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ABSOLUTE RATE COEFFICIENTS FOR F + H2 AND F + D2 AT T = 295 K.(U)
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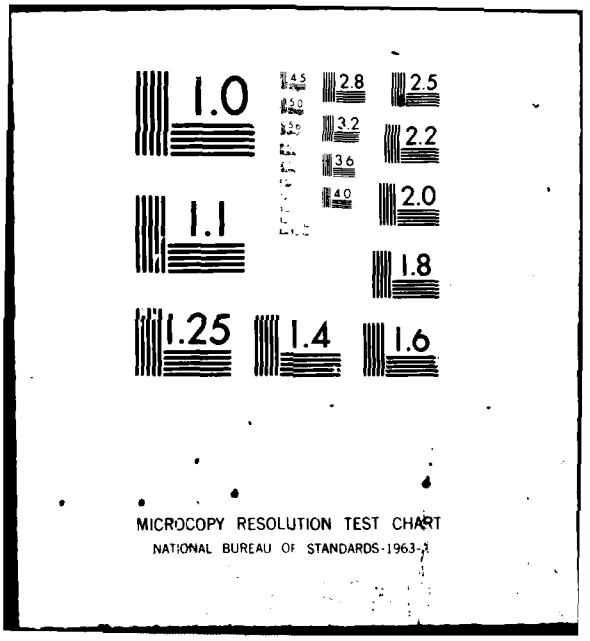
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REPORT SD-TR-80-1

Absolute Rate Coefficients for $F + H_2$ and $F + D_2$ at T = 295 K

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1 May 1980

Interim Report

Prepared for

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This interim report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-79-C-0080 with the Space Division, Deputy for Technology, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009. It was reviewed and approved for The Aerospace Corporation by W. R. Warren, Jr., Director, Aerophysics Laboratory. Lieutenant J. C. Garcia, SD/YLXT, was the project officer for Technology.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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(17) REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (18) SD-TR-80-1	2. GOVT ACCESSION NO. AD-A085 808
3. RECIPIENT'S CATALOG NUMBER (9)	
4. TITLE (and Subtitle) (6) ABSOLUTE RATE COEFFICIENTS FOR F + H_2 AND F + D_2 AT T = 295 K.	5. TYPE OF REPORT & PERIOD COVERED Interim rept.,
	6. PERFORMING ORG. REPORT NUMBER (14) TR-0080(5606)-1
7. AUTHOR(s) (7) Raymond F. Heidner III, Jerry F. Bott, Carrol E. Gardner, and James E. Melzer	8. CONTRACT OR GRANT NUMBER(s) (15) F04701-79-C-0080
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (12) 30
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Weapons Laboratory Kirtland Air Force Base N. Mex. 87117	12. REPORT DATE 1 May 1980
	13. NUMBER OF PAGES 29
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Space Division Air Force Systems Command Los Angeles, Calif. 90009	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Absolute Rate Coefficients
Deuterium
F Atoms
Hydrogen
Kinetic Isotope Effect
Multiphoton Dissociation
Time-Resolved Chemiluminescence

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The rate coefficients for the F + H_2 and F + D_2 reactions were determined to be $(1.8 \pm 0.3) \times 10^{13}$ and $(9.5 \pm 1.7) \times 10^{12}$ cm^3/mol-sec, respectively. The absolute values and the resultant ratio of H-atom to D-atom abstraction of 1.92 ± 0.23 are in agreement with earlier determinations. Fluorine atoms were generated under isothermal conditions in excess argon by means of the infrared multiphoton dissociation of SF_6. The reaction between F and H_2(D_2) was monitored by means of the time-resolved infrared emission from $HF^\dagger$($DF^\dagger$). The validity of the experimental method is discussed.

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I. INTRODUCTION

Accurate modeling of the HF and DF chemical lasers requires a reliable set of reaction rate coefficients. Cohen[1] has reviewed the literature to provide a standardized rate package for use with computer codes. In addition an excellent review of gaseous fluorine reactions has been recently presented by Foon and Kaufman.[2] The rates of the so-called "cold" reactions, $F + H_2$ and $F + D_2$, are among the most important parameters in the laser systems:

$$F + H_2 \xrightarrow{k_1} HF^\dagger + H \qquad (1)$$

$$F + D_2 \xrightarrow{k_2} DF^\dagger + D \qquad (2)$$

A number of measurements, both relative and absolute, have been reported in the last several years. Just recently, Quick and Wittig[3] and Preses et al.[4] reported that the infrared multiphoton dissociation of SF_6 is a convenient F-atom source for time-resolved kinetic measurements. In the present work this technique was used under demonstrably isothermal experimental conditions to obtain extremely precise rate coefficients for these two reactions. The accuracy of the determinations critically depends on the use of the total HF(DF) fundamental chemiluminescence as a diagnostic for the extent of reaction. This assumption is examined both analytically and with the use of The Aerospace Corporation numerical modeling code NEST.[5]

