small time constant is a function only of the V-V transfer; the large time constant depends on both V-T(R) processes (DF(1) deactivation by D_2 and $D_2(1)$ deactivation by DF). Since D_2 self-relaxation by V-T(R) processes is slow compared with DF self-relaxation, it is assumed that D_2 relaxation in the presence of DF as chaperone is also slow; therefore, the long DF time constant is essentially a function only of DF(1) relaxation by D_2.

Bott (1974b) has made use of these relationships to determine the value of $k_6^{D_2}$ over the 295 to 436 K temperature range. He obtained a value of 100 ± 40 $\sec^{-1}$ Torr^{-1} throughout that range; the scatter in the data was too large to permit a meaningful estimate of the temperature dependence. In the case of the HF-H_2 system where high-temperature data are available, it was found that data can be fitted reasonably well if it is assumed that the deactivation of HF(1) by H_2 and by HF has the same temperature dependence. If we make the analogous assumption in this case, we arrive at a $T^{2.4}$ temperature dependence for $k_6^{D_2}$; thus, $k_6^{D_2} = 1.4 \times 10^3 T^{2.4}$ cm^3/mol-sec. The v dependence of this rate coefficient has not been measured or studied theoretically; we assume a linear v dependence until such data become available.

B. VIBRATIONAL-VIBRATIONAL ENERGY TRANSFER INVOLVING DF

In general, the rate of energy transfer increases as the magnitude of vibrational energy converted to translational energy decreases; consequently, V-V energy transfer, in which only a small surplus of energy is transformed to translational energy, is generally much faster than V-T(R) transfer. In the case of homonuclear diatomics, the ratio of V-T to V-V transfer rates is generally several orders of magnitude; HF and DF are unusual in that the difference between V-T and V-V rates is only one order of magnitude. This anomaly makes the experimental separation of V-V from V-T processes difficult. In a typical laboratory experiment designed to measure energy transfer, only the population of the vibrationally excited reagent is monitored; the fate of the energy transferred is only inferred. Therefore, one typically measures a sum of $k_6^{AB} + k_7^{AB}$, where the rate coefficients refer, respectively, to the processes shown:

$$DF(v_1, j_1) + AB(v_2, j_2) \rightleftharpoons DF(v_1', j_1') + AB(v_2, j_2') \qquad \text{V-T } k_6^{AB}$$

$$DF(v_1, j_1) + AB(v_2, j_2) \rightleftharpoons DF(v_1', j_1') + AB(v_2', j_2') \qquad \text{V-V } k_7^{AB}$$

In the V-T(R) process, j_2 may change, but v_2 is constant; in the V-V process, v_2 changes. The simplest assumption to make is that k_7^{AB} is much larger than k_6^{AB} for such parallel processes, and this is the case for $v_1 = 1$. However, in the case of DF and HF, recent evidence indicates that the V-T(R) rate coefficients k_6^M can scale up with v much faster than the harmonic oscillator rate law predicts. Thus, for upper vibrational levels, the assumption that V-V processes dominate over V-T(R) is probably not valid. Interpretation of data is further complicated by the probable occurrence of multiquantum transfer processes, which also seem to occur in the HF and DF systems with non-negligible probabilities. These and related matters have been discussed in more detail by Cohen and Bott (1976a, 1976b).

1. DF

DF V-V relaxation measurements were reported almost simultaneously by Bott (1973) and by Ernst et al. (1973). Bott used the shock-tube, laser-induced fluorescence (STLIF) technique to measure the energy transfer rate for the process

$$DF(2) + DF(0) \rightleftharpoons DF(1) + DF(1) \tag{7}$$

over the 295 to 720 K temperature range. Ernst et al. studied the process at room temperature only. Bott found the rate coefficient $k_{7(1,1;2,0)}$ for the exothermic reaction (the reverse of the process written above) to vary as T^{-1} when expressed in units of cm^3/mol-sec, with $k = 6 \times 10^{15}\ T^{-1}$, indicating an exchange probability of approximately 0.2 at room temperature. Ernst et al. obtained $1.1 \times 10^{13}\ cm^3$/mol-sec for the endothermic reaction, or 1.7×10^{13} in the exothermic direction. This is about 15% smaller than Bott's room-temperature value.

Measurements on higher vibrational levels have not yet been made. However, it might be useful to point out that in the case of HF-HF V-V exchange, recent trajectory calculations by Wilkins indicate that log $k_{v,v;v-1,v+1}$ decreases linearly with v: thus, the rate coefficient for $2 + 2 \rightleftharpoons 1 + 3$, $k_{2,2;1,3}$ is about $0.5\ k_{1,1;0,2}$, and $k_{5,5;4,6}$ is $0.1\ k_{1,1;0.2}$ (Wilkins, private communication). The same behavior would be expected to occur in the case of DF. Thus, in the absence of any experimental data, we assume Wilkins' HF findings to be valid for DF and write $k_{7(v,v;v+1,v-1)} = (1.8)^{1-v}\ k_{7(1,1;2,0)}$.

2. D_2

Three experiments designed to measure quenching of DF(v) by D_2 have been published.

$$DF(1) + D_2(0) \rightleftharpoons DF(0) + D_2(1) \tag{8}$$

Bott (1974) used the STLIF technique at temperatures from 295 to 732 K. In this procedure, a mixture of DF, D_2, and diluent (Ar in this case) is shock heated to an appropriate temperature; measurements are made behind the reflected shock and consist of monitoring the decay of fluorescence induced by a DF laser pulse. Hinchen (1973a) used laser-induced fluorescence in a stationary cell at 295 K. Kwok and Wilkins (1975) used a medium-pressure (1 Torr), large-diameter flow tube (10 cm), in which DF(v) was produced chemically (described above) at 298 K. They were able to observe the decay of DF(v) for v = 1, 2, 3, 4. The results are given in Table 4. The results indicate that k

Table 4. DF(v) + D_2 Relaxation Rate Coefficients

10^{11} cm^3/mol-sec

v	Kwok and Wilkins (1975)	Bott (1974)	Hinchen (1973a)
1	2.5 ± 1.0 (3.8)[a]	3.3	3.8
2	3.5 ± 1.2 (8.3)		
3	4.0 ± 1.5 (14.6)		
4	4.5 ± 1.6 (24.9)		

[a] Values in parentheses are for the exothermic direction (calculated assuming all species in J = 0 rotational levels).

increases slightly faster with v than the linear harmonic oscillator rule would predict, but there is considerable uncertainty in the data. When Bott's results are converted to the exothermic rate for V-V transfer from $D_2(1)$ to DF, they suggest a temperature-independent value for k_{-8} of 5×10^{11} cm^3/mol-sec (Fig. 4).

