The rate of the F + H₂ reaction at very low temperatures

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The prototypical F + H₂ → HF + H reaction possesses a substantial energetic barrier (~800 K) and might therefore be expected to slow to a negligible rate at low temperatures. It is, however, the only source of interstellar HF, which has been detected in a wide range of cold (10–100 K) environments. In fact, the reaction does take place efficiently at low temperatures due to quantum-mechanical tunnelling. Rate constant measurements at such temperatures have essentially been limited to fast barrierless reactions, such as those between two radicals. Using uniform supersonic hydrogen flows we can now report direct experimental measurements of the rate of this reaction down to a temperature of 11 K, in remarkable agreement with state-of-the-art quantum reactive scattering calculations. The results will allow a stronger link to be made between observations of interstellar HF and the abundance of the most common interstellar molecule, H₂, and hence a more accurate estimation of the total mass of astronomical objects.

The F + H₂ → HF + H reaction, and its isotopic variants, is perhaps one of the most intensively investigated chemical reactions. Because of its simplicity and experimental accessibility, it has become the paradigm for exothermic triatomic chemical reactions. Sophisticated crossed molecular beam methods²⁻³ provide details of the dynamics of this reaction and reveal the existence and influence of reactive resonances—short-lived metastable quantum states⁴⁻⁶. This experimental work, as well as the availability of high-quality ab initio FH₂ potential energy surfaces (PESs)⁵⁻⁷, has stimulated many theoretical studies of this reaction⁸⁻¹². Because it involves transfer of a light hydrogen atom and because of the high barrier to reaction (~800 K)⁹, only quantum-mechanical simulations can provide an accurate description of the dynamics, particularly at low temperatures, where the reaction occurs exclusively through quantum-mechanical tunnelling⁵⁻¹².

The discovery of interstellar HF in 1997¹³, and the realization of its ubiquity in the Universe thanks to very recent observations by the Herschel Space Observatory¹⁴⁻²⁰, has engendered renewed interest in the F + H₂ reaction, which is the sole source of HF in these generally very cold environments. Molecular hydrogen is essentially unobservable at low temperatures²¹ and a common proxy is the CO molecule, which is easily observable, abundant and chemically stable, but suffers from photodissociation at lower H₂ column densities²¹. The HF molecule can serve as an alternative tracer for H₂ in these more diffuse regions owing to its high stability. Recent observations reveal¹⁶,²⁰ that HF is the main reservoir of fluorine in the interstellar medium (ISM) due to the large exothermicity of the F + H₂ reaction²² and the inefficiency of processes that destroy the HF molecule. Reactions of HF with most of the interstellar elements are substantially endothermic and negligibly slow at the low temperatures that characterize molecular clouds. Only the reaction of HF with C⁺, leading to the formation of CF⁺, is expected to take place in the ISM²³.

There have been, to our knowledge, only two direct determinations of the rate of the F + H₂ reaction rate below room temperature²⁴⁻²⁵ and none below 190 K, far above the temperatures in the ISM where HF is observed (10–100 K). Aquilanti et al.¹⁰ have used theoretical simulations to estimate the rate coefficients down to 10 K, but with an uncertainty too great for use in astrophysical modelling.

We report here the first experimental determination of the rate coefficient of the title reaction at temperatures between 11 and 295 K. The results are compared to state-of-the-art quantum reactive scattering calculations involving multiple PESs, which, in addition, shed light on the importance of non-adiabatic effects at low temperatures. Our results will enable a more accurate prediction of the abundance of HF in the different interstellar regions where it has been observed, resulting in a better calculation of the abundance of the commonest interstellar molecule, H₂, and therefore of the total mass distribution.