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The measurements were performed in a room-temperature flow system. Argon and calibrated mixtures of SF_6 in argon (10.24%), H_2 in argon (10.14%), and D_2 in argon (10.37%) were of the highest purity available in bulk-gas form. Molar flow rates were measured with rotameter flowmeters calibrated against pressure-rise measurements in a standard volume. The total pressure was measured with a capacitance manometer gauge (MKS Tru-Torr) with a resolution of 1×10^{-3} Torr. All data were taken at 3.95 ± 0.03 Torr pressure. SF_6 partial pressures of 6.5×10^{-3} and 33×10^{-3} Torr were used, and the $H_2(D_2)$ partial pressure was varied from 2.5 to 75×10^{-3} Torr. Argon constituted the balance of the flow.

The fluorescence cell incorporated into the flow system was a 10-cm-i.d. brass cube internally coated with teflon (Fig. 1). Radiation from a pulsed CO_2 laser (Lumonics K-202-2) entered and exited the cell through 15-cm-long, 2.5-cm-i.d. side arms fitted with NaCl windows. The laser was focused with a 38-cm focal length f.l. ZnSe lens into the center of the cell. In this region the beam diameter was constant at approximately 2 mm over 5 cm of optical path length. The reported data were taken with the use of the P(20) CO_2 line at 10.59 μm at an energy of 1.5 J/pulse. No visible emission was detected with a GaAs photomultiplier when argon alone, $Ar + SF_6$, or $Ar + H_2$ was flowed through the cell. Thus gas breakdown was eliminated as a consideration in these experiments. Substantial HF $3 \rightarrow 0$ overtone emission was observed at 8900 Å when H_2 and SF_6 were simultaneously present.

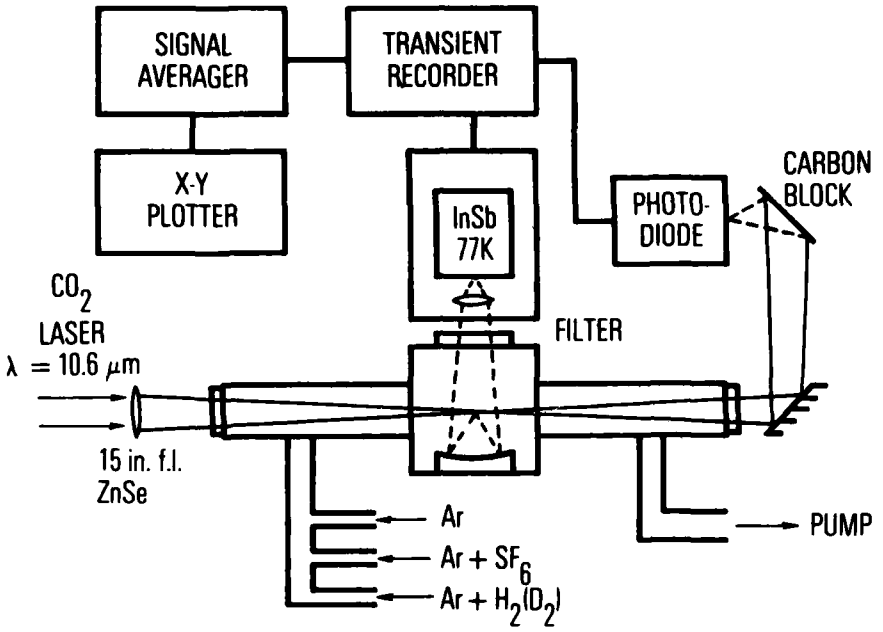

Fig. 1. Multiphoton Dissociation Infrared Fluorescence Apparatus

The chemiluminescence from $HF^{\dagger}$ or $DF^{\dagger}$ was collected by an internal 2-in.-diameter f/2 aluminum mirror overcoated with MgF_2. The radiation, after appropriate filtering, was focused onto a 77 K InSb detector (Texas Instruments). The amplified signal was recorded with a Biomation 805 transient recorder and stored in a Nicolet 1072 digital signal averager. The data represent an average of eight laser pulses. A typical trace is shown in Fig. 2 with the rise and fall of the chemiluminescence recorded on separate time bases. The measured rise time was always greater than 10 times the detector-amplifier response time of 1.5 μsec. The gas mixture was replaced approximately five times between laser shots in order to eliminate the possible effects of product accumulation on the measured rates. Although the experimental arrangement is nominally a flow system, the measured fluorescence times are orders of magnitude shorter than the transit time of gas through the cell. Thus the data are analyzed in terms of a laser-irradiated static mixture.