3. OTHER DIATOMICS

With the STLIF technique, Bott (1974) measured the deactivation of DF(1) in the presence of N_2, O_2, HCl, HBr, CO, and NO over the 300 to 800 K temperature range. Hinchen (1973) studied deactivation by H_2 and N_2 at 295 K in a stationary cell. Earlier, Blauer, Solomon, and Owens (1972a) and Bott and Cohen (1973b) reported high-temperature relaxation data obtained by shock heating DF-N_2 mixtures; these results give relaxation rates slightly slower than those obtained by Bott, who argued that the high-temperature results represented $k_6^{N_2}$, whereas the STLIF results actually measured $k_6^{N_2} + k_7^{N_2}$. Wendelken et al. (1974) also reported room-temperature deactivation rates for N_2. The results are plotted in Figs. 4 and 5.

4. CO_2

Because of the great interest in the DF-CO_2 transfer laser, a brief review of the kinetics of this process is appropriate, even though the stated scope of this paper includes only reactions in the D_2-F_2 system.

The various experimental results for the relaxation of DF(v) in the presence of CO_2 are shown in Fig. 6. Stephens and Cool (1972), Lucht and Cool (1974b, 1975), Bott and Cohen (1973c), and Hinchen and Hobbs (1975) all used laser pumping to produce the DF(v), then monitored the induced fluorescence. Hinchen and Hobbs observed the emission from $CO_2(001)$ as well and reported values for $k_7^{CO_2}$ directly, with no contributions from $k_6^{CO_2}$. This is valid only if $k_6^{CO_2}$ is small, which is generally believed to be the case (i.e., V-V transfer predominates over V-T(R) transfer). Airey and Smith (1972) produced DF(v) by chemical reaction between D and F_2 and observed the decay of DF(v) for v = 1, 2, and 3. Hinchen and Hobbs were

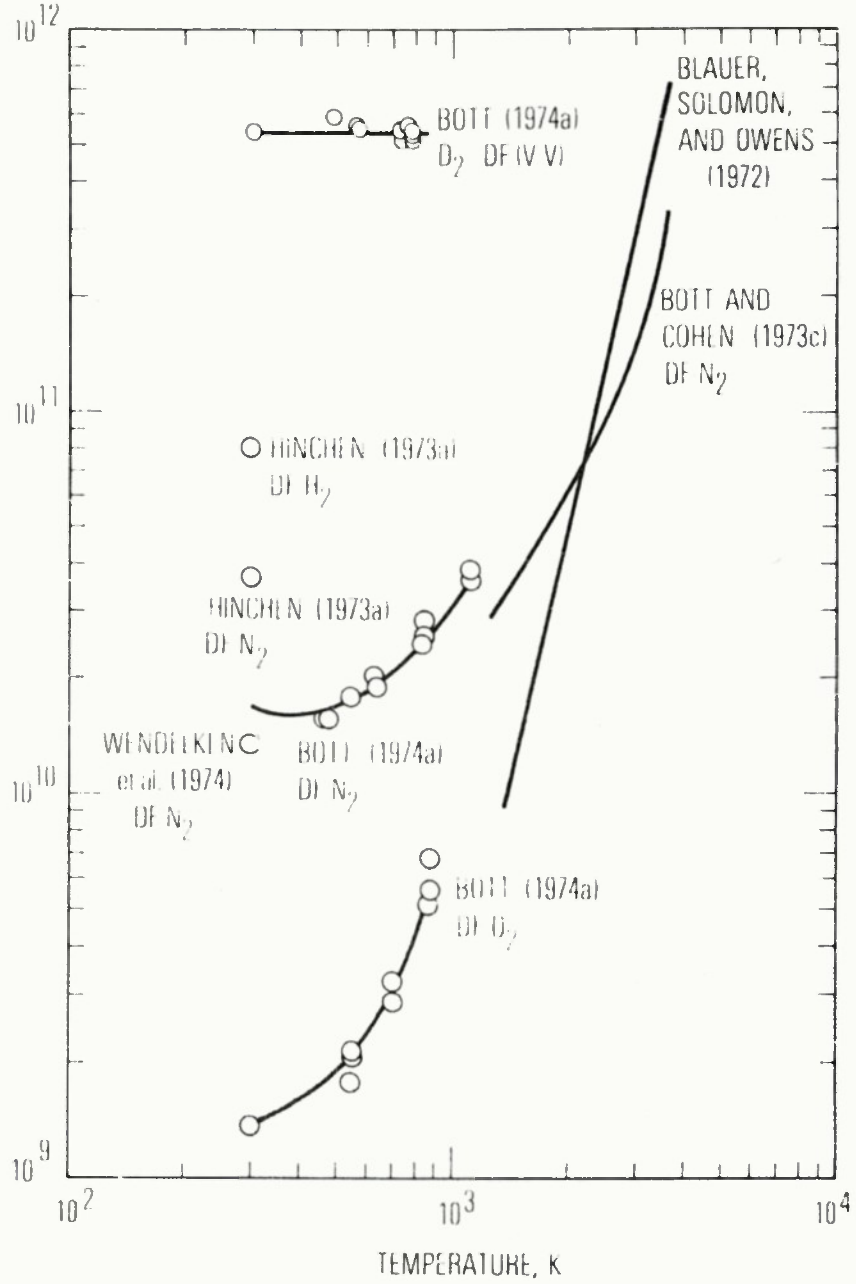

Fig. 4. Energy Transfer Rates From DF(v = 1) to N_2, H_2, and O_2. (Data for DF-D_2 are converted to exothermic rate for V-V transfer from D_2(v = 1) to DF.)

