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Room Temperature Rate Constant For H + F$_2$

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ABSTRACT

The rate constants for H atom reactions with Cl$_2$ and F$_2$ have been measured by monitoring the loss rate of hydrogen atoms in the presence of excess [Cl$_2$] and [F$_2$] via time-resolved, laser-induced Lyman-α fluorescence. The rate constants for H + F$_2$ and H + Cl$_2$ were found to be 2.4 ± 0.4 (2σ) x 10^{-12} and 2.52 ± 0.18 (2σ) x 10^{-11} cm^3 molecules^{-1} s^{-1}, respectively. The result for H + F$_2$ is consistent with the recommendation of Baulch et. al. (J. Phys. Chem. Ref. Data **10** (suppl. 1) (1981)) and our k(H + Cl$_2$) value is consistent with the majority of previous measurements.

1. INTRODUCTION

A chemical HF laser can be used to produce a high power 2.7 μm beam. Vibrationally excited HF is generated primarily by the F atom reaction with molecular hydrogen

$$F + H_2 \rightarrow HF(v = 0 - 3) + H. \tag{1}$$

or via the secondary reaction

$$H + F_2 \rightarrow HF(v = 0 - 9) + F. \tag{2}$$

The rate constant[1,2] and nascent HF(v) distribution[3,4] for reaction [1] are well established, k$_1$(T) = 1.1 ± 0.1 x 10^{-10} exp(-(450±50)/T) cm^3 molecules^{-1} s^{-1} and 0.0 : 0.15 : 0.55 : 0.30 for P$_0$:P$_1$:P$_2$:P$_3$. The detailed dynamics of reaction [1] have been exhaustively studied, both theoretically[5,6] and experimentally[7-12] by numerous investigators.

Surprisingly, the same cannot be said for reaction [2]. The 1981 kinetics review by Baulch et. al.[13] lists only 8 previous measurements of the rate constant (compared to 22 for reaction [1]) and recommends k$_2$(T)= 1.46 x 10^{-10} exp(-1210/T) cm^3 molecules^{-1} s^{-1} and k$_2$(298 K) = 2.5 x 10^{-12} cm^3 molecules^{-1} s^{-1}. A 1983 review by Cohen & Westberg[14] evaluated the same ensemble of measurements and selected k$_2$(T) = 4.8 x 10^{-15} T$^{1.4}$ exp(-667/T) cm^3 molecules^{-1} s^{-1} and k$_2$(298 K) = 1.5 x 10^{-12} cm^3 molecules^{-1} s^{-1}. Both recommendations are based primarily on mass-spectrometric experiments by Dodonov and co-workers.[15,16] (k$_2$(T) = 2.0 ± 0.2 x 10^{-10} exp((-1210 ± 100)/T) cm^3 molecules^{-1} s^{-1} for T = 294 - 565 K) and Homann, et. al.[17] (k$_2$(T) = 6.6 ± 1.7 x 10^{-11} exp((-1110 ± 50)/T) for T = 224 - 493 K). The activation energies of both expressions are essentially the same but the pre-exponential factors differ by a factor of 3. Additional measurements by Levy & Copeland[18], Rabideau et al.[19], and Sung, et al.[20] have also been reported. Levy and Copeland[18] measured F$_2$ consumption following UV irradiation of a H$_2$, F$_2$, N$_2$ and O$_2$ mixture. They did not measure k$_2$ directly; rather, they report the rate constant ratio between reaction [2] and H + O$_2$ + M $\rightarrow$ HO$_2$ + M. Using the accepted value for the reference reaction[13], their result corresponds to k$_2$(298 K) = 1.0 x 10^{-12} cm^3 molecules^{-1} s^{-1}. Rabideau, et. al. added molecular fluorine to a fast-flowing mixture of H and H$_2$ diluted in He, while monitoring the concentration of F and H atoms via EPR. The room temperature rate constants for reactions [1] and [2] were determined to be 6.6 ± 1.7 x 10^{-12} and 4.2 ± 0.3 x 10^{-12} cm^3 molecules^{-1} s^{-1}, respectively. Their result for k$_1$ is approximately a factor of 4 lower than the recommended value of Baulch[13]. Sung et al.[20] measured the infrared chemiluminescence from HCl(v) and HF(v) products generated by H atom reactions with Cl$_2$, F$_2$, ClF, and ICl. Although they "make no strong claim on the reliability of the H + F$_2$ rate constant," they report a ratio of k$_2$ / k$_3$ = 0.053, where k$_3$ is the rate constant for

$$H + Cl_2 \rightarrow HCl(v = 0 - 4) + Cl. \tag{3}$$

If the recommended value for k$_3$ is used (1.9 x 10^{-11} cm^3 molecules^{-1} s^{-1} at 298 K)[13], k$_2$ = 1.0 x 10^{-12} cm^3 molecules^{-1} s^{-1}. Considering the importance of reaction [2], and the scarcity of experimental data, a new direct measurement of k$_2$ seems timely.