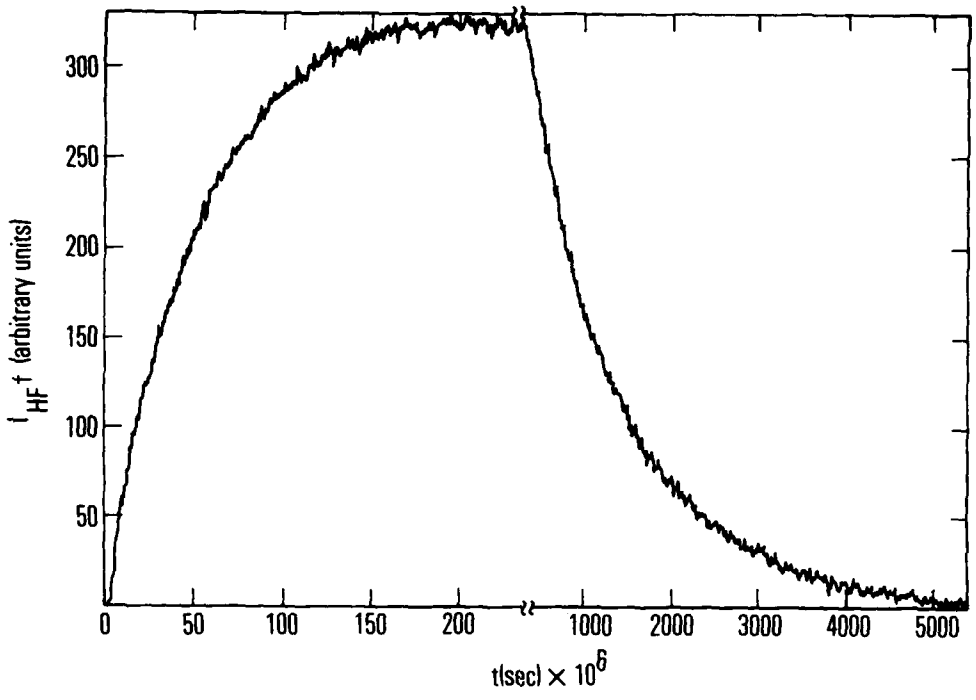

Fig. 2. Time-Resolved Infrared Chemiluminescence Trace. Channels 1-256, 0.5 μsec/channel; Channels 513-1024, 10 μsec/channel. Partial Pressures: SF_6 = 33 mTorr, H_2 = 24.3 mTorr, Ar = 3.87 Torr.

III. DATA ANALYSIS

The rate coefficient k_1 can be determined directly from the rise time of the fluorescence from $HF^\dagger$ produced by Reaction (1). This technique has been used previously for the measurement of reaction rate coefficients for reactions of Cl atoms with HBr(DBr) and HI(DI).[6] It provides an accurate value of the rate coefficient, if certain spectroscopic and kinetic conditions are met. These conditions are described in this section. The total fluorescence I(t) is related to the individual vibrational level populations by

$$I(t) = \sum_v A_v[HF(v)] \tag{3}$$

where A_v is the radiative lifetime of the v^{th} vibrational level. The initial vibrational populations are produced by Reaction (1):

$$F + H_2 \xrightarrow{k_1(v)} HF(v) + H, \quad v = 1, 2, 3$$

These levels are removed by a variety of processes; however, the following analysis focuses on single-quantum deactivation by quenching partners such as H_2 and argon, whose concentration remains essentially constant during the experiment ($[F] \ll [H_2]$).

$$HF(v) + M \xrightarrow{k_4(v)} HF(v - 1) + M \tag{4}$$

Process (4) can populate certain of the lower vibrational levels.

Radiative loss of $HF^{\dagger}$, V → V coupling between excited HF levels, and back transfer of vibrational energy from $H_2(v)$ to $HF(v')$ are omitted from the analysis. The result is an analytic expression that is tractable. The omitted terms were included in the NEST computer calculations and found to have little quantitative effect for the experimental conditions of this study. In this context, the rate equation for $[HF(v)]$ is

$$\frac{d}{dt}[HF(v)] = k_1(v)[H_2][F] - k_4(v)[HF(v)][M] + k_4(v+1)[HF(v+1)][M] \tag{5}$$

and the rate equation for total fluorescence intensity can be written as

$$\frac{dI(t)}{dt} = \frac{d}{dt}\sum_v A_v[HF(v)] = [H_2][F]\sum_v k_1(v)A_v - \sum_v k_4(v)A_v[HF(v)][M] + \sum_v k_4(v+1)A_v[HF(v+1)][M] \tag{6}$$

Equation (6) reduces exactly to Eq. (7)

$$\frac{dI(t)}{dt} = [H_2][F]\sum_v A_v k_1(v) - k_4(1)[M]I(t) \tag{7}$$

when the deactivation rate coefficients and the Einstein coefficients are related by Eq. (8).