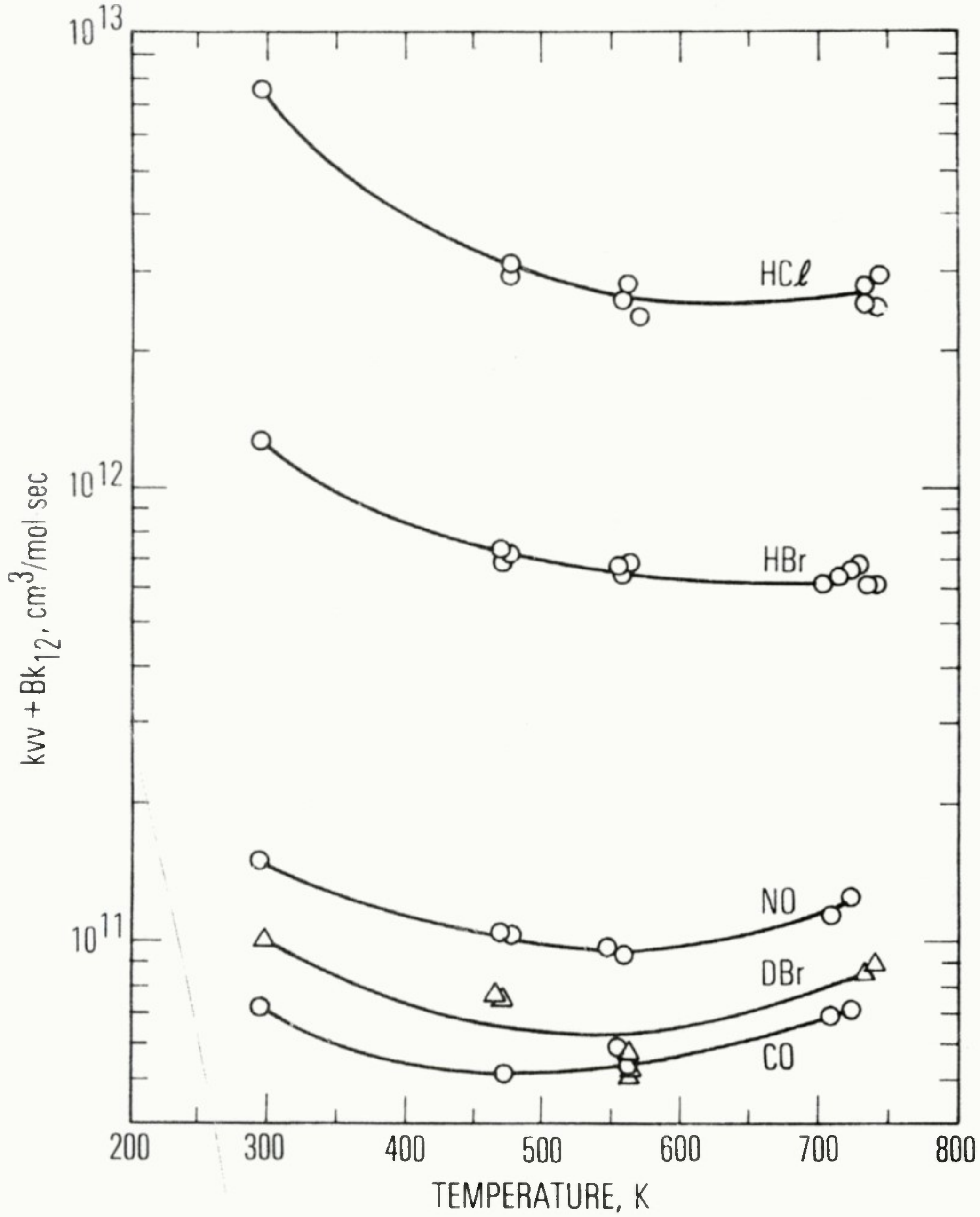

Fig. 5. Energy Transfer Rates From DF(v = 1) to Several Heteronuclear Diatomics. B = 0 for HCl; $0.64 < B < 0.79$ for HBr; and B = 1 for NO, DBr, and CO.