In addition to reaction [2], we have also re-examined the rate constant for reaction [3] which is an important source of HCl(v) in the HCl chemical laser system. Reaction [3] was also used as a reference for competitive H atom reaction studies[20,21]. Dobis and Benson[22] recently applied their very low-pressure reactor (VLPR) technique to this reaction and measured k$_3$(298 K) = 0.96 ± 0.04 x 10^{-11} cm^3 molecules^{-1} s^{-1}. This result is a factor of 2 smaller than the generally accepted value given by Baulch, et. al. as k$_3$(T)= 1.4 x 10^{-10} exp(-590/T) for T = 250 - 730 K and k$_3$(298 K) = 1.9 x 10^{-11} cm^3 molecules^{-1} s^{-1}. Even though Baulch assigns the uncertainty for reaction [3] at ± 50%, Dobis and

Benson's value seems anomalously small relative to numerous previous measurements, and another measurement of k_3 seems appropriate.

We report the direct measurement of the rate constants for the reaction of H atoms with molecular fluorine and chlorine. We generate low concentrations of H atoms via photolysis of H_2S in the presence of a large excess of F_2 or Cl_2 and monitor the loss rate of [H] by laser induced fluorescence of the Lyman α transition. Typically, the initial pool of H atoms is consumed in 100 - 200 microseconds or less, and complications related to secondary reactions with products of the primary reaction and wall losses are avoided. Our ability to produce H atoms without H_2 is particularly important for the measurement of k_2. All previous measurements have used molecular hydrogen as their H atom source. In some cases a discharge is applied to the H_2 directly, while in others a discharge based F atom source and F + H_2 pre-reactor are used to generate a known flow of H atoms. Undissociated H_2 rapidly reacts with atomic fluorine to regenerate H atoms. This not only complicates the analysis, but also ties the accuracy of the measurement to some assumption about the rate constants for the secondary reactions. Our method eliminates these considerations and simple pseudo first-order kinetics can be applied.

2. EXPERIMENTAL METHODS

Ground state hydrogen atoms were generated by pulsed photolysis of H_2S. To observe the reaction with F_2 or Cl_2, the H_2S was present as a minor constituent (approximately 6.5 x 10^{14} moleclues cm^{-3} or less) of H_2S/F_2 or Cl_2 (in He)/Ar mixtures. Various partial pressures of the halogen/He mixtures were used. Pseudo first-order conditions were achieved by adding 0.5 - 6.0 Torr of a 5% Cl_2 in He mixture (Matheson) or 0.5 - 1.75 Torr of a 10% F_2 in He mixture (Matheson). The main carrier gas was Ar and the total reactor pressure was typically 100 Torr. The flow rates of H_2S and Ar were controlled by needle valves while a mass flow controller was used for F_2 or Cl_2 addition.

Hydrogen sulfide was photolyzed at 193 nm by a Lumonics TE-860-4 excimer laser operating at 10 Hz. The laser emission (~60 mJ/pulse) was focused by a 50 cm focal length lens, providing a power density that was sufficient to dissociate all of the H_2S in the focal region. Photodissociation at 193nm produces translationally hot H and SH fragments[23,24]. The high pressure of Ar buffer gas was used to thermalize the H atoms and limit their diffusion out of the detection region. Both F_2 and Cl_2 have very weak absorption cross-sections at 193 nm, and were not photodissociated to any significant degree.

LIF detection of H atoms was accomplished by two-photon excitation of the $2s$-$1s$ transition of atomic hydrogen. Collisions with Ar rapidly quench the $2s$ state to $2p$, which then emits Lyman α radiation as it relaxes back to the ground state. A tunable dye laser (Lambda-Physik EMG-203/FL3002 system) was used to generate 486 nm light. This was frequency doubled using a BBO crystal. A short (20 cm) focal length lens was used to focus the UV in the center of the photolysis cell. The photolysis and LIF lasers were arranged in an overlapping, counter-propagating configuration, see Figure 1. The delays between the photolysis and probe laser pulses were controlled with a precision pulse delay generator (SRS model DG535). A Hammamatsu R6835 solar blind photomultiplier tube and narrow band interference filter (121 nm, 10 nm FWHM) combination was used to detect the vacuum ultraviolet fluorescence while discriminating against scattered UV light from the photolysis and probe lasers. The probe laser was scanned across the Lyman-α spectrum to measure the linewidth, 1.2 cm^{-1}, confirming a thermal H atom translational distribution.