The study of the title reaction at low temperatures is challenging. Because it possesses an energetic barrier, its rate coefficient is expected to be small (k ≈ 1 × 10⁻¹² cm³ molecule⁻¹ s⁻¹), in contrast to the majority of barrierless chemical reactions, which have rate coefficients at temperatures below 100 K often exceeding 1 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. In addition, the Born–Oppenheimer (BO) forbidden reaction of the spin–orbit excited F atom, F(2P₁/₂), can have a significant influence on the reaction rates at low temperature²⁵. For the experimental measurements reported here, we used the CRESU (cinétique de réaction en écoulement supersonique uniforme, or reaction kinetics in uniform supersonic flow) technique to provide a low-temperature gas-phase environment, employing for the first time pure hydrogen flows to compensate for the relatively slow F + H₂ reaction rate and pulsed laser photolysis–pulsed laser-induced fluorescence (PLP–LIF) to measure rate constants. The reaction was monitored by following the increase in product hydrogen atoms. These experiments, as well as complementary quantum reactive scattering calculations on multiple PESs, are fully described in the Methods and in Supplementary Section 1.

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overcome the energy barrier in a preferential fashion to react immediately with the nearby H$_2$ molecule in the complex.

The nature of the initial prompt signal was verified as being due to the rapid production of hydrogen atoms (within the pulse duration of the excimer laser). A spectroscopic line profile recorded at a very short delay time (50 ns) yielded a width (full-width at half-maximum, FWHM) of 3.8 pm, significantly wider than the laser-limited 2.3 pm line width observed at longer delay times, indicating that these ‘prompt’ hydrogen atoms are produced with significant excess energy (a pure Doppler line width of 3.8 pm for the Lyman $\alpha$ transition at 121.57 nm would correspond to a temperature of 1,940 K).

A potential source for these prompt, hot hydrogen atoms could be photolysis of low levels of hydrogen-containing impurities. However, the fact that this prompt, hot hydrogen-atom signal is not observed at 77 K and 295 K would be difficult to understand in this case. Instead, we propose that this prompt signal is due to a reaction initiated within a small concentration of F$_2$–H$_2$ van der Waals complexes, which could be formed during the expansion and subsequent cold flow, in a similar way to a number of reactions studied within the Wittig group, among others$^{37}$. Although the formation of such weakly bound complexes would be slow under the relatively low pressure conditions of CRESU flow, photolysis of F$_2$ within the complex would yield two fluorine atoms with high translational energy, one of which would almost immediately encounter an H$_2$ molecule in a potentially favourable orientation for reaction and with a favourable impact parameter and relatively high energy. This would result in a prompt signal, the magnitude of which would increase in comparison with the normal concentration of F$_2$–H$_2$ complexes in the very low-temperature supersonic flow. These complexes are then photodissociated by the photolysis laser, yielding translationally ‘hot’ fluorine atoms that may be able to

Results

Figure 1a presents the LIF trace of hydrogen atoms formed during the reaction at 77 K for a given density of H$_2$ introduced into the flow. This trace was fitted using a sum of exponential functions, which included the first-order rate coefficient for hydrogen atom formation ($k_{1st}$) as well as the rate coefficient for loss of hydrogen atoms by diffusion in the flow ($k_{\text{diff,H}}$). The values of $k_{1st}$ were plotted as a function of n-H$_2$ (normal hydrogen, see later) density to yield a straight line with slope corresponding to the second-order rate coefficient at 77 K (Fig. 1b).

Results at 295 K are provided in Supplementary Fig. 3. Figure 2 shows the fitted LIF traces of hydrogen atoms formed during reaction at 11.3 K and 20.4 K. Because n-H$_2$ was used as the buffer gas at these temperatures, it was not possible to vary its density. However, second-order rate coefficients could be obtained as the ratio of the first-order rate coefficients extracted from the fits of the LIF traces and corrected for diffusive loss both of product hydrogen atoms and reagent fluorine atoms (Supplementary Section 1.4), divided by the respective n-H$_2$ densities. The measured rate coefficients at the four temperatures are listed in Table 1 and plotted as a function of temperature in Fig. 3, together with the results of the theoretical calculations.

