

The F + H₂ reaction at very low temperatures

Meryem Tizniti,¹ Sébastien D. Le Picard,^{1,*} François Lique,² André Canosa and Ian R. Sims^{1,*}

¹ Institut de Physique de Rennes, UMR CNRS-UR1 6251, Université de Rennes 1, 263 Avenue du Général Leclerc, 35042 Rennes Cedex, France

² LOMC – Université du Havre, 25 Rue Philippe Lebon, BP 540 – 76 058 Le Havre Cedex, France

* Corresponding authors: sebastien.le-picard@univ-rennes1.fr, ian.sims@univ-rennes1.fr

The use of the CRESU (a French acronym for Reaction Kinetics in Uniform Supersonic Flow) technique coupled with pulsed laser photochemical kinetics methods (1) has shown that radical-radical, radical-unsaturated molecule and even radical-saturated molecule reactions can be rapid down to the temperatures of dense interstellar clouds (10–20 K), and the results have had a major impact in astrochemistry and planetology, as well as proving an exacting test for theory (2). Rate coefficients have been measured as low as 5.8 K for the reaction S(¹D) + H₂ (3). Until now, all of the fast chemical reactions whose rate coefficients have been measured in this way have taken place on attractive potential energy surfaces with no overall barrier to reaction.

The reaction F + H₂ → HF + F has long served as a benchmark for comparison between dynamics and kinetics experiments and quantum scattering calculations (4). It is also believed to be the primary production route for interstellar HF (5). Recent observations by the Herschel space telescope (6) have indicated that HF is the dominant reservoir of interstellar fluorine under a wide range of conditions and has the potential to become an excellent tracer of molecular hydrogen, and provides a sensitive probe of small H₂ column density clouds. However, the F + H₂ reaction possesses a small energetic barrier (~7 kJ mol⁻¹), and around 300 K its rate coefficient falls quite steeply with decreasing temperature. Calculations show, however, that tunnelling plays an increasingly dominant role as the temperature falls, and the rate constant becomes essentially temperature-independent below 20–30 K. The tunnelling calculations are sensitive not only to the barrier height, but also its precise form, with resonances and non-adiabatic effects also playing a strong role (7).

In this contribution, we will present completely new experimental measurements of the rate coefficient for the F + H₂ reaction at temperatures between 10 K and 300 K, along with a detailed comparison with new quantum reactive scattering calculations on the new hybrid new hybrid Li-Werner-Alexander-Lique potential surface. The experimental measurements of this rate coefficient, two orders of magnitude slower than typical barrierless reactions at 10 K, necessitated the use of new Laval nozzles operating with pure hydrogen buffer gas. The reaction was initiated by pulsed 248 nm excimer laser photolysis of F₂, and followed in real time by pulsed VUV LIF detection of H-atom products at 121.6 nm.

References

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