Some difficulty was encountered in finding appropriate conditions for the H + F_2 reaction. Early on, it was discovered that H_2S and F_2 could not be mixed too far upstream of the photolysis region due to a slow pre-reaction between F_2 and H_2S (k $\leq$ 6.4 x 10^{-16} cm^3 molecules^{-1} s^{-1})[25]. This problem was manifested by a total loss of the H atom LIF signal at high [F_2]. To limit the consumption of [H_2S], the reaction time was minimized by mixing the reagents just prior to their injection into the photolysis reactor. A second and more troublesome complication for the collection of reliable H + F_2 data was then discovered. For moderate to high [F_2] and long delays between the photolysis and probe laser pulses, the LIF signal deviated significantly from single exponential decay. Vibrationally excited HF is produced by H + F_2. The bond strength of HF is 136.3 kcal mol^{-1} and a single 243 nm photon can photolyze HF(v $\geq$ 2). The deviation from single exponential decay was associated with the regeneration of H atoms from probe laser photolysis of vibrationally excited HF. This problem was minimized by considering only the first 50- 100 μs of the decay curve and keeping [F_2] relatively low.

Measurements for the H+Cl_2 system were straightforward. We did not see any evidence of a pre-reaction between H_2S and Cl_2, and the H atom decay curves were single exponentials for all of the conditions investigated.

3. RESULTS AND DISCUSSION

3.1. H + F_2

A pair of representative H atom decay curves are shown in the upper panel of Figure 2. For our conditions, the slow decay in the absence of added F_2 (Γ~2700 s^{-1}) was dominated by diffusion out of the small volume sampled by the

probe laser. The addition of $[F_2] = 2.5 \times 10^{15}$ molecules cm^{-3} clearly increased the H atom loss rate. Within the 0 - 100 μs range the decay curves were single exponential and the rate constant was extracted by fitting the data to the expression

$$y = y_0 + Ae^{-bt}$$ [a]

where

$$b = k_2 [F_2] + \Gamma.$$ [b]

and Γ is the loss rate when $[F_2]$ is not present. The baseline intensity, y_0, was determined from the pre-photolysis pulse signal level. For the case shown in Figure 2, an exponential fit gives $b = 8927$ s^{-1}. The decay rate vs. $[F_2]$ data are summarized in Table 1 and plotted in Figure 3. The slope of Figure 3 gives the rate constant, $k_2 = 2.4 \pm 0.4$ (2σ) $\times 10^{-12}$ cm^3 molecules^{-1} s^{-1}.

Table 2 summarizes the results from the 8 previous reports of k_2. Our result compares well with the recommended value of Baulch et al.[13] and the experimental results of Dodonov et al.[15]. The agreement with Homann et al.[9] is marginal (just inside the combined error bars), and we are in poor agreement with Sung et al.[20], Levy and Copeland[18], and Rabideau et al.[19]. Interestingly, Baulch et al.[13] chose a k_2 value that lies halfway between the results of Homann et al.[9] ($k_2(298$ K$) = 1.6 \pm 0.4 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}) and Dodonov et al.[7,8] ($k_2(298$ K$) = 3.0 \pm 0.4 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}). Although Dodonov et al.'s method has been criticized for its poor definition of the reaction time and the unknown role of mixing[17], the results appear to be accurate not only for the H + F$_2$ reaction but also for H + Cl$_2$, see Table 4 and the discussion below.
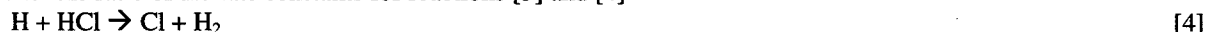
3.2. H + Cl$_2$

We tested the reliability of our method by applying it to the well-studied H + Cl$_2$ reaction. As the rate constant for H atom removal is large, this system should be less sensitive to variations in Γ, the baseline decay rate. Representative temporal profiles of the [H] dependent VUV fluorescence signal with and without added Cl$_2$ are shown in the upper panel of Figure 4. The addition of [Cl$_2$] (~50 mTorr) dramatically increased the H atom decay rate and the entire time history was consistent with a single exponential decay. Clearly, the reaction does not yield products that, on photolysis by the probe laser, produce H atoms.