As can be seen in Fig. 2, a prompt formation of hydrogen atoms was observed within the first microsecond at the lowest temperatures of 11.3 and 20.4 K. We attribute this to the formation of a small concentration of F$_2$–H$_2$ complexes in the very low-temperature supersonic flow. These complexes are then photodissociated by the photolysis laser, yielding translationally ‘hot’ fluorine atoms that may be able to

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**Figure 1** | Results for the determination of the F + H$_2$ reaction rate coefficient at 77 K. **a.** Hydrogen atom product LIF intensity $I_{\text{LIF}}$ as a function of photolysis–probe laser delay time at 77 K for an H$_2$ concentration of 6.91 × 10$^{15}$ cm$^{-3}$, fit to a function of the form $I_{\text{LIF}} = A \exp(-k_{1st}t) - \exp(-k_{\text{diff,H}}t)$ (red line). **b.** Pseudo-first-order rate coefficients $k_{1st}$ obtained from a series of such experiments plotted against the concentration of normal hydrogen, [n-H$_2$]. Error bars correspond to twice the standard error in $k_{1st}$.

**Figure 2** | Hydrogen atom product LIF intensity as a function of photolysis-probe laser delay time. **a.** LIF signal at 11.3 K for a density of [n-H$_2$] = 3.92 × 10$^{16}$ cm$^{-3}$ (a) and at 20.4 K for a density of [n-H$_2$] = 5.10 × 10$^{16}$ cm$^{-3}$ (b). The traces are fit (red line) by an exponential growth (reaction) and decay (loss by diffusion), including an initial prompt component, as described in Supplementary Section 1.5.
reactive signal as the temperature decreased and the formation of F₃–H₂ van der Waals complexes was thereby enhanced. Such a dependence was indeed observed, with negligible prompt signal at 77 and 295 K and a prompt signal at 20 K of about 40% of the fitted magnitude of the reactive signal, rising to be as large as the reactive signal at 11 K. Measurements were also made using a hydrogen flow at 5 K, but the prompt signal had grown so large in comparison with the reactive signal that it was impossible to measure the rate constant accurately for the F + H₂ reaction at this temperature.

To test this explanation, we performed ab initio calculations to determine the dissociation energy of the F₃–H₂ van der Waals complex, as detailed in Supplementary Section 2.1. The complex was indeed found to have a global minimum in a T-shaped configuration, with the F₃ normal to the H–H bond, and a value for the dissociation energy (Dₒ) on the order of 100 cm⁻¹. The F₃–H₂ van der Waals complex will therefore form at low concentrations via three-body collisions at the very low temperatures of the CRESU flow. Photodissociation of F₃ within this complex will result in F + H₂ collisions that are favourably oriented for reaction, providing a plausible explanation for the prompt hydrogen atom signal.

**Discussion**

Excellent agreement was obtained between our experimental rate coefficients and previous measurements down to 221 K obtained by Stevens and colleagues. As can be seen by comparison with the extrapolated recommendation from the review of Persky and Kornweitz, also shown in Fig. 3, our results at the lowest temperatures display a strongly non-Arrhenius temperature dependence. This confirms the importance of tunnelling in this reaction.

The results of the simulation shown in Fig. 3 demonstrate excellent agreement with the experimental measurements, confirming the importance of using an appropriate theoretical description. In particular, it is essential to take into account the open-shell character of the fluorine atom. In our experiment the F(2P) excited spin–orbit state is collisionally relaxed on a timescale much shorter than the reaction, especially at low temperature. This is fully discussed in Supplementary Section 1.2. Thus, reaction occurs only on the ground adiabatic PES (Supplementary Fig. 4). Nevertheless, a correct multi-state scattering treatment includes coupling between the three FH₂ PESs (Supplementary Fig. 4) and the presence of non-zero electronic and spin angular momenta, all neglected in the usual (BO) single-PES treatment. Consequently (Fig. 3), even at low temperature, the multi-state cross-sections and rate coefficients are lower than those obtained within a single-PES treatment.

Aquilanti et al. have discussed in detail the inadequacies in the original Stark–Werner PES, adding modifications to include the spin–orbit Hamiltonian and to describe better the long-range F–H₂ interaction. The rate constants predicted by calculations with this PES (which they designate PES III) are also shown in Fig. 3. They appear to be a significant underestimate at low temperatures.