$$\frac{k_4(2)}{k_4(1)} = \frac{A_2}{A_2 - A_1}$$

$$\frac{k_4(3)}{k_4(1)} = \frac{A_3}{A_3 - A_2} \tag{8}$$

In the case of harmonic oscillators, $A_v \propto v$ and $k_v \propto v$ such that Eq. (8) is satisfied exactly. HF is not harmonic, so $k_4(v)$ must increase as 1/2.4/4.93 to satisfy Eq. (8) with accepted values of the Einstein coefficients. Since $[F] = [F]_0 \exp(-k_1[H_2]t)$, Eq. (7) can be integrated to yield

$$I(t) = \frac{Ck_1[H_2][F]_0}{k_1[H_2]-k_4(1)[M]} \left\{\exp(-k_4(1)[M]t) - \exp(-k_1[H_2]t)\right\} \qquad (9)$$

where C is given by $(\sum_v A_v k_1(v))/k_1$. Therefore, the rise time of the fluorescence intensity τ_r is directly related to the rate coefficient k_1 by $\tau_r = (k_1[H_2])^{-1}$, and the decay time can be expressed as $\tau_f = (k_4(1)[M])^{-1}$. Equation (9) can be rewritten as:

$$I(t) = \frac{C\tau_r^{-1}[F]_0}{\tau_r^{-1} - \tau_f^{-1}} \left\{\exp\left(\frac{-t}{\tau_f}\right) - \exp\left(\frac{-t}{\tau_r}\right)\right\} \qquad (10)$$

At long times the intensity is represented by

$$I_L(t) = \frac{C\tau_r^{-1}[F]_0}{\tau_r^{-1} - \tau_f^{-1}} \exp\left(\frac{-t}{\tau_f}\right) \qquad (11)$$

The short-time intensity difference between Eqs. (10) and (11) is given by

$$I_S(t) = I_L(t) - I(t) = \frac{C\tau_r^{-1}[F]_o}{\tau_r^{-1} - \tau_f^{-1}} \exp\left(\frac{-t}{\tau_r}\right) \qquad (12)$$

Both Eq. (11) and Eq. (12) have the same intercept, which can be related to the initial F-atom concentration

$$[F]_0 = \frac{I_L(0)}{C} \frac{\tau_r^{-1} - \tau_f^{-1}}{\tau_r^{-1}} \qquad (13a)$$

$$= \frac{I_S(0)}{C} \frac{\tau_r^{-1} - \tau_f^{-1}}{\tau_r^{-1}} \qquad (13b)$$

Numerical modeling calculations were performed with the NEST[5] computer code with input parameters corresponding to the present experimental conditions in order to test the accuracy of these analytic approximations. Recommended values of A_v, the reaction rate coefficients $k_1(v)$ for the $F + H_2 \rightarrow HF(v) + H$ reactions, and the HF(v)-HF deactivation processes $k_4(v)$ were taken from Reference 1. Rate coefficients for HF(v) deactivation by H and H_2 were taken from References 7 and 8, respectively.

The computer code calculated a time-dependent fluorescence profile from which a rise time and a decay time were extracted by the same method applied to the laboratory data. The limitations of the analytical equations were revealed by comparing the derived rate coefficients with the input values. The most important conclusion is that $\tau_r = (k_1[H_2])^{-1}$ is a good approximation even when Eq. (8) is not valid, as long as $\tau_r \ll \tau_f$. The computed fluorescence profiles obey this latter criterion to a high degree of accuracy. Results of these calculations are shown in Table I for three different H_2 pressures.

The experimental decay times τ_f are somewhat shorter than those computed with the standard rate coefficients. The ratio τ_f/τ_r ranged

from 6 to 30 for the experimental data. The measured decay times were sensitive to gas purity and handling techniques; impurity deactivation of HF(v), e.g., by H_2O, may play a role in these experiments. Artificially fast decay rates were inserted into the calculations in order to reproduce the experimental decay times and determine the effect of additional deactivation on the derived rise times. Three methods of scaling this increased deactivation with v were examined: (1) $k_4(v)$ = constant, (2) $k_4(v) \alpha v^2$, and (3) $k_4(v)$ scaling by Eq. (8). The normalized rise times and decay times determined from the fluorescence profiles are listed in Table I for these three cases. The first two cases did not decay with single exponential rates; therefore the decay times are approximate force fits. The calculated rise time for 0.001 Torr F and 0.005 Torr H_2 was lengthened somewhat by the removal of 20% of the H_2 during the chemical reaction. From these calculations the systematic error in relating the fluorescence rise time to the rate coefficients k_1 and k_2 is estimated to be ±5%.

