ABSOLUTE RATE COEFFICIENTS FOR F + H2 AND F + D2 AT T = 295 K (U)

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Absolute Rate Coefficients for F + H\(_2\)
and F + D\(_2\) at T = 295 K

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Interim Report

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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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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 $1.92 \pm 0.23$ 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$^+(DF^+)$. The validity of the experimental method is discussed.
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III. Absolute and Relative Rate Coefficients for F + D₂ → DF⁺ + D at T = 298 K
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, \(F + \text{H}_2\) and \(F + \text{D}_2\), are among the most important parameters in the laser systems:

\[
\begin{align*}
\text{(1)} & \quad F + \text{H}_2 & \rightarrow & \text{HF}^+ + \text{H} \\
\text{(2)} & \quad F + \text{D}_2 & \rightarrow & \text{DF}^+ + \text{D}
\end{align*}
\]

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 \(\text{SF}_6\) 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 $\text{SF}_6$ in argon (10.24%), $\text{H}_2$ in argon (10.14%), and $\text{D}_2$ 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 $1 \times 10^{-3}$ Torr. All data were taken at $3.95 \pm 0.03$ Torr pressure. $\text{SF}_6$ partial pressures of $6.5 \times 10^{-3}$ and $33 \times 10^{-3}$ Torr were used, and the $\text{H}_2(\text{D}_2)$ partial pressure was varied from 2.5 to $75 \times 10^{-3}$ 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 $\text{CO}_2$ 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 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) $\text{CO}_2$ 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, $\text{Ar} + \text{SF}_6$, or $\text{Ar} + \text{H}_2$ was flowed through the cell. Thus gas breakdown was eliminated as a consideration in these experiments. Substantial HF 3→0 overtone emission was observed at 8900 Å when $\text{H}_2$ and $\text{SF}_6$ were simultaneously present.
Fig. 1. Multiphoton Dissociation Infrared Fluorescence Apparatus
The chemiluminescence from HF⁺ or DF⁺ was collected by an internal 2-in.-diameter \( f/2 \) aluminum mirror overcoated with MgF₂. 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 \( \mu \)sec. 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: SF₆ = 33 mTorr, H₂ = 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 $\text{HF}^+$ 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

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

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

$$\text{F} + \text{H}_2 \xrightarrow{k_1(v)} \text{HF}(v) + \text{H}, \; v = 1, 2, 3$$

These levels are removed by a variety of processes; however, the following analysis focuses on single-quantum deactivation by quenching partners such as $\text{H}_2$ and argon, whose concentration remains essentially constant during the experiment ($[\text{F}] \ll [\text{H}_2]$).

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

Process (4) can populate certain of the lower vibrational levels.
Radiative loss of HF$^+$, $V \rightarrow V$ 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

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

(5)

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

$$\frac{dI(t)}{dt} = \sum_{v} A_v[HF(v)] = [H_2][F] \sum_{v} k_1(v)A_v - \sum_{v} k_4(v)A_v[HF(v)][M]$$

$$+ \sum_{v} k_4(v + 1)A_v[HF(v + 1)][M]$$

(6)

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

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

(7)

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

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

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

(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

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

(9)

where $C$ is given by $(\sum A_v k_1(v))/k_1$. Therefore, the rise time of the fluorescence intensity $\tau_r$ 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:

$$I(t) = \frac{C\tau^{-1}_r[F]_0}{\tau^{-1}_r - \tau^{-1}_f} \left| \exp\left(-\frac{t}{\tau_r}\right) - \exp\left(-\frac{t}{\tau_f}\right) \right|$$

(10)

At long times the intensity is represented by

$$I_L(t) = \frac{C\tau^{-1}_r[F]_0}{\tau^{-1}_r - \tau^{-1}_f} \exp\left(-\frac{t}{\tau_f}\right)$$

(11)

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

$$I_S(t) = I_L(t) - I(t) = \frac{C\tau^{-1}_r[F]_0}{\tau^{-1}_r - \tau^{-1}_f} \exp\left(-\frac{t}{\tau_r}\right)$$

(12)

Both Eq. (11) and Eq. (12) have the same intercept, which can be related to the initial $F$-atom concentration.
\[
[F]_0 = \frac{L_l(0)}{C} \frac{\tau_{r}^{-1} - \tau_{f}^{-1}}{\tau_{r}^{-1}} \quad (13a)
\]
\[
= \frac{L_s(0)}{C} \frac{\tau_{r}^{-1} - \tau_{f}^{-1}}{\tau_{r}^{-1}} \quad (13b)
\]

Numerical modeling calculations were performed with the NEST 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 \(k_4(v)\) 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 \(\tau_{r} = (k_4[H_2])^{-1}\) 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 \(\tau_{f}\) are somewhat shorter than those computed with the standard rate coefficients. The ratio \(\tau_{f}/\tau_{r}\) 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$_2$O, 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 $\pm 5\%$. 

