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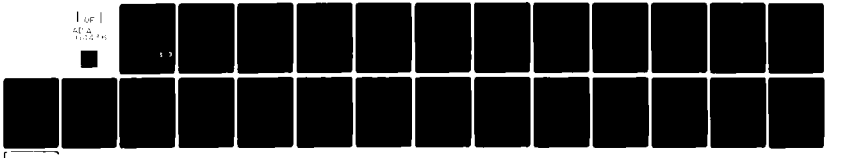

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The Removal of DF (v = 3 and 4) by H and D Atoms

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The deactivation rate coefficients for the removal of DF(v = 3) and DF(v = 4) by H and D atoms have been measured at 295 K by the technique of laser-induced fluorescence in a discharge flow-tube apparatus. The rate coefficients were found to increase dramatically with vibrational level v. Data obtained for the removal of DF(v = 4) in the presence of H atoms have been used to infer a rate coefficient of $(5 \pm 2) \times 10^{11}$ $cm^3/mol\text{-}s$ for the reaction

$$H + DF(v = 4) \rightarrow HD + F$$

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19. KEY WORDS *(Continued)*

20. ABSTRACT *(Continued)*

This is in excellent agreement with a previous measurement of the F + HD rate coefficient obtained by Berry.

CONTENTS

FIGURES

TABLES

I. INTRODUCTION

The deactivation of vibrationally excited DF by the products of the F + D_2 reaction directly affects the performance of the DF chemical laser. Discussions of the various deactivation processes and their recommended rate coefficients can be found in Refs. 1-3. In the cold-reaction DF laser, one D atom is produced for each DF molecule, and the effects of DF(v) deactivation by D atoms must be considered. The analogous case of HF(v) deactivation by H atoms has been studied in several laboratories.[4-8] Of particular importance is the observation[6-8] that the removal rates of HF(v) by H increase very dramatically for $v > 3$.

The only measured rates of DF(v) deactivation by H and D atoms to be reported[5] to date are for $v = 1$. In the present study we have measured the removal rates of DF($v = 3$ and 4) by H and D atoms at 295 K. The experiments were performed in the same apparatus as the previous HF(v) -H experiments[6,7] using the technique of laser-induced fluorescence. Helium, D_2, and a small amount of DF flow through a fluorescence cell in which a pulsed DF laser pumps a small fraction of the DF($v = 0$) to $v = 3$ and 4 by sequential photon absorption. Before reaching the cell the helium and D_2 flow through a microwave discharge which produces D atoms. The difference in the decay rates of the DF overtone fluorescence obtained with and without D atoms is used to determine the deactivation coefficients.

The removal of DF($v = 4$) by D atoms can proceed by three channels:

$$D' + DF(v = 4) \rightarrow D' + DF(v < 4) \quad (1)$$

$$\rightarrow D + D'F(v < 4) \quad (2)$$

$$\rightarrow DD' + F \quad (3)$$

These channels, nonreactive deactivation (1), reactive deactivation by D-atom exchange (2), and the back reaction of the F + D_2 reaction (3), are discussed in Section IV.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The experiments were performed in the fluorescence cell-flow system described in Ref. 6 and shown schematically in Fig. 1. The photomultiplier was positioned at the end of the flow tube so that fluorescence from the entire length of the cell would contribute to the signal. Because of the low signals for DF(v = 3, 4), it was not possible to place the photomultiplier transverse to the laser beam. The required position of the photomultiplier precluded direct measurements of the H(D) atom concentrations with the catalytic probe used in Ref. 6. Therefore, the density of the H and D atoms was inferred from their effect on the decay time of the HF(3) fluorescence and the previously measured removal rate coefficients.[7] Experiments were performed in which the HF impurity in the DF was pumped to the v = 3 level with an HF laser. The subsequent decay rate of HF(v = 3) was measured with and without the atoms present.

An RCA GaAs photomultiplier was used to monitor the fluorescence from HF(v = 3) and DF(v = 4). A Kodak Wratten filter (87B) and a 0.62-cm sheet of Plexiglas were used to attenuate scattered light from the microwave discharge and the laser pulse. A DuMont Type 6911 (S-1 response) photomultiplier behind a Corning CS7-56 filter and 0.62 cm of Plexiglas was used to monitor DF(v = 3). Typically, 256 or 512 pulses were averaged for DF(v = 3) and DF(v = 4), whereas only 32 to 64 were required for HF(v = 3). Other apparatus, such as the DF-pulsed laser and the signal processing instruments, have been previously described.[9]

The experiments were performed at room temperature (295 K) and at a total pressure of 5.5 Torr. The bulk of the gas flow was helium with partial pressures of ~ 0.02 Torr DF, ~ 0.04 Torr $D_2(H_2)$, and ~ 0.02 Torr D(H) atoms.