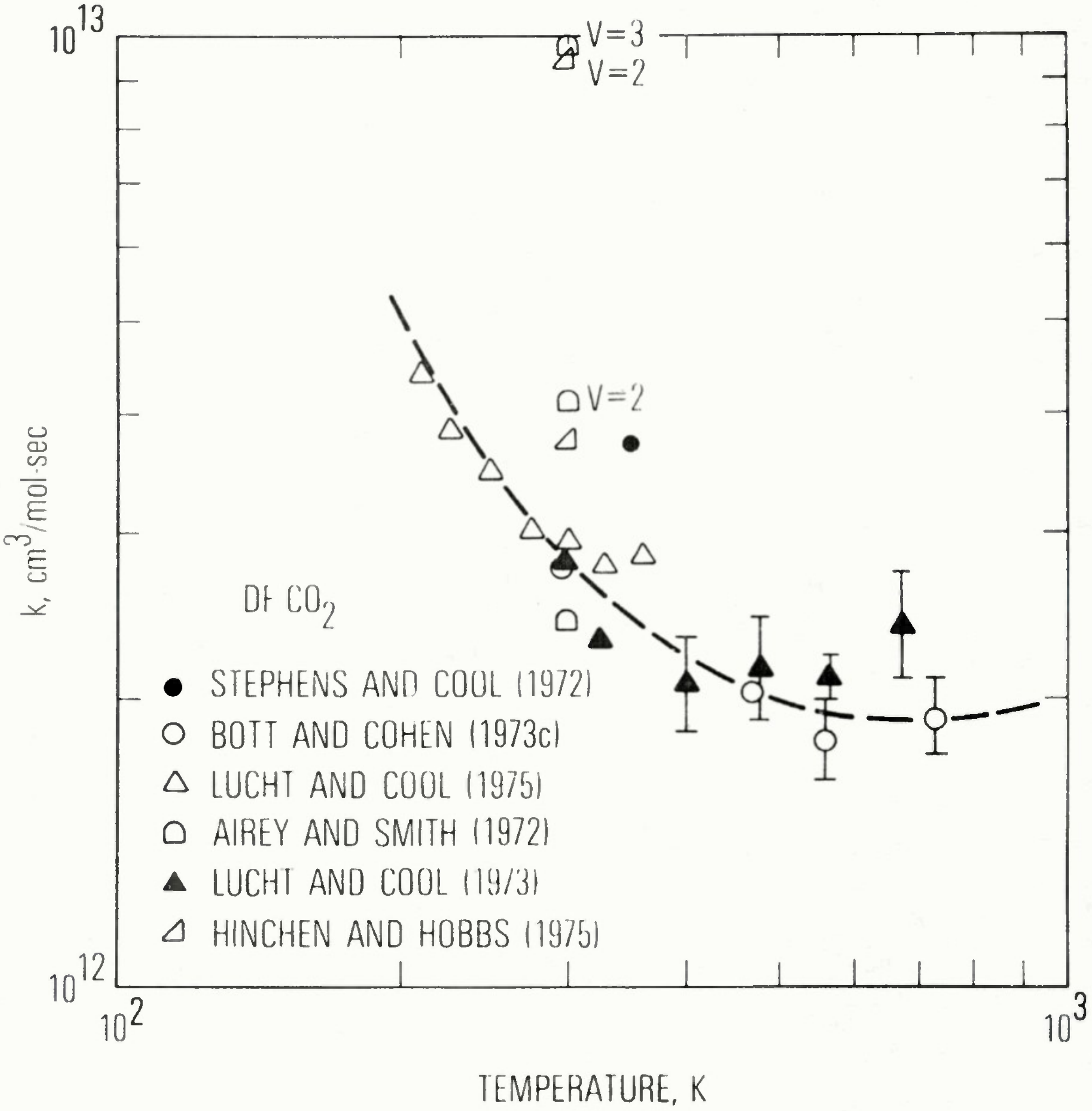

Fig. 6. Experimental Rate Coefficients for Vibrational Relaxation of DF(v) in the Presence of CO_2 for v = 1, 2, and 3. (Dashed curve is best fit for data for v = 1.)

able to observe $v = 2$ emission. Although the agreement between these two experiments is not good in absolute terms, both papers indicate that k increases with v, with an approximately first-order dependence.

Figure 6 indicates that the temperature dependence of $k_7^{CO_2}$ varies approximately as T^{-1} for temperatures below 350 K and is nearly independent of T in the 350 to 750 K range. The data can be fitted, within experimental error, by the expression

$$k_7^{CO_2} = 5.8 \times 10^9 \, T^{0.76} \exp(10,800/RT)$$

Also of interest in DF-CO_2 systems is the rate of deactivation of $CO_2(00^\circ1)$ by DF. Measurements have been made by Stephens and Cool (1972), Chang, McFarland, and Wolga (1972), Bott and Cohen (1973c), and Lucht and Cool (1975). These measurements are plotted in Fig. 7.

5. OTHER POLYATOMIC SPECIES

The vibrational relaxation of DF(1) has been studied in the presence of several other polyatomic chaperones — principally hydrocarbons and halides — at room temperature. In Table 3, most of the data are collected. The last column shows that there is no simple ratio relating the relaxation rates of HF and of DF by the same chaperone; in some cases, DF relaxation is faster, but not always. Correlations have been made in the case of HF vibrational relaxation between the relaxation rate coefficient and some function of the energy mismatch between the HF fundamental and some vibrational mode (usually a strong, fundamental infrared active one) of the chaperone [Bott, private communication: Kwok and Cohen (1974)]. The correlations are reasonably good (with a factor of 3 deviation from linear plots), indicating that the principal mode of deactivation is in all probability a V-V transfer, rather than just V-T,R transfer. A very simple correlation for DF relaxation, in which relaxation rate coefficient is plotted versus ΔE based on the closest-to-resonant mode of the chaperone, is shown in Fig. 8. There is considerable scatter, but the graph does show that there is a strong dependence of k on ΔE.