A sample exponential fit is shown in the lower panel of Figure 4. For the sake of comparison, a simulated curve for $k_3 = 9.6 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1} is also shown. Figure 5 and Table 3 summarize the conditions and results for reaction [3]. The slope of the plot in Figure 5 gives $k_3 = 2.52 \pm 0.18$ (2σ) $\times 10^{-11}$ cm^3 molecules^{-1} s^{-1} and the intercept is consistent with the measured decay rate in the absence of Cl$_2$.

Our result is in good agreement (i.e. within the combined error bars) with the recommended value of Baulch et. al.[13], and other previous measurements, see Table 4. The difference between Dobis and Benson's[22] value and ours is outside of the combined uncertainty.

Table 4 shows that the results from previous measurements of k_3 can be roughly separated into two groups. A majority of the previous studies report $k_3 = 2 \pm 1 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}, while a smaller number give $k_3 \leq 1 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}. A more detailed examination of this second group of experiments shows that nearly all were performed under conditions where secondary reactions were important and the primary data must be carefully processed to extract k_3. For example, the experiments of Klein and Wolfsberg[26] and Armstrong and co-workers[27,28] provided estimates for the ratio of the rate constants for reactions [3] and [4]

H + HCl $\rightarrow$ Cl + H$_2$ [4]

by measuring the yield of H$_2$ following long-term irradiation (i.e. many minutes of reaction time) of a variety of gaseous mixtures containing HCl. Their results[26,28] range from $k_4/k_3 = 1.07 \pm 0.15 \times 10^{-2}$ to $8.8 \pm 0.5 \times 10^{-3}$. If the Baulch et al.[13] recommendation for k_4 is adopted ($k_4(298$ K$) = 4.25 \times 10^{-14}$ cm^3 molecules^{-1} s^{-1}), then k_3 ranges from $4.1 \pm 0.6 \times 10^{-12}$ to $4.8 \pm 0.3 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}. Because of the long reaction times and the chemical complexity of the system, a complicated mechanism must be deconvoluted to extract the ratio k_4/k_3. In addition, the role of wall reactions could not be determined and considerable error can occur if the model is not complete.

The present result is also in disagreement with the k_3 value reported by Whytock and co-workers[29,30] ($k_3(298) = 0.7 \pm 0.22 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}). The accuracy of this measurement has been examined on several occasions[22,31,32]. Most attribute the disagreement with their results to the lack of pseudo first-order conditions in Whytock's experiments and the fact that Whytock was working in an extremely difficult H atom detection regime for his electron spin resonance instrument.

The most recent measurement of k_3 by Dobis and Benson[22] gives $k_3 = 0.96 \pm 0.04 \times 10^{-11}$ cm^3 molecules^{-1} s^{-1}. In their experiment, a phosphoric acid coated discharge tube was used to create a small [H] ($\sim 10^{10}$ atoms cm^{-3}) to which Cl_2 was added. Mass spectrometry was used to monitor $[Cl_2]$, [Cl], and [HCl]. Dobis and Benson attribute the difference between their result and the larger k_3 values listed in Table 4 to un-accounted for wall reactions that remove H atoms. The difference between our result, which is unaffected by wall effects, and Dobis and Benson's is not entirely clear. We note that Dobis & Benson's[33,34] application of their VLPR apparatus to the Cl + HBr reaction also resulted in a rate constant that was a factor of two smaller than the majority of previous results[35-37].

4. SUMMARY

The H+F_2 and H+Cl_2 reactions were examined under pseudo first order conditions. Pulsed photolysis of low concentrations of H_2S was used to generate H atoms. The subsequent removal of H atoms was monitored by two-photon laser induced fluorescence. For H+Cl_2, simple exponential decay curves were observed, and a rate constant of 2.52 ± 0.18 (2σ) x 10^{-11} cm^3 molecules^{-1} s^{-1} was obtained. This value was in good agreement with several earlier determinations.