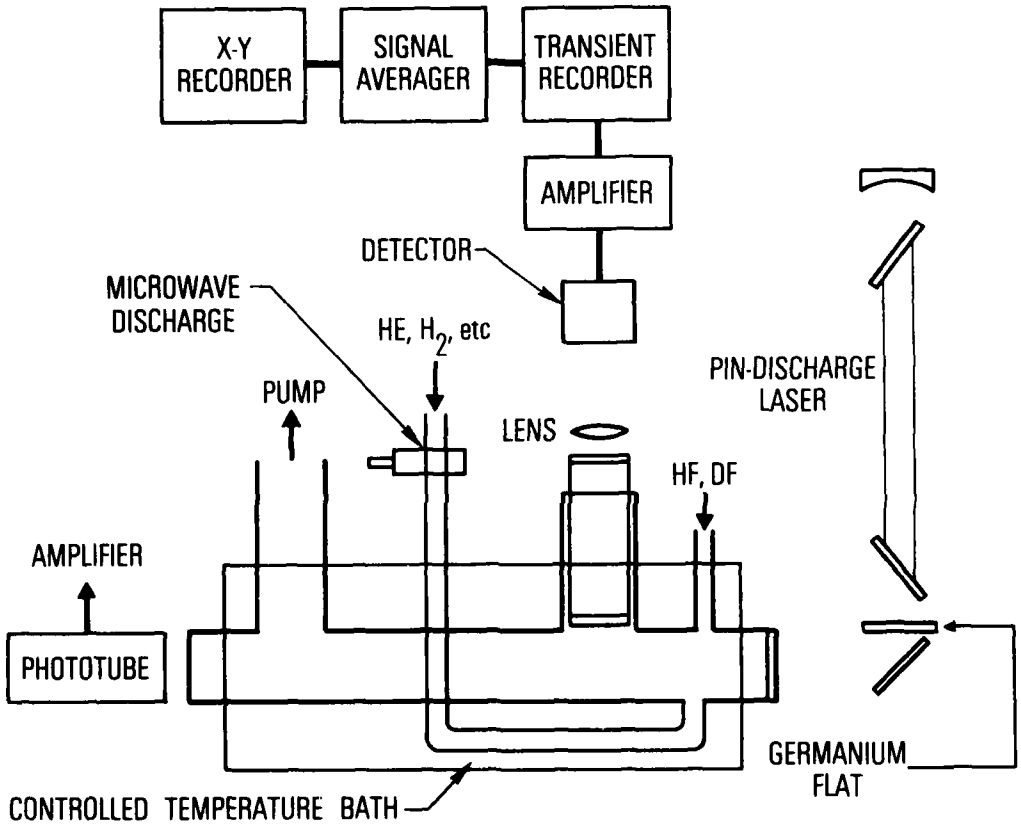

Fig. 1. Schematic of Apparatus

III. RESULTS

A. VIBRATIONAL RELAXATION OF DF(v = 3) BY D ATOMS

The DF 3 → 0 overtone fluorescence was recorded with and without the D atoms produced by the microwave discharge. The fluorescence decay times were ~ 25% shorter with the D atoms present. As described in Ref. 6,

$$\Delta\left(\frac{1}{\tau}\right) = \tau_{on}^{-1} - \tau_{off}^{-1} = \left(k_{DF-D} - \frac{1}{2} k_{DF-D_2}\right)[D] \qquad (4)$$

The exponential decay times of the fluorescence traces and the calculated values of $\Delta(1/\tau)$ are presented in Table 1. The latter have an average value of 6×10^{-3} μs^{-1} if all five values are included, or 5.3×10^{-3} μs^{-1} if the high and low values are excluded. This compares to a value of 6.3×10^{-2} μs^{-1} obtained under the same conditions for HF(v = 3) removal by D atoms. Using the previously measured value[7] of 5.9×10^{13} $cm^3/mol\text{-}s$ for the HF(3)-D removal rate, we estimate $5 \pm 2 \times 10^{12}$ $cm^3/mol\text{-}s$ for the value of $k_{DF-D} - 1/2\ k_{DF-D_2}$. The value[9] of $k_{DF-D_2} = 2.8 \times 10^{11}$ $cm^3/mol\text{-}s$ is small compared to the uncertainty in the measurement and can be neglected.