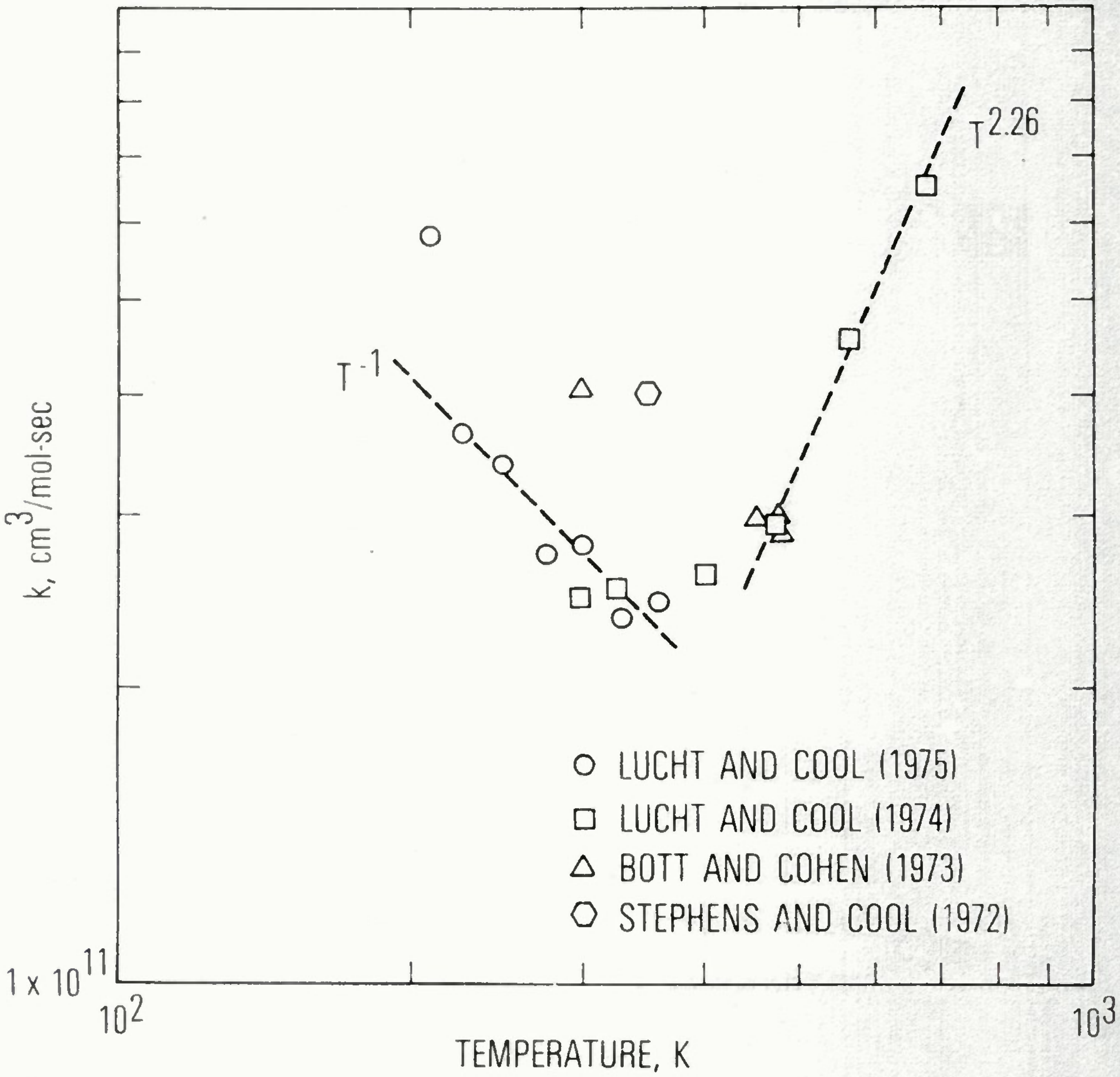

Fig. 7. Vibrational Relaxation of CO_2 (00°1) by DF

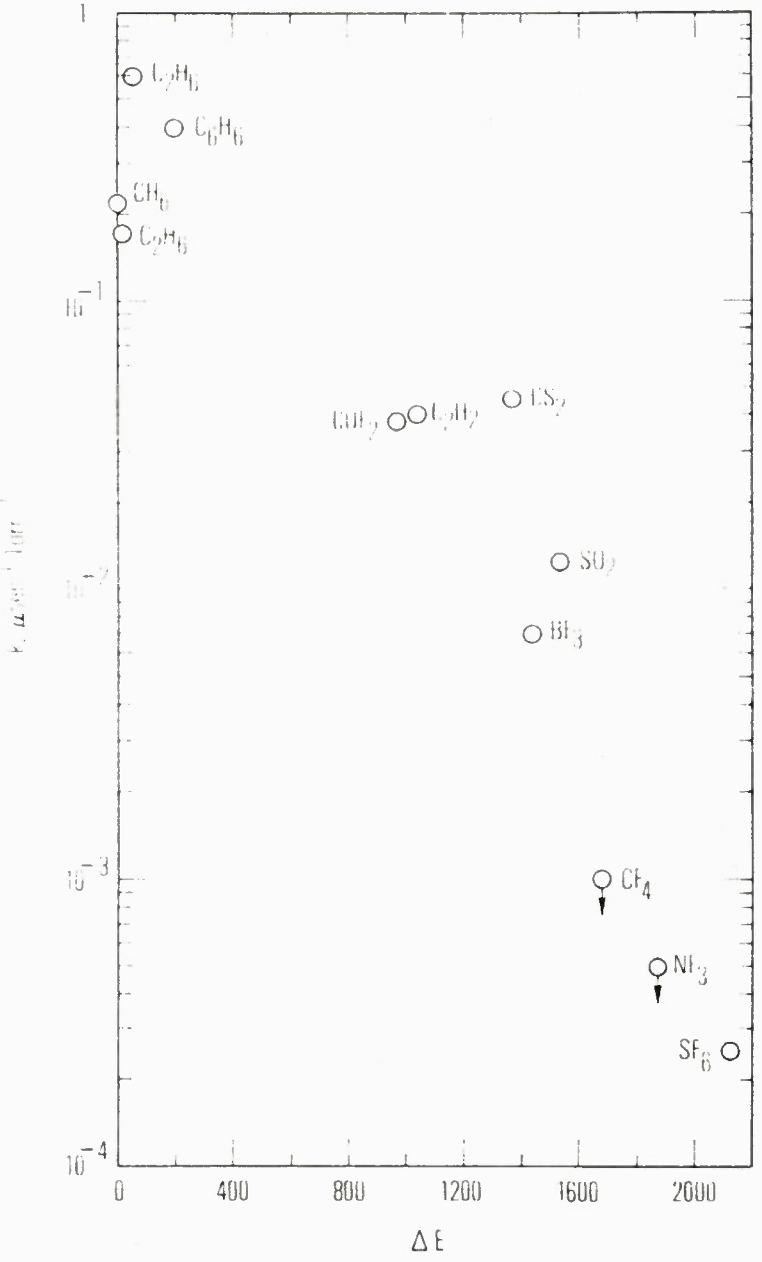

Fig. 8. Correlation Diagram for Vibrational Relaxation of DF(1) by Various Polyatomics, k in sec^{-1} Torr^{-1} Versus ΔE in cm^{-1}. (ΔE is the difference in energy between DF fundamental transition and nearest infrared active transition in the chaperone.)

In the case of CH_4 as chaperone, Bott measured the temperature dependence of the relaxation rate coefficient and found it to decrease slightly with increasing temperature (approximately as $T^{-0.5}$) when expressed in units of $cm^3/mol\text{-}sec$ (Fig. 9).

C. VIBRATIONAL ENERGY TRANSFER INVOLVING D_2

Because of the near-resonant energy levels of DF and D_2, V-V transfer between the two molecules is an important energy channel in a DF laser system with molecular deuterium present. Therefore, the fate of the vibrationally excited D_2 is of interest: if transfer back to DF is the only rapid process, then the D_2 can act as an energy reservoir and retard the DF vibrational relaxation. On the other hand, if the D_2 itself relaxes very rapidly, then it can provide an additional effective mechanism for DF relaxation.