-17-
Table I. Numerical Modeling Results for Representative Conditions of 0.001 Torr F and 4.0 Torr Ar + H₂

<table>
<thead>
<tr>
<th>Case</th>
<th>0.005 Torr H₂</th>
<th>0.025 Torr H₂</th>
<th>0.10 Torr H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>τ⁻¹ /k₁[H₂]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>1.00</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>2b</td>
<td>0.85</td>
<td>0.97</td>
<td>0.98</td>
</tr>
<tr>
<td>3</td>
<td>1.09</td>
<td>1.12</td>
<td>1.06</td>
</tr>
<tr>
<td>4</td>
<td>0.98</td>
<td>0.96</td>
<td>0.95</td>
</tr>
<tr>
<td>1</td>
<td>na</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>1.00</td>
<td>0.98</td>
</tr>
<tr>
<td>3</td>
<td>1.02</td>
<td>1.14</td>
<td>1.05</td>
</tr>
<tr>
<td>4</td>
<td>0.69</td>
<td>0.69</td>
<td>0.60</td>
</tr>
</tbody>
</table>

aCase 1 = Standard reaction rate coefficients (see text).
Case 2 = k₄(v) scaled from Eq. (8), 1/2.4/4.93/14.3.
Case 3 = k₄(v) ∝ v².
Case 4 = k₄(v) = constant.

bIn Cases 2 through 4, k₄(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 $SF_6^+ + H_2(D_2)$ collisions do not contribute to $[F]_0$ or, by implication, to the time history of HF$^+$. These results agree with previous deductions about the system. 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, $SF_6^+ - SF_6$ 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$^+$ and DF$^+$ (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 $\tau_f^{-1}$ for (a) HF$^+$ as Function of $H_2$ Pressure and (b) DF$^+$ as Function of $D_2$ Pressure
earlier, the measured quenching rates are faster than the computed rates. 
A low-level H₂O impurity in the H₂(D₂) is the most likely explanation for 
these results, but additional experiments are in progress.

The inverse rise time $\tau^{-1}$ 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 $k_2 = (9.46 \pm 0.30) \times 10^{12}$ cm³/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 $\sigma_1$ and $\sigma_2$ 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 $\tau^{-1}$ for (a) HF$^+$ as Function of H$_2$ Pressure and (b) DF$^+$ as Function of D$_2$ Pressure
Table II. Absolute Rate Coefficients for $F + H_2 \rightarrow HF^+ + H$ at $T = 298$ K