B. VIBRATIONAL RELAXATION OF DF(v = 3) BY H ATOMS

The H atoms had a smaller effect on the DF(v = 3) fluorescence decay times than the D atoms. The values of $\Delta(1/\tau)$ for DF(v = 3) are smaller by a factor of about 35 than the values for HF(v = 3) (see Table 2). Using a value of 6.3×10^{13} for the HF(v = 3)-H removal rate,[6] we obtain a value of about 2×10^{12} $cm^3/mol\text{-}s$ for $(k_{DF-H} - 1/2\ k_{DF-H_2})$. The small value[9] of 0.8×10^{11} $cm^3/mol\text{-}s$ for k_{DF-H_2} makes it a negligible contribution. Since the decay times with and without the atoms differ only by about 10%, there is a large uncertainty in the measured value of $k_{DF-H} = 2 \pm 2 \times 10^{12}$ $cm^3/mol\text{-}s$.

C. VIBRATIONAL RELAXATION OF DF(v = 4) BY D ATOMS

The data for DF(v = 4) removal by D atoms are listed in Table 3. The exponential decay times of the fluorescence traces obtained with and without the D atoms differ by about a factor of 2. The decay rates for HF(v = 3) are

Table 1. Removal Rates of DF(v = 3) by D Atoms

Run	τ_{on}, μs	τ_{off}, μs	$\Delta(1/\tau) \times 10^3$, μs^{-1}	$\Delta(1/\tau)$ for HF(v = 3), μs^{-1}
1	44	97	12.4	$(5.5 \pm 1) \times 10^{-2}$
2	51.6	69.5	5.0	
3	54.4	78	5.6	
4	59	66	1.8	
5	54	75.1	5.2	
			6 ± 2	

Table 2. Removal Rates of DF(v = 3) by H Atoms

Run	τ_{on}, μs	τ_{off}, μs	$\Delta(1/\tau) \times 10^3$, μs^{-1}	$\Delta(1/\tau)$ for HF(v = 3), μs^{-1}
1	73.1	66.6	-1.4	$(5.0 \pm 1) \times 10^{-2}$
2	52.2	56.2	1.3	
3	45.7	49.1	1.5	
4	49.5	56	2.3	$(8.0 \pm 1) \times 10^{-2}$

Table 3. Removal Rates of DF(v = 4) by D Atoms

Run	τ_{on}, μs	τ_{off}, μs	$\Delta(1/\tau) \times 10^2$, μs^{-1}	$\Delta(1/\tau)$ for HF(v = 3), μs^{-1}
1	40.4	95	1.43	$(3.0 \pm 0.5) \times 10^{-2}$
2	36.5	85	1.56	
3	40.9	82	1.23	
4	43	92	1.23	
5	36.1	100	1.77	$(4.1 \pm 0.5) \times 10^{-2}$
6	33.9	100	1.95	
7	29.9	98	2.34	$(4.7 \pm 0.5) \times 10^{-2}$
8	29.9	98	2.34	
9	34.2	118	2.23	$(5.4 \pm 0.5) \times 10^{-2}$
10	40	125	1.70	$(5.0 \pm 0.5) \times 10^{-2}$
11	33.8	130	2.19	$(4.6 \pm 0.5) \times 10^{-2}$

plotted versus those of DF(v = 4) in Fig. 2. The value of $\Delta(1/\tau)$ for DF(v = 4) averaged 0.46 times the values of $\Delta(1/\tau)$ for HF(v = 3). Using the previously measured value[7] of 5.9×10^{13} $cm^3/mol\text{-}s$ for the HF(3)-D removal rate, we obtain a value of $(2.6 \pm 1) \times 10^{13}$ $cm^3/mol\text{-}s$ for the removal rate of DF(v = 4) by D atoms. The values of 9.1×10^{11} $cm^3/mol\text{-}s$ and 3.4×10^{11} $cm^3/mol\text{-}s$ for the deactivation rates[9,10] of HF(v = 3) and DF(v = 4) by D_2 can be neglected.