Table I. Numerical Modeling Results for Representative Conditions of 0.001 Torr F and 4.0 Torr Ar + H_2

	Case	0.005 Torr H_2	0.025 Torr H_2	0.10 Torr H_2
$\tau_r^{-1}/k_1[H_2]$	1[a]	1.00	0.99	0.98
	2[b]	0.85	0.97	0.98
	3	1.09	1.12	1.06
	4	0.98	0.96	0.95
$\tau_f^{-1}/k_4(1)[Ar]$	1	na	na	na
	2	1.00	1.00	0.98
	3	1.02	1.14	1.05
	4	0.69	0.69	0.60

[a]Case 1 = Standard reaction rate coefficients (see text).

Case 2 = $k_4(v)$ scaled from Eq. (8), 1/2.4/4.93/14.3.

Case 3 = $k_4(v) \propto v^2$.

Case 4 = $k_4(v)$ = constant.

[b]In Cases 2 through 4, $k_4(1)$ is adjusted to provide reasonably close agreement between calculated and measured decay times.

IV. RESULTS

The analytic description of the infrared chemiluminescence is approximate, and numerous checks on the accuracy of the analysis were performed. The linearity of $\ln I_L(t)$ and $\ln I_S(t)$ versus t is shown in Fig. 3, which represents a deconvolution of the trace presented in Fig. 2. The deviations from linearity predicted in Table I for certain deactivation rate scalings are barely discernible within the experimental scatter. The intercepts $I_L(0)$ and $I_S(0)$ were typically the same (within 10%), as predicted. Plots of $[F]_0$, calculated with Eq. (13), versus $[H_2]$ or $[D_2]$ were constant to ±15% for nominally constant laser conditions. Thus $SF_6^\dagger + H_2(D_2)$ collisions do not contribute to $[F]_0$ or, by implication, to the time history of $HF^\dagger$. These results agree with previous deductions about the system.[3] Although each data set was collected for constant $[SF_6]$, a plot of $\ln[F]_0$ versus $\ln[SF_6]$ had a slope of 1.06, demonstrating that the formation of F atoms is linearly dependent on the $[SF_6]$. As expected, $SF_6^\dagger$-$SF_6^\dagger$ collisions do not play a role in F-atom formation.

The fall time of the infrared chemiluminescence was plotted versus the $[H_2]$ and $[D_2]$ and compared with computer simulations that were based on the known collisional, radiative, diffusional, and convective losses of $HF^\dagger$ and $DF^\dagger$ (Fig. 4). The last three removal processes are held constant in these plots. Thus the slope should represent the collisional quenching of the coupled HF(v) levels by H_2 and the DF(v) levels by D_2. As discussed

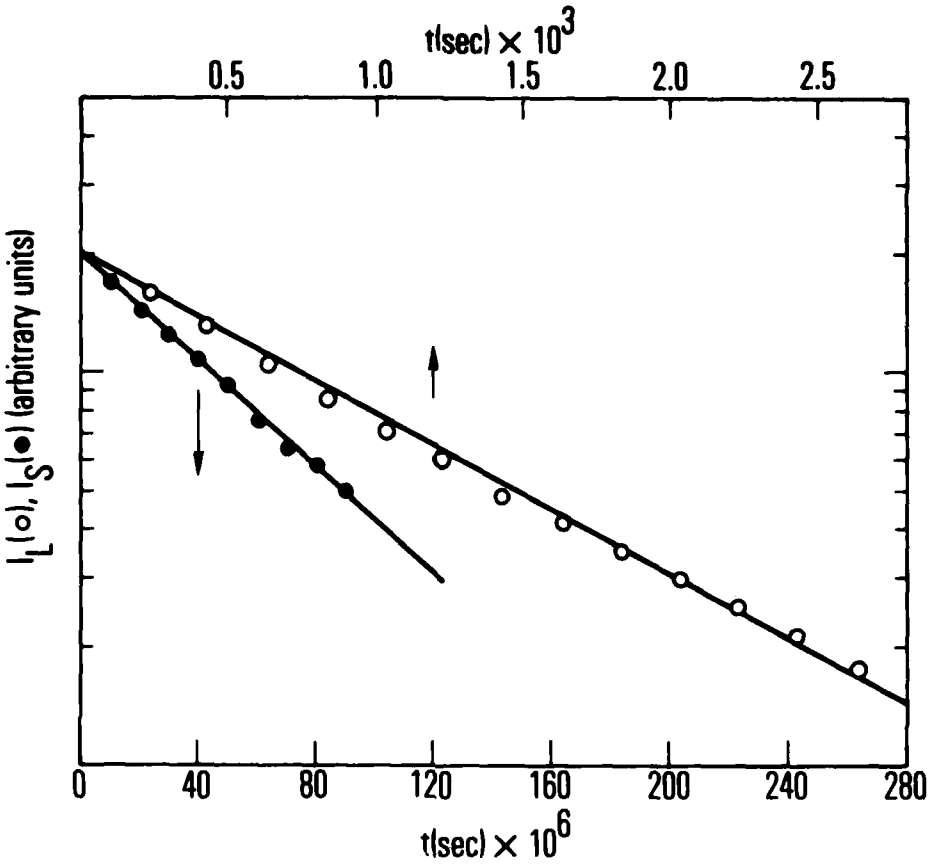

Fig. 3. Plots of I_L Versus t [(Eq. 11)] and I_S Versus t [(Eq. (12)] from Trace in Fig. 2

