CHEMISTRY OF HYDROGEN FLUORIDE IN THE INTERSTELLAR MEDIUM

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ABSTRACT

A comprehensive account is given of the chemistry of HF in interstellar clouds. Calculations are presented of the rate coefficients for the quenching of $F(^2P_{1/2})$ and for the reaction of $F(^2P_{3/2})$ atoms in collisions with H_2. They confirm the conclusions of Neufeld and coworkers that gaseous fluorine exists in interstellar clouds almost entirely in the form of the molecule HF.

Subject headings: astrochemistry — ISM: molecules — molecular data — molecular processes

1. INTRODUCTION

Hydrogen fluoride has been detected in sunspots (Hall & Noyes 1969; Wallace & Livingston 1991; Wallace, Livingston, & Bernath 1994), in the atmospheres of Venus (Connes et al. 1967), α Ori (Spinrad et al. 1970), and red giants (Jorissen, Smith, & Lambert 1992), and in the interstellar medium (Neufeld et al. 1997). It was discovered in the interstellar medium through the observation of an absorption line at 121.6973 μm attributed to the $J = 2$–1 rotational transition of HF (Neufeld et al. 1997). The line was detected in the line of sight toward the far-infrared continuum source Sgr B2. The fractional abundance relative to H_2 derived is 3×10^{-10}. Neufeld et al. (1997) present a brief discussion of the fluorine chemistry, and they conclude that most of the fluorine will be taken up as HF, the small observed abundance of HF then implying that fluoride is substantially depleted onto interstellar grains. Neufeld et al. (1997) based their discussion of the chemistry on the reactions

$$F + H_2 \rightarrow HF + H \qquad (1)$$

and

$$F + H_2O \rightarrow HF + OH . \qquad (2)$$

Measurements of the rate coefficients have been carried out at temperatures above 200 K (Wurzberg & Houston 1980; Heidner et al. 1980; Stevens, Brune, & Anderson 1989). Neufeld et al. (1997) concluded that only reaction (1) was important in the astrophysical environment, except possibly at very cool temperatures. They extrapolated the rate coefficient k_1 of reaction (1) to temperatures below 200 K using the representation

$$k_1 = 1.4 \times 10^{-10} \exp(-500/T) \ \text{cm}^3 \ \text{s}^{-1} , \qquad (3)$$

recommended by Atkinson et al. (1992). The chemistry is more complicated because the rate coefficient of reaction (1) depends on the fine-structure population of the fluorine atom and because it may also depend on the rotational state of the hydrogen molecule.

The fine-structure population is determined by a balance between the radiative decay of $F(^2P_{1/2})$ and collision-induced transitions

$$F(^2P_{1/2}) + H_2 \leftrightarrow F(^2P_{3/2}) + H_2 . \qquad (4)$$
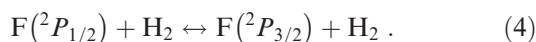
We present here the results of fully quantum-mechanical calculations of the rate coefficients of processes (1) and (4) and discuss the resulting modifications to the chemistry of HF.

2. FINE-STRUCTURE COLLISIONS

There have been several theoretical studies of transitions between fine-structure levels of F induced by collisions with H_2 (Rebentrost & Lester 1976; Fitz & Kouri 1981; McNutt & Wyatt 1981; Gilibert & Baer 1995) with results that show some sensitivity to the interaction potentials. A reliable interaction potential has been calculated by Alexander, Manolopoulos, & Werner (2000), and we adopt it here. The relevant quantum-mechanical scattering theory has been developed by Baer (1975), Alexander (1993, 1995), Dubernet & Hutson (1994a, 1994b), and Alexander et al. (2000). Details of the analytical and numerical procedures that we followed to calculate the collision cross sections are given by Alexander et al. (2000) and Krems & Dalgarno (2002).

It was discovered by Rebentrost & Lester (1976) that the relaxation of $F(^2P_{1/2})$ colliding with H_2 in the lowest rotational level $j = 0$ at energies between 35 and 700 cm^{-1} is dominated by the near-resonance reaction

$$F(^2P_{1/2}) + H_2(j = 0) \rightarrow$$
$$F(^2P_{3/2}) + H_2(j = 2) + 49.82 \ \text{cm}^{-1}, \qquad (5)$$
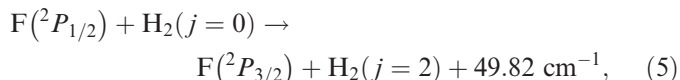
in which H_2 is excited from the $j = 0$ to the $j = 2$ level. Our calculations confirmed that process (5) occurs much more rapidly than the reaction

$$F(^2P_{1/2}) + H_2(j = 0) \rightarrow F(^2P_{3/2})$$
$$+ H_2(j = 0) + 404 \ \text{cm}^{-1}, \qquad (6)$$
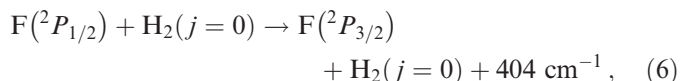
in which H_2 does not undergo any change in its rotational level. The near-resonance occurs only for $j = 0$, so that quenching of $F(^2P_{1/2})$ in collisions with H_2 in higher rotational levels $j \geq 1$,

$$F(^2P_{1/2}) + H_2(j \geq 1) \rightarrow F(^2P_{3/2}) + H_2 , \qquad (7)$$
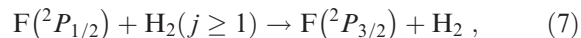
is also relatively slow.