D. THE REMOVAL RATE OF DF(v = 4) BY H ATOMS

The DF(v = 4) fluorescence decayed exponentially in the gas flows containing H_2 without the microwave discharge. However, with the microwave discharge on and, therefore, H atoms present, the observed fluorescence rose to a maximum at about 30 μs before beginning its exponential decay. A fluorescence trace is shown in Fig. 3. Since DF 4 → 0 fluorescence and HF 3 → 0 fluorescence fall within the spectral bandpass of our photomultiplier-filter system, a logical interpretation is the following. DF(v = 4) is removed by the three reactions

$$H + DF(4) \xrightarrow{k_5} HD + F \tag{5}$$

$$H + DF(4) \xrightarrow{k_6} H + DF(3, 2, 1, 0) \tag{6}$$

$$DF(4) + M \rightarrow DF(3, 2, 1, 0) + M \tag{7}$$

where M = H_2, DF, etc. The F atoms react with the abundant H_2 to produce HF(v = 3) in the reaction

$$F + H_2 \rightarrow HF(v = 1, 2, 3) + H \tag{8}$$

Only DF(v = 4) emission produces the photomultiplier signal immediately after the laser pumping of DF. However, at longer times both DF(v = 4) and HF(v = 3) fluorescences contribute to the signal. Analytical expressions are derived in the Appendix for the fluorescence intensities of these two species. They indicate that the exponential decay rate at long times can be related to the total removal rate of DF(v = 4) by H atoms. Because of the rapid quenching