**Table 1 | Rate coefficients for the reaction between F(2P) atoms and n-H₂ between 11 and 295 K.**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Buffer gas</th>
<th>Total density (10¹⁶ molecule cm⁻³)</th>
<th>[H₂] (10¹⁶ molecule cm⁻³)</th>
<th>k (10⁻¹³ cm³ molecule⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.3</td>
<td>H₂</td>
<td>4.02</td>
<td>3.92</td>
<td>2.48±1.90*</td>
</tr>
<tr>
<td>20.4</td>
<td>H₂</td>
<td>5.15</td>
<td>5.10</td>
<td>2.18±0.72</td>
</tr>
<tr>
<td>77</td>
<td>He</td>
<td>101</td>
<td>0.364–3.41</td>
<td>23.2±4.8</td>
</tr>
<tr>
<td>295</td>
<td>He</td>
<td>28.1</td>
<td>0.100–0.390</td>
<td>249±37</td>
</tr>
</tbody>
</table>

*Errors correspond to 95% statistical confidence limits combined with an estimated 10% systematic error (20% at 77 K).
temperature, probably a consequence of an overestimate of the height of the barrier to reaction. We explore this disagreement further in Supplementary Section 2.2, where we compare our results with the full set of calculations of Aquilanti and colleagues.

At the four temperatures investigated, the new rate coefficients are between 1.5 and 5 times lower than those used in the interstellar fluorine chemistry model of Neufeld and Wolfire. As an example of the likely impact of this work upon astrochemical models, we have taken the simplified interstellar fluorine chemistry model based on the work of Neufeld and Wolfire and used by Godard et al. to calculate the ratio of abundances of (HF) to (H₂) in diffuse clouds. This can then be used to relate observations of HF by the Herschel Space Observatory to the difficult-to-observe hydrogen abundance and hence the total mass of the object under study. Under such conditions, the abundance of HF is controlled by four chemical reactions:

\[
F + H_2 \rightarrow HF + H \quad (k_1)
\]

\[
HF + h\nu \rightarrow F + H \quad (\epsilon_{HF})
\]

\[
HF + C^+ \rightarrow CF^+ + H \quad (k_2)
\]

\[
CF^+ + e^- \rightarrow F + C \quad (k_3)
\]

Godard et al. used the value for the rate coefficient \( k_1 \) calculated by Zhu et al. and communicated to Neufeld and Wolfire, namely

\[
k_{1et al.} = 1.00 \times 10^{-10}[\exp(-450 K/T) + 0.078 \exp(-80 K/T) + 0.0155 \exp(-10 K/T)] \text{ cm}^3 \text{s}^{-1}
\]

This is claimed to be valid down to 10 K, and is plotted in Fig. 4 together with the results of our calculations for \( H_2 \) in \( j = 0 \) and \( j = 1 \) rotational states and a thermally averaged value (LTE, local thermodynamic equilibrium). We have fitted this thermally averaged value of \( k_1 \) to give the following equation, which we recommend for use in astrochemical models:

\[
k_{1This work} = 4.71 \times 10^{-11}[\exp(-0.364 K/T) + 3.38 \exp(-38.9 K/T) + 212 \exp(-881 K/T) + 124 \exp(-414 K/T)] \text{ cm}^3 \text{s}^{-1}
\]

This fit is also plotted in Fig. 4, and differs from the value of Zhu et al. by a factor of ~3 in the range 10–100 K. The ratio of abundances of (HF) to (H₂) under typical diffuse interstellar cloud conditions is given by equation C.3 from ref. 31:

\[
n(HF) = \frac{([C]k_2 + \epsilon_{HF} n_{H_2})}{k_1} \frac{f_{H_2}}{2} \left( 1 + \frac{k_2}{k_3} \right)
\]

Using their values for \( \epsilon_{HF} \), \( k_2 \), \( k_3 \) and the fluorine and carbon elemental gas-phase abundances relative to hydrogen nuclei, \( [F] \) and \( [C] \) (see ref. 31 for the values), and typical diffuse cloud conditions with atomic hydrogen density \( n_{H} = 50 \text{ cm}^{-3} \), visual extinction \( A_v = 0.3 \) and molecular fraction \( f_{H_2} = 1 \), we calculated the ratio of abundances using both the Zhu et al. expression for \( k_1 \) and the new value from this work. The results are presented in Fig. 5 and show that our new values result in a significant lowering of the predicted (HF) to (H₂) abundance ratio over the temperature range 10–100 K, by up to a factor of two. Thus, for a given observation of HF, the predicted value of the total H₂ abundance would be significantly increased (by up to a factor of two) using the new data.