Study of the reaction H+F_2 was complicated by the production of vibrationally excited HF, which could be photodissociated by the probe laser. Measurements were made under conditions that minimized the influence of this secondary process. The initial H atom decay rate as a function of [F_2] defined a rate constant of 2.4 ± 0.4 (2σ) x 10^{-12} cm^3 molecules^{-1} s^{-1}. This result is in good agreement with the value obtained by Baulch et al.[13] from a critical review of previous determinations. We recommend continued use of the Baulch et al.[13] Arrhenius parameters in computational models of HF chemical lasers.

5. ACKNOWLEDGMENTS

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Table 1: Conditions and Results for H + F_2 measurements

[F_2] 10^{15} molec cm^{-3}	H atom decay rate[a] 10^5 s^{-1}	[F_2] 10^{15} molec cm^{-3}	H atom decay rate 10^5 s^{-1}
1.063	0.044	3.928	0.114
1.578	0.070	3.928	0.117
1.578	0.038	3.928	0.119
2.318	0.067	4.540	0.141
2.415	0.088	4.991	0.164
2.512	0.074	5.120	0.189
2.512	0.089	5.152	0.150
3.252	0.092	5.571	0.145
3.928	0.084		

[a] These are the raw observed decay rates, uncorrected for the decay rate (Γ) in the absence of F_2

Table 2: Comparison of measured rate constants for H+F_2 at 298 K

Reference	k_2(298 K) (x 10^{-12} cm^3 molecules^{-1} s^{-1})
Experiments	
Homann, et. al.[17]	1.6 ± 0.4
Albright, et. al.[15,16]	3.0 ± 0.4
Sung, et. al.[20]	1.0[a]
Levy & Copeland[18]	1.0 ± 0.15[b]
Rabideau, et. al.[19]	4.2 ± 0.3
This work	2.4 ± 0.4
Reviews	
Cohen & Westberg[14]	1.5[c]
Baulch, et. al.[13]	2.5[c]

[a] authors reported $k_2 / k_3 = 0.053$, absolute value calculated using $k_3 = 1.9$ x 10^{-11} from ref. 13. [b] authors reported $k_2 / k(H+O_2+M)[M] = 4.6 ± 0.7$, absolute value calculated using $k(H+O_2+M)[M]$ from ref. 13. [c] recommendation based on literature review.

Table 3: Conditions and Results for H + Cl$_2$ measurements[a]

[Cl$_2$] 10^{15} molec cm^{-3}	Fluorescence decay rate 10^5 s^{-1}	[Cl$_2$] 10^{15} molec cm^{-3}	Fluorescence decay rate 10^5 s^{-1}
0.74	0.32	4.81	1.27
1.66	0.40	5.02	1.11
1.66	0.50	5.23	1.56
1.98	0.56	5.47	1.53
2.11	0.60	5.55	1.67
2.11	0.64	5.59	1.50
2.13	0.59	6.44	1.83
2.29	0.79	6.50	1.77
2.83	0.71	7.12	2.06
2.83	0.88	7.28	1.74
3.22	0.90	7.53	1.56
3.27	0.89	7.63	1.98
3.75	0.64	8.60	2.47
4.06	1.28	8.63	2.22
4.31	1.32	9.05	2.34
4.35	1.15	10.55	2.79
4.73	0.87		

[a] These are the raw observed decay rates, uncorrected for the decay rate (Γ) in the absence of Cl$_2$

Table 4: Comparison of measured rate constants for H+Cl$_2$ at 298 K

Reference	k_3(298 K) (10^{-11} cm^3 molecules^{-1} s^{-1})
Klein & Wolfsberg[26]	0.46 ± 0.19[a,b]
Davidow, Lee, & Armstrong[28]	0.49 ± 0.03[b,c]
Jardine, Ballash, & Armstrong[27]	0.43 ± 0.04[b,d]
Ambidge, Bradley, & Whytock[29]	0.70 ± 0.14
Dobis & Benson[22]	0.96 ± 0.04
Dodonov, et. al.[15,16]	2.97 ± 0.89
Stedman, Steffenson, and Niki[38]	3.5 ± 1.2
Wagner, Welzbacher and Zellner[9,32]	1.91 ± 0.25
Bemand & Clyne[31]	2.19 ± 0.32
Michael & Lee[39]	1.6 ± 0.1
Jaffe and Clyne[40]	2.13 ± 0.78
Kita and Stedman[41]	1.7 ± 0.26
Seeley, Jayne, and Molina[42]	1.8 ± 0.5[e]
This work	2.52 ± 0.18