The vibrational self-relaxation of D_2 was studied over the 50 to 400 K temperature range by Lukasik and Ducuing (1974a, 1974b), who used the Raman excitation technique. Kiefer and Lutz (1966a, 1966b), using a Schlieren technique, studied D_2 relaxation in D_2-Ar mixtures in a shock tube. They reported

$$p\tau_{D_2-D_2} = (2.7 \pm 0.3) \times 10^{-10} \exp[(110.5 \pm 1.5)/T^{1/3}] \text{ atm-sec}, \quad 1100 < T < 3000 \text{ K}$$

and

$$p\tau_{D_2-Ar} = (1.0 \pm 0.7) \times 10^{-9} \exp[(118 \pm 10)/T^{1/3}] \text{ atm-sec}, \quad 1600 < T < 3000 \text{ K}$$

The D_2-D_2 results of Kiefer and Lutz agree reasonably well with the lower-temperature work of Lukasik and Ducuing when the two sets of data are extrapolated into a common intermediate temperature range. Hopkins and Chen (1972) observed the laser-induced fluorescence in relaxing mixtures

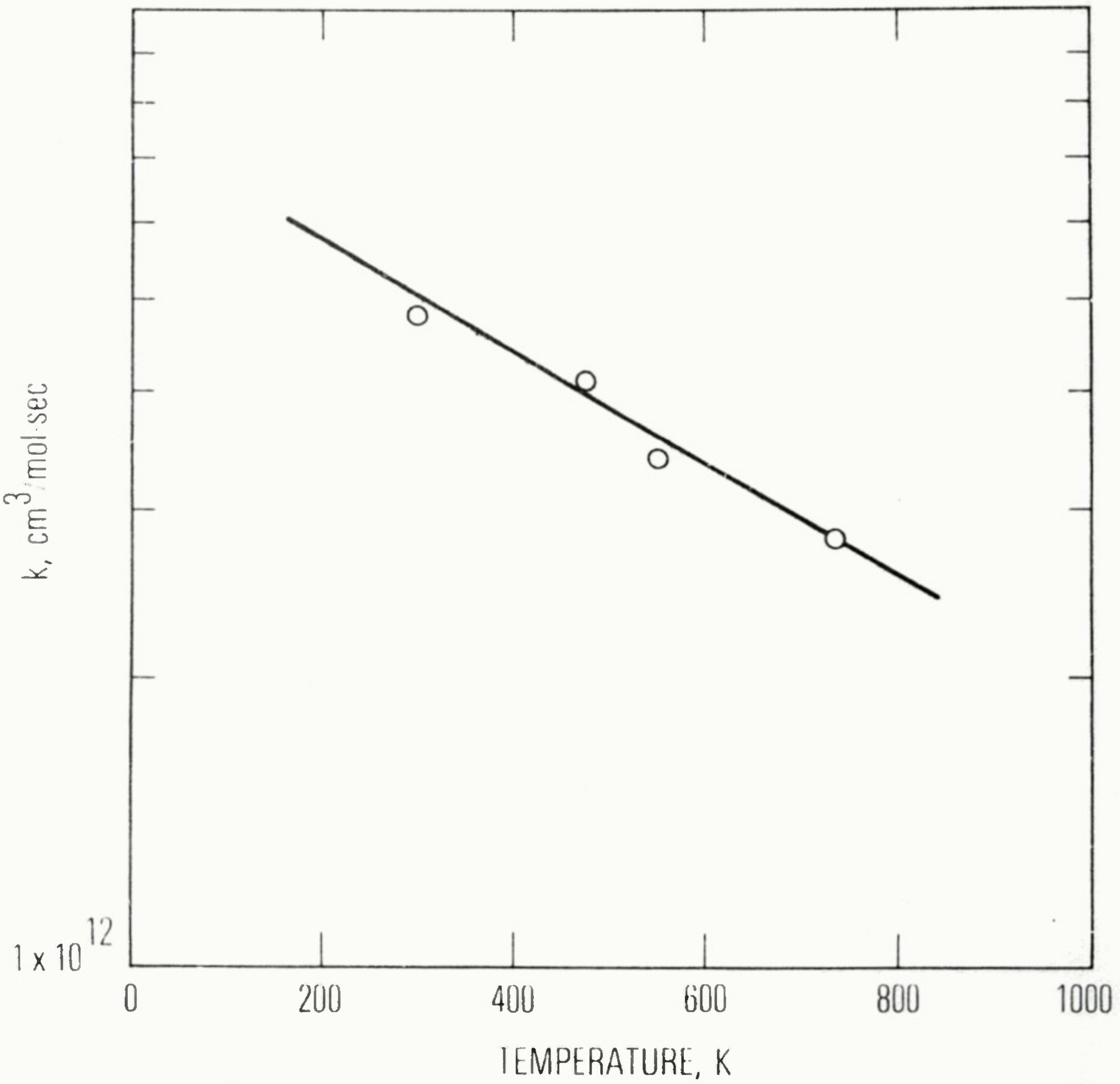

Fig. 9. Experimental Rate Coefficients for Vibrational Relaxation of DF(1) in the Presence of CH_4 (Bott, 1976)

of D_2 and HCl at 295 K and deduced rate coefficients for the several relaxation processes taking place. For deuterium self-relaxation, they obtained a value for $p\tau$ of $1.58 \pm 0.13 \times 10^3$ μsec-atm, or 1.5×10^7 cm^3/mol-sec. This is faster by a factor of about 3 than the value at that temperature obtained by Lukasik and Ducuing (Fig. 10). In view of the greater complexity in the D_2-HCl system, we take the results to Lukasik and Ducuing to be the more reliable at this time.

The data of Lukasik and Ducuing can be fitted throughout most of their temperature range by the expression $k = 1.5 \times 10^{-6}\ T^{5.33} \exp(526/RT)$ cm^3/mol-sec, although no theoretical significance is to be attached to these Arrhenius parameters. This expression deviates from the experimental curve by over 50% at temperatures above approximately 375 K. Therefore, for higher temperatures, a different expression should be used, one based on an extrapolation from 200 K up.