In passing, we note that Godard et al., in their calculations, have in fact neglected the left-hand side of the denominator of their equation C.3, and used a constant value for the abundance ratio (3.6 × 10⁻⁸), which overestimates the new value for the abundance ratio by more than an order of magnitude at low temperatures.

Fluorine chemistry is less well understood in the densest (10⁻¹⁰⁻¹⁰⁻⁸ cm⁻³) and coldest environments (T = 10–50 K) where a significant fraction of HF is expected to condense on dust grains. A better knowledge of this chemistry, in which the reaction F + H₂ plays a central role, is crucial to interpret new observations of HF in such cold, dense regions of the ISM.

In summary, we have reported the experimental determination of rate coefficients for the F + H₂ reaction down to 11 K, where the reaction takes place exclusively by quantum-mechanical tunneling. The results agree very well with the predictions of non-adiabatic, multiple-PES quantum scattering calculations, confirming the importance of non-BO effects. The new rate coefficients should significantly improve the estimation of the density of interstellar molecular hydrogen by means of observations of HF.

**Methods**

We used the CRESU technique to measure rate coefficients for the title reaction over temperatures ranging from 11 to 295 K. This method uses isotropic supersonic expansions of a buffer gas through convergent–divergent Laval nozzles to generate a cylinder of cool, thermalized gas that can be used as a reactant to perform kinetics experiments. Fluorine atoms were generated by excimer laser photolysis of molecular fluorine at 248 nm, followed by rapid removal of any non-thermal distribution of fluorine spin–orbit states by collision with the buffer gas, as discussed in Supplementary Section 1.2. The rate coefficients were measured by monitoring the hydrogen atoms formed using resonant vacuum ultraviolet LIF at a wavelength of 121.6 nm. A schematic diagram of the experimental apparatus is shown in Supplementary Fig. 1.

Experiments were performed at 295, 77, 20 and 11 K. At 11 and 20 K, where we anticipated small rate coefficients, we used pure hydrogen as both the buffer gas and reagent. This required the use of Laval nozzles, which, together with the hydrogen gas, were precooled to 77 K using liquid nitrogen to avoid problems associated with incomplete rotational relaxation. The high quality of the uniform supersonic flows can be seen in the temperature profiles shown in Supplementary Fig. 2. The measurements at 77 and 295 K were performed by introducing various densities of H₂ into a supersonic flow of helium obtained by reducing the pumping speed. In all cases, a room-temperature population ratio of 3:1 was maintained for...
the orthopara spin isomers of H₂ (so-called normal hydrogen, n-H₂). The use of pure hydrogen gases in the ABCU technique is considered in more detail in Supplementary Section 1.1.

A full theoretical description of the F + H₂ reaction requires three BO PESs as well as an off-diagonal coupling potential and the dependence on geometry of the spin–orbit coupling between atomic states (Supplementary Fig. 4). Time-independent, fully quantum, reactive scattering calculations were carried out to predict rate coefficients, based on a formalism presented earlier⁶ and incorporating the very recent Li–Werner–Alexander–Lique (LWAL) PESs, which are a fit to highly correlated ab initio calculations. In particular, and of crucial importance at low temperature, the external correlation energy was scaled so that the calculated F + H₂ (v = 0, j = 0) → HF(ψ = j = 0) + H endothermicity (22.73 meV) agrees with experiment (22.33 meV) and the current best estimate of 70.86 meV (ref. 36). This is an indication of the high accuracy and quantitative nature of the PES. All scattering calculations were performed with the ABC code of Manolopoulos and co-workers⁶, extensively modified to include the three F-H₂ PESs as well as the spin–orbit and non-adiabatic coupling between them. The resulting state-to-state reaction cross-sections were transformed into thermal rate coefficients by appropriate averaging over reactant and product rovibrational states and collision energies, as described in Supplementary Section 1.7. Further details of the experimental and theoretical methods can be found in the Supplementary Information.

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References