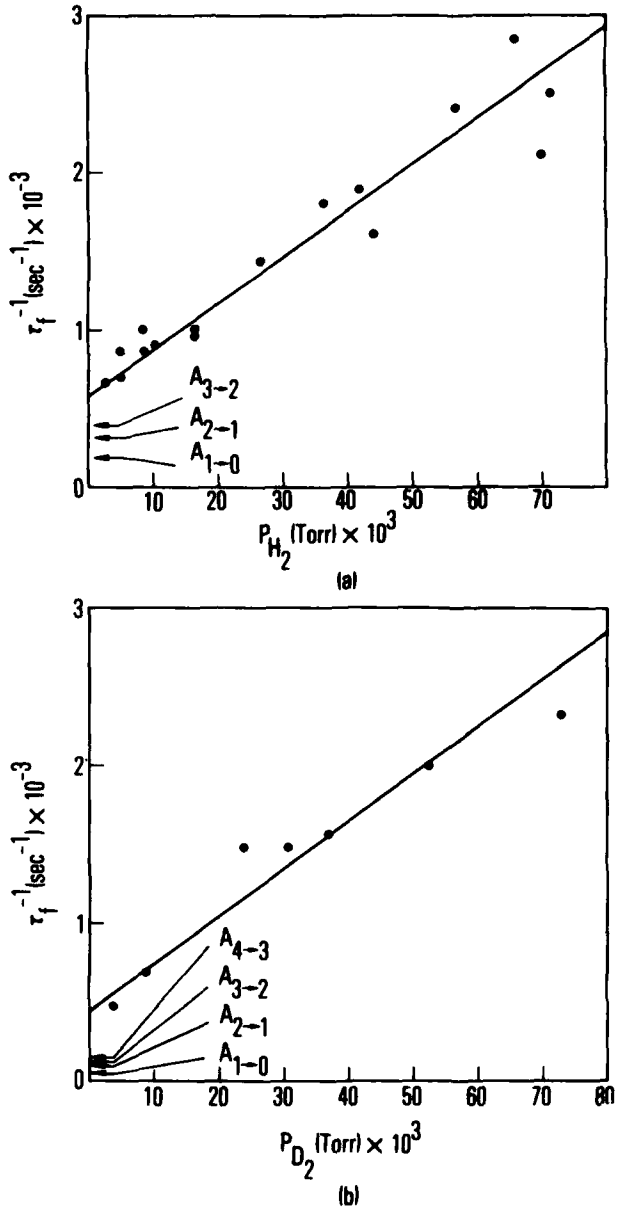

Fig. 4. Inverse Fall Times τ_f^{-1} for (a) $HF^\dagger$ as Function of H_2 Pressure and (b) $DF^\dagger$ as Function of D_2 Pressure

earlier, the measured quenching rates are faster than the computed rates. A low-level H_2O impurity in the $H_2(D_2)$ is the most likely explanation for these results, but additional experiments are in progress.

The inverse rise time τ_r^{-1} of the infrared chemiluminescence is given by $k_1[H_2]$ and $k_2[D_2]$. These quantities are plotted versus $[H_2]$ and $[D_2]$ in Fig. 5. An unweighted linear least-squares fit to these data results in the rate coefficients $k_1 = (1.81 \pm 0.07) \times 10^{13}$ and $k_2 = (9.46 \pm 0.30) \times 10^{12}$ cm^3/mol-sec. The values given in Tables II and III have stated errors that reflect the statistical error previously given and a systematic error of ±15%.

The determination of k_1/k_2 (Table III) is extremely insensitive to systematic errors in the various calibration procedures. The proposed value $k_1/k_2 = 1.92 \pm 0.23$ has an error given by $k_1/k_2\ (\sigma_1/k_1 + \sigma_2/k_2 + 0.05)$, where σ_1 and σ_2 are the standard deviations of k_1 and k_2 (Fig. 5). The term $0.05\ k_1/k_2$ reflects the uncertainty in the use of infrared chemiluminescence from HF or DF as an F-atom disappearance diagnostic.