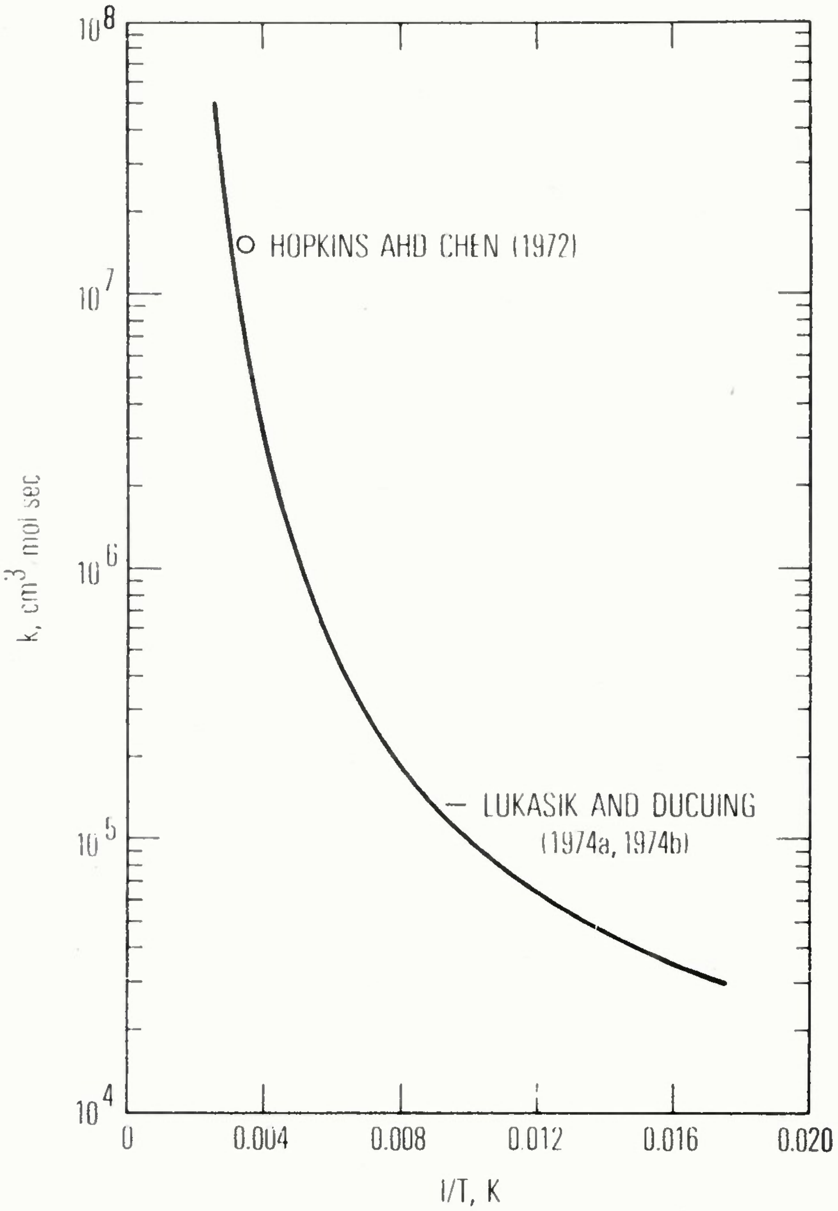

Fig. 10. Experimental Rate Coefficients for Self-Relaxation of D_2:$D_2(1) + D_2(0) \rightarrow D_2(0) + D_2(0)$

V. CONCLUSIONS

In spite of the work accomplished on the kinetics of the HF and DF systems in recent years, there are still several areas that need further attention.

Among the dissociation-recombination reactions, the rates of greatest uncertainty involve those with atomic chaperone species: $D_2 + D$ (k_1^D), $F + H$ (k_2^H), $F_2 + F$ (k_2^F), $DF + D$ (k_3^D), and $DF + F$ (k_3^F). None of these has been measured with any degree of precision, and all are expected to be considerably faster than recombination-dissociation with the parent molecule as chaperone. The estimated room-temperature rate coefficients assigned in Section II of this review are uncertain by a probable factor of at least 2 or 3.

For both of the overall pumping reactions, $F + D_2$ (k_4) and $D + F$ (k_5), there are no direct experimental data. In the former case, measurements have been made relative to the isotopic reaction, $F + H_2$; uncertainties in the value of the rate coefficient for that process, therefore, directly affect the derived value of k_4, and the room-temperature value of k_4 should be regarded as uncertain by a factor of 2 to 3. Because of uncertainties in the activation energies for both k_4 and the isotopic analog, the rate coefficient uncertainty at lower temperatures is even larger. In the case of the $D + F_2$ reaction, there are no experimental data on the pumping distribution, and distributions have been estimated on the basis of the analogous $H + F_2$ reaction. It seems unlikely that the $H + F_2$ room-temperature distribution fractions will change by more than 20% to 25% from the current best values. It also seems unlikely that the $D + F_2$ distribution will differ significantly from that for $H + F_2$ once the appropriate corrections have been made (principally because of the different vibrational energy spacing in DF and HF). However, there are no data on pumping distributions at temperatures other than 300 K for either $D + F_2$ or $H + F_2$.

The principal vibrational relaxation processes of concern are those with DF itself and with D atoms as chaperones. In the case of DF(1) + DF, the relaxation rate coefficient is well-known at all temperatures of interest. The principal problem is the variation of k_v with v. At this time, the uncertainties in upper vibrational relaxation rate coefficients can be as large as a factor of 2 to 3. The temperature dependence of the upper vibrational relaxation rate coefficients is completely unmeasured, but there is little reason to expect significant differences in the temperature dependence for the different v levels. Similar uncertainties in the variation in k with v and with T exist in the case of D as chaperone. In this instance, though, the temperature dependence of the different levels can be significantly different, particularly if the mechanism responsible for relaxation of high levels is different from that for the low levels ($v \le 4$), as seems to be the case.