[a] authors reported k_4 / k_3 = 0.143 ± 0.033 exp(-(1540 ± 130)/RT).
[b] k_3(298 K) calculated from k_4(298 K)[13] = 4.25 x 10^{-14} cm^3 molecules^{-1} s^{-1}.
[c] authors reported k_4 / k_3 = 0.0088 ± 0.0005 at 298 K.
[d] authors reported k_4 / k_3 = 0.01 ± 0.001 at 298 K.
[e] authors do not give a numerical result, value in table is estimated from Figure 16 of reference 42.
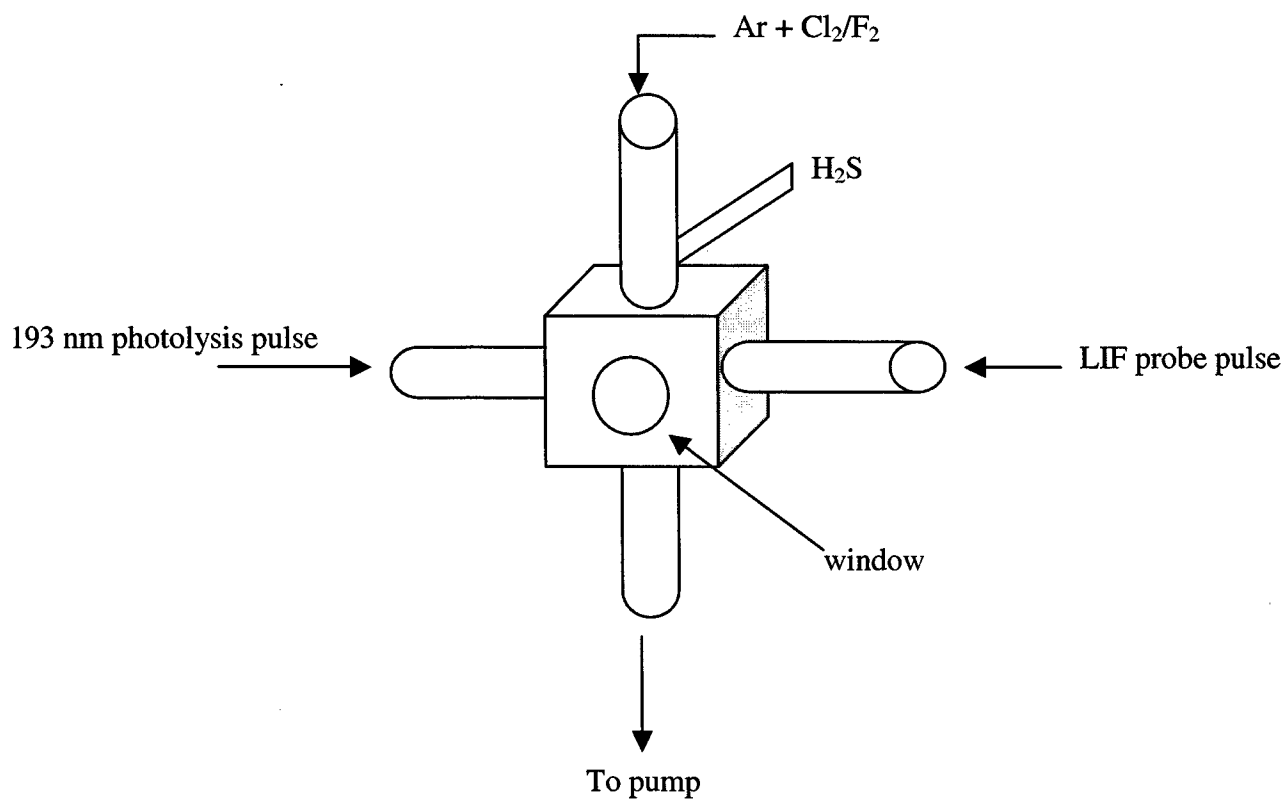
Figure 1. Schematic diagram of the experimental apparatus. The reaction between hydrogen atoms and molecular F_2 or Cl_2 was pulse initiated by 193 photolysis of a $H_2S/Cl_2(F_2)/Ar$ mixture. The time history of the H atoms was monitored by laser induced fluorescence of the Lyman-α transition.

Figure 2. Representative H + F_2 data is shown. The slow decay in the absence of F_2 in the upper panel is attributed to diffusion and H atom loss via reactions with photoproducts. The lower panel demonstrates the quality of the fit to a single exponential decay. The best least squares fit gives $k_2 = 2.47 \pm 0.11$ cm^3 molecules^{-1} s^{-1}. For the sake of comparison, the background-corrected decay curve for $k_2 = 1.0 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1} is shown.