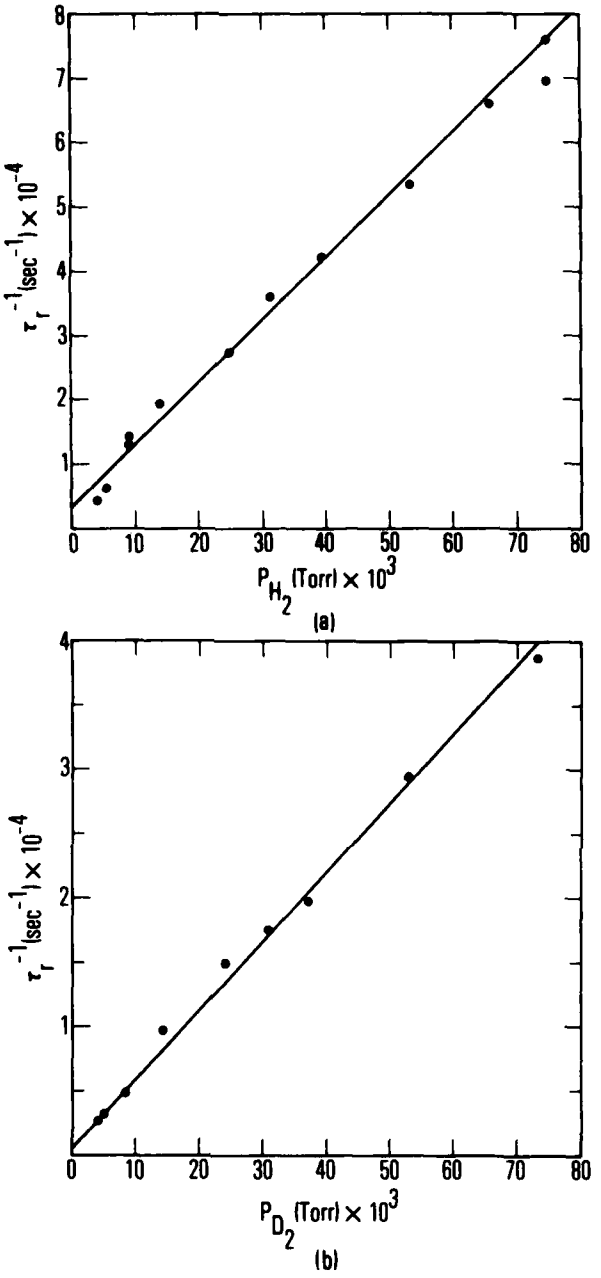

Fig. 5. Inverse Rise Times τ_r^{-1} for (a) $HF^\dagger$ as Function of H_2 Pressure and (b) $DF^\dagger$ as Function of D_2 Pressure

Table II. Absolute Rate Coefficients for $F + H_2 \rightarrow HF^{\dagger} + H$ at T = 298 K

k (cm^3/mol-sec)	Technique		Reference
	F-Atom Source	Detection Method	
1.1×10^{13}	$N + NF_2$	Mass Spectrometry	9
$(1.8 \pm 0.4) \times 10^{13}$	F_2 Discharge	Mass Spectrometry	10
3.8×10^{13}	WF_6 Flash Photolysis	HF Laser Emission	11
$(1.5 \pm 0.4) \times 10^{13}$		Molecular Beam Mass Spectrometry	12
1.0×10^{13}	F_2 Thermal Dissociation	ESR	13
1.5×10^{13} (±50%)	CF_4 Discharge	F by ClNO Titration, H_2 by Mass Spectrometry	14
$(1.00 \pm 0.08) \times 10^{13}$	F_2 Discharge	ESR	15
1.3×10^{13}	MoF_6 Flash Photolysis	HF Laser Emission	16
2.1×10^{13}	SF_6 Multiphoton Dissociation	$HF^{\dagger}$ Chemiluminescence	3
$(2.0 \pm 0.3) \times 10^{13}$	SF_6 Multiphoton Dissociation	$HF^{\dagger}$ Chemiluminescence	4
$(1.8 \pm 0.3) \times 10^{13}$	SF_6 Multiphoton Dissociation	$HF^{\dagger}$ Chemiluminescence	This Work