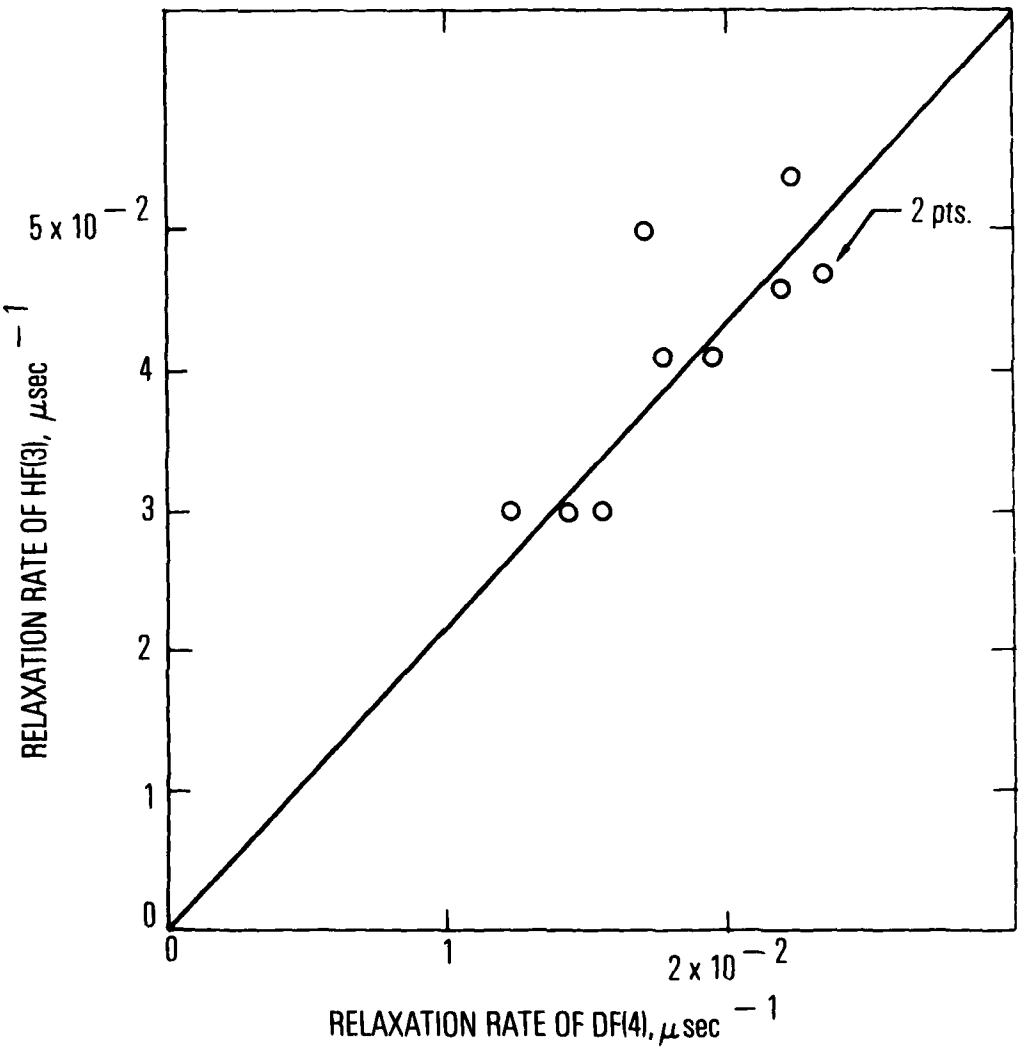

Fig. 2. Rates of HF(v = 3) Removal by D Atoms Versus Rates of DF(v = 4) Removal by D Atoms

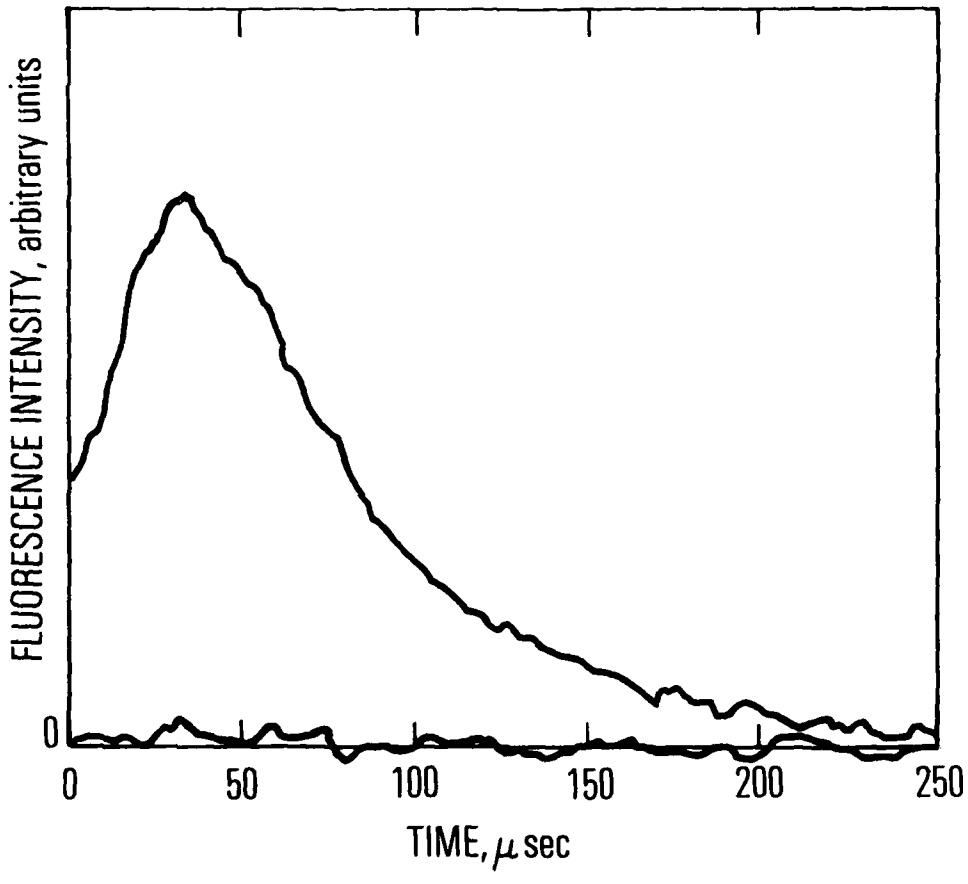

Fig. 3. Fluorescence Signal Obtained with DF Pumped to DF(v = 4) in the Presence of H Atoms

rate of HF(v = 3) by H atoms, the HF(v = 3) fluorescence is essentially proportional to the DF(v = 4) concentration. The total fluorescence intensity at long times (extrapolated back to time = 0), and the initial DF(v = 4) fluorescence intensity can be used to estimate the contribution of Reaction (5) to the total removal rate. From the Appendix we have