[F_2] = 0.0 molecules cm^{-3}

[F_2] = 2.51 x 10^{15} molecules cm^{-3}

Intensity (arb. units)

time (μs)

k_2 = 1.0 x 10^{-12} cm^3 molecules^{-1} s^{-1}

k_2 = 2.47 x 10^{-12} cm^3 molecules^{-1} s^{-1}

Intensity (arb. units)

time (μs)

fluorescence decay rate (10^5 s^{-1})

[F_2] (10^{15} molecules cm^{-3})

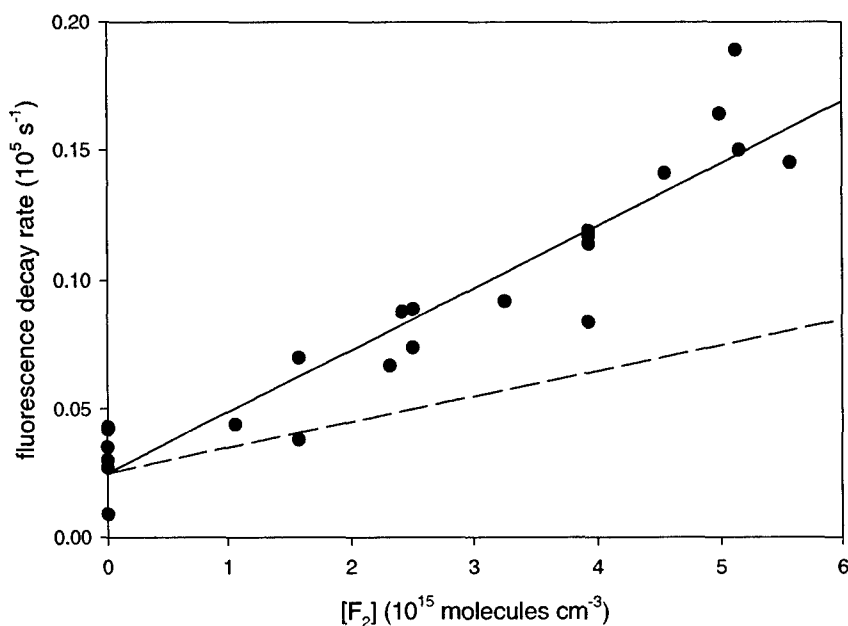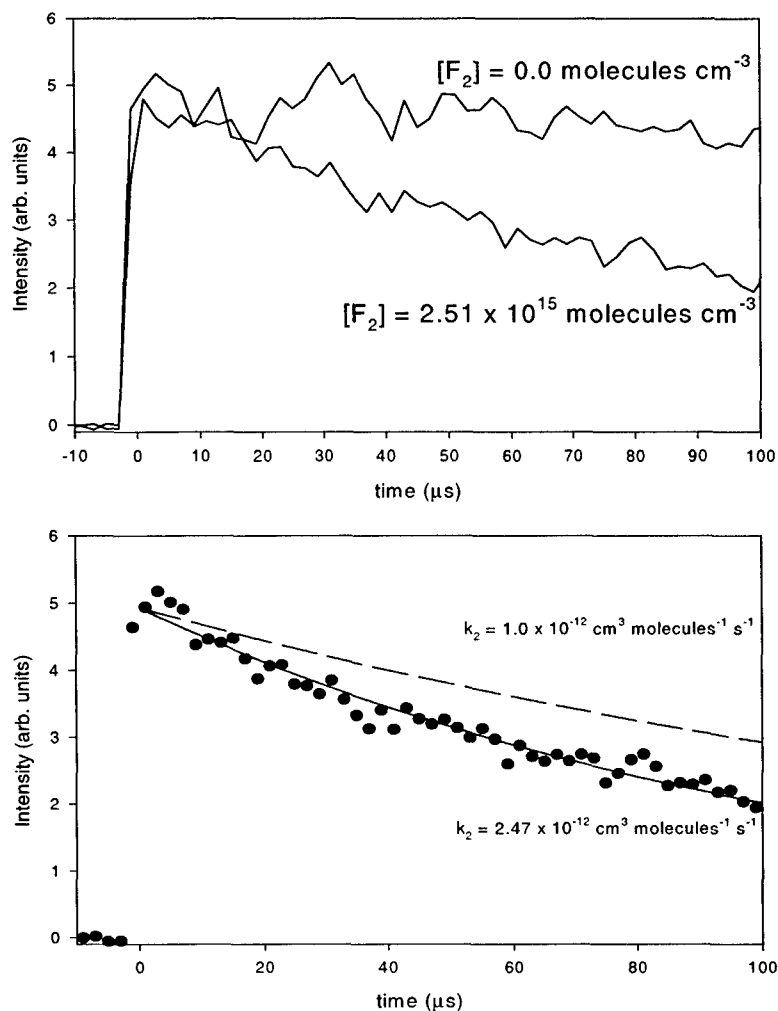**Figure 3.** H atom decay rate vs. [F_2]. The rate constant for reaction [2] is given by the slope, $k_2 = 2.4 \pm 0.4$ (2σ) x 10^{-12} cm^3 molecules^{-1} s^{-1}. This result agrees with the previous measurements by Dodonov and co-workers[15,16] and the recommended value of Baulch, et. al[13]. The broken line represents $k_2 = 1.0 \times 10^{-12}$ cm^3 molecules^{-1} s^{-1}.
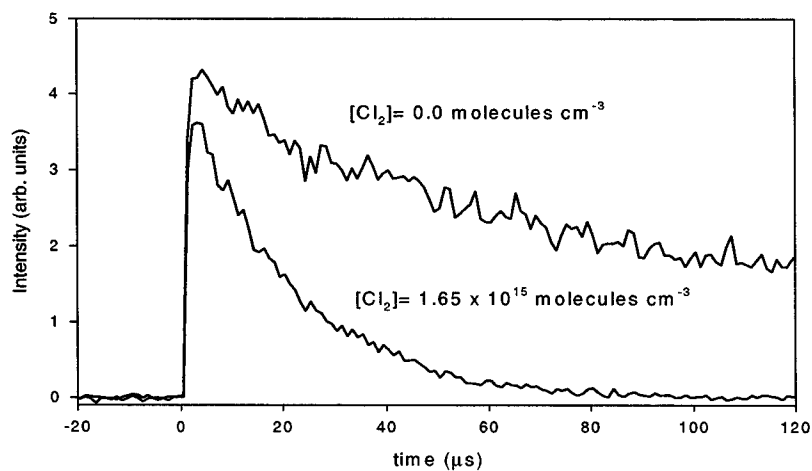