Table III. Absolute and Relative Rate Coefficients for

$F + D_2 \rightarrow DF^{\dagger} + D$ at T = 298 K

k_2 (cm^3/mol-sec)	$\frac{k_1}{k_2}$	Technique		Reference
		F-Atom Source	Detection Method	
	2.0 (T = 293 K)	F_2 Equilibrium Dissociation	EPR of H and D from Discharged Product HF and DF	17
	1.7 ± 0.4 (1.9)[a]	F_2 Equilibrium Dissociation	Gas Chromatography	18
	1.79 ± 0.10	Flash Photolysis	Chemical Laser Emission	19
	1.8 ± 0.4 (T = 283 K)	Nuclear Recoil $^{19}F(n, 2n)^{18}F$	Radio Gas Chromatography	20
	1.91 ± 0.08	Microwave Discharge	Mass Spectrometry	21
	1.16 ± 0.1	Pulsed Electrical Discharge	Chemical Laser Emission	22
	1.94 ± 0.04	Nuclear Recoil $^{19}F(n, 2n)^{18}F$	Radio Assay	23
$(1.19 \pm 0.18) \times 10^{13}$	1.65 ± 0.35	Multiphoton Dissociation (SF_6)	IR Chemiluminescence	4
$(9.5 \pm 1.7) \times 10^{12}$	1.92 ± 0.23	Multiphoton Dissociation (SF_6)	IR Chemiluminescence	This Work

[a]Derived from temperature-dependent fit to k_1/k_2 in Reference 18.

V. DISCUSSION

The result for k_1 obtained in this study is in excellent agreement with those determined by Quick and Wittig[3] and by Preses et al.[4] Although in all three studies the same basic experimental technique was used, in the present study an attempt was made to establish well-defined conditions for kinetic rate measurements. Unlike the earlier studies data were collected for a constant pressure of inert buffer gas (argon) with a ratio of $[Ar]/[F]_0 \sim 4 \times 10^3$, which eliminates the possibility of hot-atom reactions[24] between F and $H_2(D_2)$ and limits the adiabatic temperature rise to approximately 2.5°C. Computer calculations made with the use of the NEST[5] code indicate that the actual temperature rise during the fluorescence rise time is <1 C for $[F]_0$ = 0.001 Torr. The change in k_1 when $[SF_6]_0$ was increased from 6.6 to 33 mTorr was not statistically significant. This observation rules out a temperature rise produced by the laser heating of nondissociating SF_6.

The other experimental determinations of k_1 (Table II) have been critically reviewed by Cohen[1] and by Foon and Kaufman.[2] Each review recommends the value $k_1 = (1.5 \pm 0.5) \times 10^{13}$ cm^3/mol-sec and cites the study by Clyne et al.[14] as the most direct. The present measurement falls within the high side of that experimental limit and disagrees principally with several precise ESR studies.[13, 15]

Absolute measurements of k_2 were nonexistent until very recently (Table III); thus the principal comparison of the multiphoton result must be with earlier measurements of the k_1/k_2 ratio. The study by Persky[21] is

the most precise determination of k_1/k_2 made under demonstrably thermalized conditions. That study is in excellent agreement with the nuclear-recoil experiments of Grant and Root[23] in which highly moderated ^{18}F atoms were used. The measurements obtained in this study are in close agreement with these results and are within the experimental error of most of the other determinations in Table III. Thus the value of $k_2 = (9.5 \pm 1.7) \times 10^{12}$ cm^3/mol-sec is both a direct determination and one that satisfies well-established values for k_1/k_2.

The temperature dependence of k_1/k_2 has been measured by Persky,[21] $[k_1/k_2 = (1.04 \pm 0.02)\exp(370 \pm 10)/RT]$, and by Grant and Root,[23] $[k_1/k_2 = (1.04 \pm 0.06)\exp(382 \pm 35)/RT]$, with upper temperature limits of 417 and 475 K, respectively. These data provide a useful standard for evaluating the results of future high-temperature studies of $F + H_2$ and $F + D_2$ by means of the multiphoton dissociation-infrared chemiluminescence technique.

VI. CONCLUSIONS

Accurate and precise rate coefficients for the $F + H_2$ and $F + D_2$ reactions have been measured under highly controlled experimental conditions. The extension of the work to temperature-dependent studies over the wide temperature range required for modeling of electron-beam-initiated HF and DF chemical lasers is in progress.

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The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military concepts and systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the Nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

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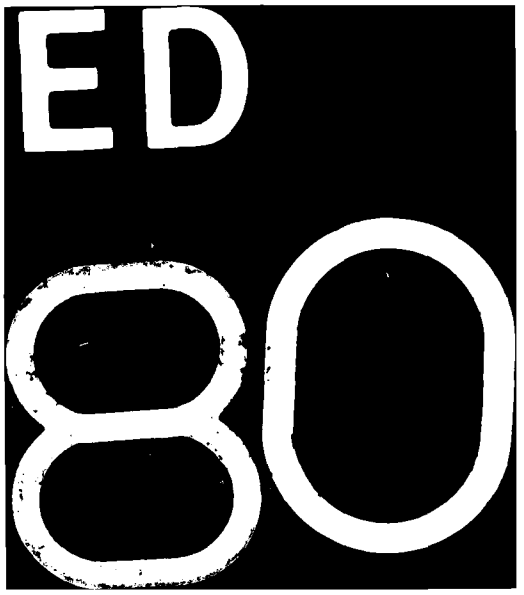
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