$$\left(\frac{I^0_{\text{total}}}{I^0_{DF}}\right) - 1 = \frac{S_{HF}}{S_{DF}} \frac{A_{HF}}{A_{DF}} F \frac{\tau_1 \tau_2}{\tau_2 - \tau_1} k_5[H] \qquad (9)$$

where I^0_{total} is the intensity obtained by extrapolating the total intensity of long times back to time = 0, I^0_{DF} is the DF intensity at time = 0, S is the relative response of the photomultiplier at the wavelengths of the HF and DF lines, A is the Einstein coefficient for the lines, F is the fraction of HF(v = 3) produced by Reaction (8), and τ_1 and τ_2 are the rise times and decay times, respectively. A value of 1.24×10^3 was determined for $(S_{HF}A_{HF}/S_{DF}A_{DF})$ by a detailed calibration of the detector, which folded in the values of A from Ref. 11. This large value means the photomultiplier is 1.24×10^3 more sensitive for HF(v = 3) detection than for DF(v = 4). F has a value[3] of 0.28. From the fluorescence trace shown in Fig. 3 we estimate τ_2 = 55 ± 3 μs, τ_1 = 20 ± 2 μs, $(I^0_{\text{total}}/I^0_{DF})$ = 5, and [H] ≈ 0.8×10^{-9} mol/cm^3 obtained from HF(v = 3) decay times. Using these values and Equation (9), we obtain $k_5 = 5 \times 10^{11}$ cm^3/mol-s. The decay time of 55 μs compares with a decay time of 130 μs obtained without the microwave discharge (and, therefore, without H atoms). From these decay times we calculate a total removal rate of $(1.3 \pm 0.3) \times 10^{13}$ cm^3/mol-s for DF(v = 4) by H atoms.

To determine the H atom concentration, the HF impurity in the DF was pumped to HF(v = 3) with the HF pulsed laser. The HF(v = 3) fluorescence decayed exponentially with a decay time of 21 μs. This decay time is consistent with the value of $\tau_1 = (k[H])^{-1}$, where k is the rate coefficient for the removal of HF(v = 3) by H atoms. The decay time of HF(v = 3) fluorescence in the first experiment is described by the same equation to a good approximation.

IV. DISCUSSION

The present data for DF(v = 3) deactivation by H and D atoms contain large uncertainties because of the relatively small changes in the decay times with and without the microwave discharge. In spite of their large uncertainties (Table 4), they are smaller by a factor of 10 than the rate coefficients for the deactivation of HF(v = 3) by H and D atoms.[7] The rates of HF(v) and DF(v) deactivation by diatomic molecules have been found to scale as v^n when the deactivation process is exothermic.[9,10] The scaling parameter is independent of the diatomic collision partner, and for DF(v) deactivation n = 1.9 ± 0.1. It is not known whether the same scaling parameter applies to DF(v) deactivation by atoms, and the present data, given in Table 4, are too imprecise to determine the dependence. It would appear, however, that the rate coefficients for DF(v = 3) deactivation by H and D atoms are faster than we would predict on the basis of the DF(v = 1) data and a $v^{1.9}$ scaling.

The rate coefficients obtained for DF(v = 4) removal by H and D atoms are given in Table 4. They are approximately five times larger than the DF(v = 3) -H, D deactivation rate coefficients, but two to four times smaller than the HF(v = 3) -H, D deactivation rates. The rate coefficient for DF (v = 4) removal by Reaction (3), the reverse of the pumping reaction, can be estimated on the basis of the overall reaction rate for F + D_2, the relative vibrational distributions, and the equilibrium constant $K_{3,-3} = k_3/k_{-3}$. Cohen and Bott[3] reviewed the data for the F + D_2 reaction and recommended a value of (0.95 ± .17) × 10^{13} cm^3/mol-s for the rate coefficient at 295 K and recommended the Perry and Polanyi value[12] of 0.26 for the branching fraction into the v = 4 level. A value of $K_{3,-3}$ = 1.03 can be calculated from the thermodynamic data in Table 5. Using these values we obtain a value of k_3 = 2.6 × 10^{12} cm^3/mol-s, with perhaps a 50% uncertainty. Since this value is almost an order of magnitude smaller than the present measured value of the total removal rate of DF(v = 4) by D atoms, it would appear that vibrational deactivation, Reactions (1) and (2), is the dominant mechanism for DF(v = 4) removal.