TABLE 1
RATE COEFFICIENTS FOR RELAXATION OF F($^2P_{1/2}$)

T (K)	Reaction (5) (cm^3 s^{-1})	Reaction (6) (cm^3 s^{-1})	Reaction (7) (cm^3 s^{-1})
50........	0.226×10^{-9}	0.249×10^{-11}	0.546×10^{-11}
100......	0.288×10^{-9}	0.528×10^{-11}	0.915×10^{-10}
150......	0.315×10^{-9}	0.876×10^{-11}	0.132×10^{-10}
200......	0.329×10^{-9}	0.127×10^{-10}	0.177×10^{-10}
250......	0.338×10^{-9}	0.169×10^{-10}	0.226×10^{-10}
300......	0.342×10^{-9}	0.213×10^{-10}	0.278×10^{-10}
350......	0.345×10^{-9}	0.260×10^{-10}	0.333×10^{-10}
400......	0.346×10^{-9}	0.309×10^{-10}	0.389×10^{-10}
450......	0.346×10^{-9}	0.358×10^{-10}	0.446×10^{-10}
500......	0.346×10^{-9}	0.409×10^{-10}	0.503×10^{-10}
550......	0.345×10^{-9}	0.459×10^{-10}	0.560×10^{-10}
600......	0.344×10^{-9}	0.510×10^{-10}	0.615×10^{-10}
650......	0.342×10^{-9}	0.560×10^{-10}	0.670×10^{-10}
700......	0.341×10^{-9}	0.610×10^{-10}	0.720×10^{-10}

NOTES.—For reactions (5) and (6) initial $j = 0$, and for reaction (7) initial $j = 1$.

In Table 1 we present the rate coefficients for processes (5) and (6) for $j = 0$ and process (7) for $j = 1$. The rates of the reverse excitation processes can be obtained by detailed balance. The calculations of the rate coefficients for reaction (5) are fully converged and the uncertainty of rate coefficients for reactions (6) and (7) due to numerical integration is within 10%. For the reverse of process (5) to be effective requires a significant population of $j = 2$ levels of H_2. In practice in the interstellar environment, given our calculated rate coefficients and the short radiative lifetime 1.10×10^3 s of F($^2P_{1/2}$) (Cheng, Kim, & Desclaux 1979), all the F atoms can be taken to reside in the ground $^2P_{3/2}$ state.

3. THE REACTION OF F($^2P_{3/2}$) WITH H_2

Reaction (1) is a benchmark case that has been the subject of extensive theoretical and experimental study (Rosenman et al. 1996; Castillo et al. 1996; Russell & Manolopolous 1996; Chapman et al. 1998; Castillo et al. 1998; Manolopolous 1997; Takayanagi & Kurosaki 1998; Alexander, Werner, & Manolopoulos 1998; Baer et al. 1999; Ma, Cai, & Deng 1999; Balakrishnan & Dalgarno 2001). Alexander et al. (2000) have shown that the reaction dynamics is represented satisfactorily by scattering on the lowest potential energy surface of Stark & Werner (1997). Our calculations of the rate coefficients are based on this assumption.

We have used the ABC quantum reactive scattering program of Skouteris, Castillo, & Manolopoulos (2000), which couples channels with a given total angular momentum quantum number J. Total angular momentum quantum numbers up to $J = 20$ were required to secure convergence for collision energies up to 0.2 eV. Many product rotational states are populated in the reaction. The individual partial cross sections show the presence of resonances in the product channels but the rate coefficients are smooth functions of temperature. We report in Table 2 the rate coefficients for the reactions
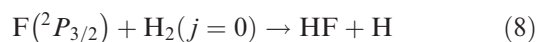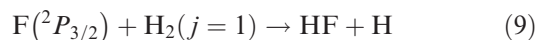
$$F\left(^2P_{3/2}\right) + H_2(j = 0) \rightarrow HF + H \qquad (8)$$

TABLE 2
RATE COEFFICIENTS FOR REACTIONS
(8) AND (9) OF F($^2P_{3/2}$)

T (K)	Reaction (8) (10^{-11} cm^3 s^{-1})	Reaction (9) (10^{-11} cm^3 s^{-1})
50........	0.312	0.184
100......	0.791	0.476
150......	1.32	0.974
200......	1.92	1.60
250......	2.54	2.29
300......	3.16	2.98
350......	3.75	3.63
400......	4.28	4.21
450......	4.74	4.72
500......	5.13	5.14

NOTES.—Reaction (8): $H_2(j = 0)$; reaction (9): $H_2(j = 1)$.

and

$$F\left(^2P_{3/2}\right) + H_2(j = 1) \rightarrow HF + H \qquad (9)$$

at temperatures between 50 and 500 K.