Figure 4. Representative H + Cl_2 data is shown. The slow decay in the absence of Cl_2 in the upper panel is attributed mainly to diffusion out of the observation zone with a minor amount of H atom loss via reactions with photoproducts. The lower panel demonstrates the quality of the fit to a single exponential decay. The corresponding rate constant is 2.47 ± 0.04 cm^3 molecules^{-1} s^{-1}.
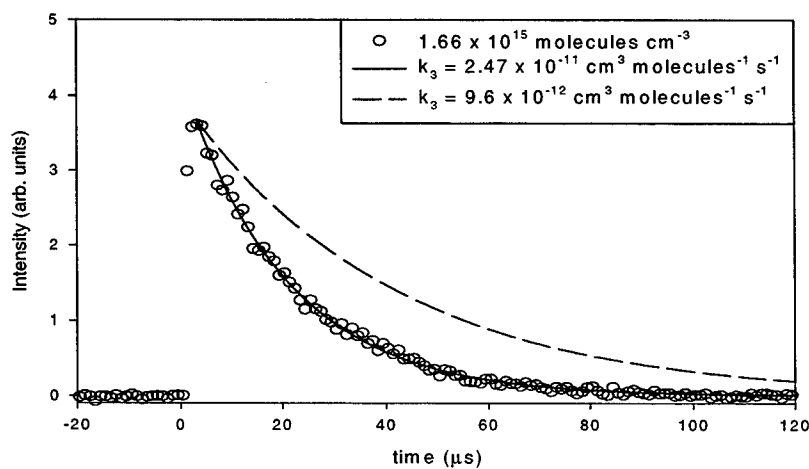
Figure 5 H atom decay rate vs. [Cl_2]. The rate constant for reaction [3] is given by the slope, $k_3 = 2.52 \pm 0.18$ (2σ) x 10^{-11} cm^3 molecules^{-1} s^{-1}. This result agrees with many previous measurements and the recommended value of Baulch, et. al[1]. Our result does not agree with the recent result of Dobis and Benson[22], who reported $k_3 = 0.96 \pm 0.04$ x 10^{-12} cm^3 molecules^{-1} s^{-1}