Berry studied the reaction[13]

Table 4. Removal Rate Coefficients

Excited Molecule	Rate Coefficients, $cm^3/mol\text{-}s$			
	H	D	H_2	D_2
DF(v = 1)	[a] $(6.7 \pm 1.8) \times 10^{10}$	[a] $(0 \pm 9) \times 10^{10}$	[b] 1.0×10^{10}	[b] 3.8×10^{11}
DF(v = 3)	[c] $(2 \pm 2) \times 10^{12}$	[c] $(5 \pm 2) \times 10^{12}$	[b] 8.2×10^{10}	[b] 2.8×10^{11}
DF(v = 4)	[c] $(1.3 \pm 0.6) \times 10^{13}$	[c] $(2.6 \pm 1) \times 10^{13}$	[b] 1.68×10^{11}	[b] 3.4×10^{11}
DF(v = 4)	[d] $(5 \pm 2) \times 10^{11}$	[e] $(3 \pm 1.5) \times 10^{12}$		

[a] Ref. 5

[b] Ref. 9

[c] Present results.

[d] Reaction (5), present results.

[e] Reaction (3), see text.

Table 5. Thermochemical Data[a]

Species	S^{o}_{298} cal/mol-K	$\Delta H^{o}_{f\ 298}$ kcal/mol
F	37.917	18.860
D	29.455	52.992
H	27.392	52.103
D_2	34.620	0.000
H_2	31.207	0.000
HD	34.343	0.077
DF(v = 0)	42.924	-65.85
DF(v = 4)	42.924	-34.160

[a]See Ref. 14.

$$F + HD \underset{k_{-10}}{\overset{k_{10}}{\rightleftarrows}} DF(4) + H \qquad (10)$$

and reported the rate of the F + DH → DF + H reaction to be 0.51 ± 0.03 of the rate of the F + D_2 → DF + D reaction. He also reported the branching fraction into DF(4) to be 0.13 ± 0.09. These values, together with the value of (0.95 ± 0.17) × 10^{13} cm^3/mol-s for the F + D_2 reaction, combine to give k_{10} = (6.3 ± 4.0) × 10^{11} cm^3/mol-s. A value of $K_{10,-10}$ = 2.0 can be calculated from the thermochemical data of Table 5. This results in a value of (3.1 ± 2) × 10^{11} cm^3/mol-s for k_{-10}, which is in agreement with the value of (5 ± 2) × 10^{11} measured in the present study. This good agreement between the directly measured value of k_{-10} and the value calculated from the value of k_{10} reinforces our confidence in the calculations of the removal rates of HF(v = 3), DF(v = 4) by H and D atoms by the reverse of the pumping reactions.

It has been suggested[8] that the fast removal rates of HF(v = 3) and DF(v = 4) by H and D atoms might be the result of the back reaction of the pumping reactions. Polanyi and coworkers[8] used the method of chemiluminescence depletion with mass spectrometry (CDMS) to study removal rates of HF(v = 1 - 6) by D atoms. With this technique they could determine relative depletion rates of the various levels and appearance rates of products. They found the depletion rates of HF(v) to increase dramatically for v = 3 through 6 from the very low rates for v = 1 and 2. When they added D atoms to a gas mixture containing HF(1), HF(2), and HF(3), they observed the fast removal of HF(3) and the appearance of HD. No HF(v = 1,2) increases were observed. Their results suggest that the removal of HF(3) by D atoms occurs solely by the isotopic analog of Reaction (1). This is inconsistent, however, with the results of the present study in which the rate coefficient of DF(v = 4) removal by D atoms was found to be almost an order of magnitude larger than that estimated above for Reaction (3) (the reverse of the F + D_2 pumping reaction). On the basis of the present data we conclude that vibrational deactivation must be the major channel for DF(v = 4) removal by H and D atoms. The dominance of vibrational deactivation was postulated by Heidner

and Bott[7] for the fast removal rates of HF(v = 3) by H and D atoms and the T^{-1} temperature dependence of these rate coefficients between 200 and 295 K.