The experimental values (Wurzberg & Houston 1980; Heidner et al. 1980; Stevens et al. 1989) refer presumably to measurements with thermal populations of fine-structure levels and rotational populations. We find little dependence on j until temperatures fall below 250 K. Alexander et al. (1998) have found that the reactivity of F($^2P_{1/2}$) is less than 10% of that of F($^2P_{3/2}$) so that in order to compare with the measured values, our calculated rate coefficients for F($^2P_{3/2}$) should be multiplied by a factor of $2/(2 + e^{-\Delta/k_B T})$, where $\Delta = 50.1$ meV is the $^2P_{1/2}$–$^2P_{3/2}$ splitting of the F atom, k_B is Boltzmann's constant, and T is the temperature. A comparison that includes this factor is given in Figure 1. The agreement between the theoretical and experimental data is good. In Figure 1, we also include some previous theoretical calcu-
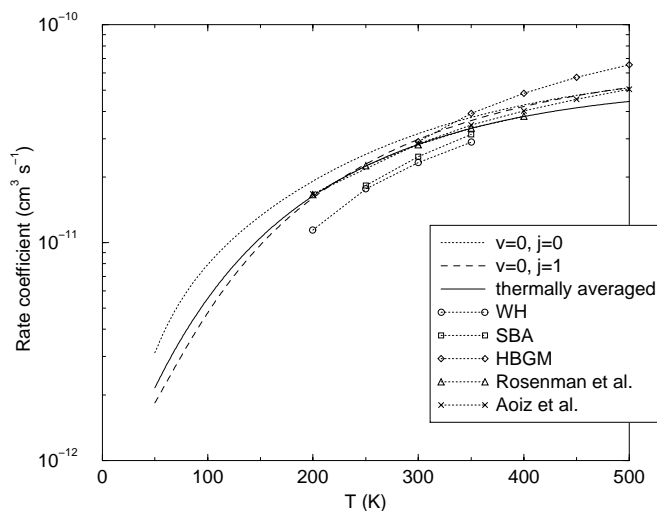

FIG. 1.—Rate coefficients for the F + H_2 reaction: solid curve, thermally averaged rate coefficients; dotted curve, F($^2P_{3/2}$) + $H_2(v = 0,\ j = 0)$ reaction; dashed curve, F($^2P_{3/2}$) + $H_2(v = 0,\ j = 1)$ reaction; circles, squares, and diamonds are the experimental data of Wurzberg & Houston (1980), Stevens et al. (1989), and Heidner et al. (1980), respectively. Triangles are the calculations by Rosenman et al. (1996), and crosses are the values by Aoiz et al. (1999).

TABLE 3

Coefficients for the Analytical Approximations (Eq. [10]) of the Temperature
Dependence of the Rate Coefficients for the Reaction of Fluorine with $H_2(j)$

i	0	1	2	3	4
$j = 0$.......	-10.9967	-289.052	22486.0	-9.57330×10^5	1.58973×10^7
$j = 1$.......	-10.9829	-278.212	12884.0	-2.09014×10^5	-6.7910×10^5

lations. The results of approximate coupled-states calculations by Roseman et al. (1996) agree very well with our calculations in the temperature range of 200–400 K, as do those of Aoiz, Banares, & Castillo (1999) at temperatures below 350 K, obtained with the adiabatic rotation approximation. The adiabatic rotation approximation treats the rotational motion of the triatomic system adiabatically by neglecting the Coriolis coupling. At higher temperatures the values of Aoiz et al. (1999) are larger than ours, indicating a loss of accuracy in their approximation at high temperatures.

At 100 K, the predicted rate coefficient is 11.8 times that given by equation (3) and adopted by Neufeld et al. (1997). The theoretical results can be represented as a function of temperature by

$$\ln k(T) = \sum_{i=0}^{4} \frac{a_i}{T^i} . \tag{10}$$

The fitting coefficients in equation (10) for the reactions of $F(^2P_{3/2})$ with $H_2(j = 0)$ and $H_2(j = 1)$ are given in Table 3.

4. CONCLUSIONS

Because in the interstellar medium the F atom resides in the $(^2P_{3/2})$ state and because it is the $(^2P_{3/2})$ state that is highly reactive in collisions with H_2, the conclusions of Neufeld et al. (1997) that F is converted almost entirely to HF is strengthened by our more comprehensive discussion of the chemistry.

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