The variation in the V-V rate coefficients with v and v′ in the general case of DF(v) + DF(v′) has not been characterized, either experimentally or theoretically. Although these processes are expected to have little effect on the total energy output of a chemical laser, they can alter the frequency distribution of the output. Formidable experimental difficulties will probably prevent meaningful experimental data from becoming accessible for several years; therefore, it is almost certain that we will have to rely on theoretical calculations of these rate coefficients, $k_7(v, v'; v + \Delta v, v' - \Delta v')$. Trajectory calculations from this Laboratory should be available in the near future; in addition, other theoretical approaches may provide further insights.

In this report, nothing has been mentioned about the possibility of chain branching in the D_2-F_2 reaction system. This topic was discussed in some detail in a previous review in the case of the H_2-F_2 system [Cohen and Bott (1976b)], and there is nothing further to add at this time.

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APPENDIX

RECOMMENDED RATE COEFFICIENTS FOR D_2-F_2 SYSTEM

Table A-1. Recommended Rate Coefficients for D_2-F_2 System

Reaction Number[a]	Reaction	Rate Coefficient (cm^3, mol, sec, cal units)	Notes
1a	$2D + Ar \rightleftharpoons D_2 + Ar$	$k_1^{Ar} = 10^{18}T^{-1}$	Use k_1^{Ar} for all M other than D, D_2
1b	$2D + D \rightleftharpoons D_2 + D$	$k_1^{D} = 3 \times 10^{17}T^{-0.5}$	
1c	$2D + D_2 \rightleftharpoons D_2 + D_2$	$k_1^{D2} = 10^{17}T^{-0.67}$	
2	$F_2 + M \rightleftharpoons 2F + M$	$k_2^{M} = 5 \times 10^{13} A_M \exp(-35,100/RT)$	$Ar = A_{D_2} = A_{DF} = 1$; $A_{F_2} = 2.7$; $A_H = 3$; $A_F = 10$
3	$DF(v) + M \rightleftharpoons D + F + M$	$k_{3,v}^{M} = 1.1/(n+1) \times 10^{19}T^{-1} A_M$ $\exp[(-137,130 + E_v - E_o)/RT]$	$A_D = A_F = A_{DF} = 5$; $A_M = 1$ for all others; $v = 1 \ldots n$
4a	$F + D_2(0) \rightleftharpoons DF(v) + D$	$k_{4,v}^{0} = g(v) \times 10^{14}T^{n(v)}$ $\exp(-1960/RT)$	$v = 1 \ldots 4$; $g(1) = 0.1$, $g(2) = 0.35$, $g(3) = 1.17$, $g(4) = 0.69$; $n(1) = n(2) = 0$; $n(3) = n(4) = -0.1$
4b	$F + D_2(v') \rightleftharpoons DF(v) + D$	$k_{-4,v}^{v'} = 10^{13} \exp(-500/RT)$	$v' \leq v - 4$, $v = 5 \ldots 9$
5	$D + F_2 \rightleftharpoons DF(v) + F$	$k_{5,v} = 6.2 \times 10^{13} g(v)$ $\exp(-2500/RT)$	$v = 5 \ldots 9$; $g(5) = 0.2$, $g(6) = 0.16$, $g(7) = 0.22$, $g(8) = 0.40$, $g(9) = 0.02$. These are approximations to theoretical values given in the text (Section III-B).
6a	$DF(v) + DF \rightleftharpoons DF(v-1) + DF$	$k_{6,v}^{DF} = g(v) (8 \times 10^{14}T^{-1.3}$ $+ 1.1 \times 10^{4}T^{2.37})$	$g(1) = 1$, $g(2) = 6$, $g(3) = 12$, $g(4) \simeq 20$, $g(5) = 35$, $g(6) = 60$
6b	$DF(v) + M \rightleftharpoons DF(v-1) + M$	$k_{6,v}^{M} = g(v) \times 7 \times 10^{-5}T^{4.3}$	$g(v) = v$, $M = Ar, F_2$
6c	$DF(v) + He \rightleftharpoons DF(v-1) + He$	$k_{6,v}^{He} = g(v) \times 4 \times 10^{-6}T^{4.75}$	$g(v) = v$
6d	$DF(v) + D \rightleftharpoons DF(v') + D$	$k_{6v,v'}^{D} = g(v,v') 5 \times 10^{11} \exp(-2000/RT)$	$v = 1 \ldots 6$; $v' = 0 \ldots (v-1)$; $g(1,0) = 1$, all other $g = 20$
6e	$DF(v) + F \rightleftharpoons DF(v') + F$	$k_{6v,v'}^{F} = 4 \times 10^{12} \frac{v}{v-v'} \exp(-3200/RT)$	$v = 1 \ldots 6$; $v' = 0 \ldots (v-1)$
6f	$DF(v) + HF \rightleftharpoons DF(v-1) + HF$	$k_{6,v}^{HF} = g(v) (5.2 \times 10^{14}T^{-1.2}$ $+ 1.35 \times 10^{2}T^{3})$	$g(v) \simeq v^{2.2}$
6g	$DF(v) + D_2 \rightleftharpoons DF(v-1) + D_2$	$k_{6,v}^{D2} = 1.4 \times 10^{3} vT^{2.4}$	
7	$DF(v) + DF(v') \rightleftharpoons DF(v+1) + DF(v-1)$	$k_{7(v,v',v+1,v-1)} = (1.8)^{1-v} \times$ $6 \times 10^{15}T^{-1}$	
8	$DF(v) + D_2(v') \rightleftharpoons DF(v+1) + D_2(v'-1)$	$k_{8(v,v')} = 5 \times 10^{11} g(v)$	$g(v) \simeq v$
9	$D_2(v) + M \rightleftharpoons D_2(v-1) + M$	$k_9^{M} = 1.5 \times 10^{-6}T^{5.33}$ $\exp(526/RT) vA_M$	$A_{D_2} = 1$; $A_F = A_{F_2} = A_{Ar} = 0.2$

[a] Reaction number as it appears in the text.

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