Of concern to laser modelers is the effect of D-atom deactivation on laser performance. In the "cold reaction" chemical laser there is one D atom produced for each DF molecule. According to the recommended rate coefficients given in Ref. 3, the V-R,T deactivation of DF(v = 3) by DF has a rate coefficient of 4×10^{12} cm^3/mol-s at 295 K, and the V-V exchange between DF(v = 3) and DF(v = 0) has a rate coefficient of 1×10^{13} cm^3/mol-s. Therefore, with the rate coefficient of $5 \pm 2 \times 10^{12}$ cm^3/mol-s obtained in the present study, the deactivation of DF(v = 3) by D atoms is significant but not dominant in determining the removal rate of DF(v = 3). On the other hand, the deactivation of DF(v = 4) by atoms may well dominate over the self-deactivation by DF. According to Ref. 3, the recommended rate coefficients for the V-R,T deactivation of DF(v = 4) by DF and for the V-V exchange between DF(v = 4) and DF(v = 0) are 7×10^{12} cm^3/mol-s and 7.4×10^{12} cm^3/mol-s, respectively. Therefore, the value of $(2.6 \pm 1) \times 10^{13}$ cm^3/mol-s obtained in the present study for the deactivation of DF(v = 4) by D atoms is larger than the sum of the V-V and V-R,T self-deactivation rate coefficients of DF(v = 4) by DF.

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APPENDIX

THE REMOVAL RATE OF DF(v = 4) BY H ATOMS

The DF(v = 4), which is produced by the laser pulse, is removed by the three reactions

$$H + DF(4) \xrightarrow{k_5} HD + F \tag{5}$$

$$H + DF(4) \xrightarrow{k_6} H + DF(3, 2, 1, 0) \tag{6}$$

$$DF(4) + M \rightarrow DF(3, 2, 1, 0) + M \tag{7}$$

where M = H_2, DF, etc. The F atoms react with the abundant H_2 to produce HF(v = 3) in the reaction

$$F + H_2 \rightarrow HF(v = 1, 2, 3) + H \tag{8}$$

The HF(3) is then deactivated by H atoms by the process

$$H + HF(3) \rightarrow H + HF(v = 2, 1, 0) \tag{11}$$

Since the reverse reactions can be neglected when compared to the forward directions of Reactions 5, 6, and 7, the DF(4) disappears exponentially. The population of DF(4) can be described by

$$[DF(4)] = [DF(4)]_o \exp\left(\frac{-\tau}{\tau_2}\right) \tag{12}$$

where $[DF(4)]_o$ is the initial DF concentration produced by the laser pulse, and τ_2 is the exponential decay time.

When the F atoms produced by Reaction (5) react quickly to form HF in Reaction (8), the formation rate of HF(v = 3) can be described by the term

F k_5[H] [DF(4)] where F is the fraction of HF produced in the v = 3 vibrational level by Reaction (8). The removal rate of HF(v = 3) is simply k_{11}[H] [HF(3)]. The rate equation for the formation and removal of HF(3) can be solved to obtain

$$[HF(3)] = F\ k_5[H]\ [DF(4)]_o \frac{\tau_1\tau_2}{\tau_2 - \tau_1} \left\{\exp\left(\frac{-t}{\tau_2}\right) - \exp\left(\frac{-t}{\tau_1}\right)\right\} \qquad (13)$$

where τ_1 is the rise time defined by $1/\tau_1 = k_{11}[H]$. The intensity of the HF(3) fluorescence, I_{HF} (actually the photomultiplier signal), is given by

$$I_{HF} = S_{HF}\ A_{HF}\ [HF(v = 3)] \qquad (14)$$

where S_{HF} is the response of the photomultiplier at the wavelengths of the HF lines, and A_{HF} is the Einstein coefficient for the lines. A similar equation holds for I_{DF}.

I^0_{total}, the total intensity of $I_{DF} + I_{HF}$ extrapolated back to time = 0 from its values at long times, and I^0_{DF}, the DF fluorescence intensity at time = 0, can be related to k_5 by the equation

$$\left(\frac{I^0_{total}}{I^0_{DF}}\right) - 1 = \frac{S_{HF}}{S_{DF}} \frac{A_{HF}}{A_{DF}} F \frac{\tau_1\tau_2}{\tau_2 - \tau_1} k_5[H] \qquad (9)$$

Therefore, the value of k_5 can be determined from the fluorescence intensity profile if [H], the density of H atoms, is known. The values of A and F are available, and the relative responses, S_{HF} and S_{DF}, can be determined by a calibration.

LABORATORY OPERATIONS

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