<table>
<thead>
<tr>
<th>$k$ (cm$^3$/mol·sec)</th>
<th>F-Atom Source</th>
<th>Detection Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.1 \times 10^{13}$</td>
<td>N + NF$_2$</td>
<td>Mass Spectrometry</td>
<td>9</td>
</tr>
<tr>
<td>$(1.8 \pm 0.4) \times 10^{13}$</td>
<td>$F_2$ Discharge</td>
<td>Mass Spectrometry</td>
<td>10</td>
</tr>
<tr>
<td>$3.8 \times 10^{13}$</td>
<td>WF$_6$ Flash Photolysis</td>
<td>HF Laser Emission</td>
<td>11</td>
</tr>
<tr>
<td>$(1.5 \pm 0.4) \times 10^{13}$</td>
<td>$F_2$ Thermal Dissociation</td>
<td>Molecular Beam Mass Spectrometry</td>
<td>12</td>
</tr>
<tr>
<td>$1.0 \times 10^{13}$</td>
<td></td>
<td>ESR</td>
<td>13</td>
</tr>
<tr>
<td>$1.5 \times 10^{13}$ (±50%)</td>
<td>CF$_4$ Discharge</td>
<td>F by CINO Titration, H$_2$ by Mass Spectrometry</td>
<td>14</td>
</tr>
<tr>
<td>$(1.00 \pm 0.08) \times 10^{13}$</td>
<td>$F_2$ Discharge</td>
<td>ESR</td>
<td>15</td>
</tr>
<tr>
<td>$1.3 \times 10^{13}$</td>
<td>MoF$_6$ Flash Photolysis</td>
<td>HF Laser Emission</td>
<td>16</td>
</tr>
<tr>
<td>$2.1 \times 10^{13}$</td>
<td>SF$_6$ Multiphoton Dissociation</td>
<td>HF$^+$ Chemiluminescence</td>
<td>3</td>
</tr>
<tr>
<td>$(2.0 \pm 0.3) \times 10^{13}$</td>
<td>SF$_6$ Multiphoton Dissociation</td>
<td>HF$^+$ Chemiluminescence</td>
<td>4</td>
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<tr>
<td>$(1.8 \pm 0.3) \times 10^{13}$</td>
<td>SF$_6$ Multiphoton Dissociation</td>
<td>HF$^+$ Chemiluminescence</td>
<td>This Work</td>
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Table III. Absolute and Relative Rate Coefficients for F + D₂ → DF⁺ + D at T = 298 K

<table>
<thead>
<tr>
<th>k₂ (cm³/mol·sec)</th>
<th>k₁/k₂</th>
<th>Technique</th>
<th>F-Atom Source</th>
<th>Detection Method</th>
<th>Reference</th>
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<tr>
<td>2.0 (T = 293 K)</td>
<td></td>
<td>F₂ Equilibrium Dissociation</td>
<td>EPR of H and D from Discharged Product HF and DF</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>1.7 ± 0.4 (1.9)³</td>
<td></td>
<td>F₂ Equilibrium Dissociation</td>
<td>Gas Chromatography</td>
<td>18</td>
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</tr>
<tr>
<td>1.79 ± 0.10</td>
<td></td>
<td>Flash Photolysis</td>
<td>Chemical Laser Emission</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>1.8 ± 0.4 (T = 283 K)</td>
<td>Nuclear Recoil ¹⁹F(n, 2n)¹⁸F</td>
<td>Radio Gas Chromatography</td>
<td>20</td>
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<tr>
<td>1.91 ± 0.08</td>
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<td>Microwave Discharge</td>
<td>Mass Spectrometry</td>
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<tr>
<td>1.16 ± 0.1</td>
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<td>Pulsed Electrical Discharge</td>
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<tr>
<td>1.94 ± 0.04</td>
<td>Nuclear Recoil ¹⁹F(n, 2n)¹⁸F</td>
<td>Radio Assay</td>
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<td></td>
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<tr>
<td>(1.19 ± 0.18) x 10¹³</td>
<td>1.65 ± 0.35</td>
<td>Multiphoton Dissociation (SF₆)</td>
<td>IR Chemiluminescence</td>
<td>4</td>
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<tr>
<td>(9.5 ± 1.7) x 10¹²</td>
<td>1.92 ± 0.23</td>
<td>Multiphoton Dissociation (SF₆)</td>
<td>IR Chemiluminescence</td>
<td>This Work</td>
<td></td>
</tr>
</tbody>
</table>

³Derived from temperature-dependent fit to k₁/k₂ 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 and by Preses et al. 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 $[\text{Ar}]/[\text{F}]_0 \sim 4 \times 10^{-3}$, which eliminates the possibility of hot-atom reactions between $\text{F}$ and $\text{H}_2(\text{D}_2)$ and limits the adiabatic temperature rise to approximately $2.5^\circ \text{C}$. Computer calculations made with the use of the NEST code indicate that the actual temperature rise during the fluorescence rise time is $<1^\circ \text{C}$ for $[\text{F}]_0 = 0.001$ Torr. The change in $k_1$ when $[\text{SF}_6]_0$ 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 $\text{SF}_6$.

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

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 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\textsuperscript{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,\textsuperscript{21} 

$$[k_1/k_2 = (1.04 \pm 0.02)\exp(370 \pm 10)/RT],$$

and by Grant and Root,\textsuperscript{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.
REFERENCES


2. R. Foon and M. Kaufman, Prog. in Reaction Kinetics 8, 81 (1975).


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