Enhanced reactivity of fluorine with para-hydrogen in cold interstellar clouds by resonance-induced quantum tunnelling

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Chemical reactions are important in the evolution of low-temperature interstellar clouds, where the quantum tunnelling effect becomes significant. The \( \text{F} + \text{para-} \text{H}_2 \rightarrow \text{HF} + \text{H} \) reaction, which has a significant barrier of \( 1.8 \text{ kcal mol}^{-1} \), is an important source of HF in interstellar clouds; however, the dynamics of this quantum-tunnelling-induced reactivity at low temperature is unknown. Here, we show that this quantum tunnelling is caused by a post-barrier resonance state. Quantum-state-resolved crossed-beam scattering measurements reveal that this resonance state has a collision energy of \(-5 \text{ meV}\) and a lifetime of \(-80 \text{ fs}\), which are in excellent agreement with a recent anion photoelectron spectroscopic study. Accurate quantum reactive scattering calculations on the new iCSZ-LWAL potential energy surfaces provides a detailed explanation of the experimental results. The reaction rate for this system was also theoretically determined accurately at temperatures as low as 1K.

In the classical picture, a chemical reaction with an energy barrier can only happen at collision energies higher than the barrier. However, at energies below the reaction barrier, chemical reactions through quantum tunnelling can play a significant role in many chemical and biological processes\(^{1-3}\). Quantum tunnelling is especially important in low-temperature environments such as the interstellar medium\(^{4-6}\). Thus, understanding quantum tunnelling in chemical reactions is of general interest and of fundamental importance to interstellar chemistry.

The \( \text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H} \) reaction has been a benchmark system for the study of chemical reaction dynamics in recent decades\(^{4,5}\). Its importance in the interstellar medium has also been recognized\(^{6,7}\). HF was first discovered in the interstellar cloud (ISC) in 1997, and recent observations by the Herschel Space Observatory found that the existence of HF is ubiquitous in the universe\(^{8-10}\). It has been used to trace key properties of the ISC, such as hydrogen column density. This discovery has generated renewed interest in the benchmark \( \text{F} + \text{H}_2 \) reaction in the low-temperature region, because it is the sole source of the observed HF in low-temperature ISC\(^{11}\). Clearly, the reaction rate of this system at temperatures close to absolute zero is very important for modelling ISC chemistry. It is already known that for reactions such as the \( \text{S}(^3 \text{D}) + \text{H}_2 \) reaction\(^{11-13}\), which has no reaction barrier, the reaction rate at very low temperatures is usually very large. However, the \( \text{F} + \text{H}_2 \) reaction is known to have a significant reaction barrier (\( E_r \approx 1.8 \text{ kcal mol}^{-1} \) or 78 meV), so its reaction rate should be negligibly small at low temperatures around \( T=10 \text{ K} \), which are quite typical in the ISC, even when the normal quantum tunnelling effect below the reaction barrier is taken into consideration. A recent rate measurement of the \( \text{F} + \text{H}_2 \) reaction at temperature as low as \( 12 \text{ K} \) showed pronounced chemical reactivity of this reaction at an extremely low temperature\(^{14}\). This rather surprising result raises an intriguing question: what is the exact mechanism of the enhanced \( \text{F} + \text{H}_2 \) reactivity at extremely low temperatures that produces HF in the low-temperature ISC?

As one of the most important prototype reactions for the study of reaction dynamics and the development of the concept of reaction resonances, the \( \text{F} + \text{H}_2 \) reaction (and its isotopic reactions) has been investigated extensively in recent decades using various advanced experimental methods and accurate quantum dynamics theories\(^{15-19}\). The existence of a reaction resonance in the \( \text{F} + \text{H}_2 \) reaction was predicted in 1973 in refs\(^{20,21}\) and \( 21 \). In 1985, a forward scattering peak for the HF(\( v' = 3 \)) product was observed in a crossed-beam scattering experiment (which was regarded as a signature of reaction resonances) from this seemingly direct abstraction reaction\(^{22,23}\). Both quasi-classical trajectory\(^{24}\) and quantum dynamics calculations\(^{25}\) on the Stark–Werner potential energy surface (SW-PES)\(^{26}\) show a forward scattering peak for HF(\( v' = 3 \)), with the quasi-classical trajectory results smaller than the experiment. In the past two decades, reaction resonances in the \( \text{F} + \text{HD} \) system have been investigated and characterized in great detail\(^{27-29}\). Even though reaction resonances in the \( \text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H} \) reaction have also been investigated quite extensively\(^{20-23}\), the lowest resonance state in the reaction has not been characterized directly in a crossed-molecular-beam study, and its role in the chemical reactivity at the cold interstellar temperature has not been clearly understood. This is largely due to the
difficulties in studying the dynamics of this reaction at very low collision energy using the crossed-molecular-beam method.

To understand the role of resonances in the F + H₂ reaction at the cold interstellar temperature, we carried out a high-resolution crossed-beam scattering study on the F + H₂ → HF + H reaction at a collision energy as low as 1.21 meV, using the H-atom Rydberg tagging time-of-flight (TOF) technique. Quantum-state-specific backward scattering spectroscopy (QSSBSS), which essentially is the collision-energy-dependent differential cross-sections (DCSs) for a specific product quantum state in the backward scattering direction, was measured in the very low collision energy region, in addition to obtaining full-dimensional DCSs at three collision energies. The present results are also compared with recent results from a high-resolution negative-ion photoelectron spectroscopic study and accurate quantum dynamics calculations in an effort to understand the nature of the F + H₂ reactivity at very low temperature. Using a combination of the QSSBSS of the crossed molecular beam scattering technique and negative ion photoelectron spectroscopic technique enables us to obtain a unique perspective on the transition-state resonance. As we show in the following sections, the experimental results agree with each other well, which demonstrates the power of these two state-of-the-art experimental methods for characterizing a transition state.

**Results and discussion**

**Crossed molecular beam and anion photoelectron spectroscopy experiment.** The crossed molecular beam apparatus used in this work was specially modified so that a reactive scattering experiment on the title reaction at very low collision energy could be carried out. Using this apparatus, TOF spectra were measured for the H-atom product in the backward scattering direction from the F(2P_j) + H₂(v = 0, j = 0) → HF(v, j') + H reaction in the low collision energy region. Three typical TOF spectra are shown in Fig. 1, with the lowest collision energy at 1.21 meV. From these spectra, it is clear that the HF products are predominantly populated in the v = 2 state in the low collision energy region.

The QSSBSS has been demonstrated to be a powerful method to probe the isolated quantum resonances in several benchmark chemical reactions, and can effectively minimize partial waves averaging in reactive scattering experiments. Here, we measured the QSSBSS for the HF(v = 2) product from the F + H₂(v = 0, j = 0) reaction for collision energies between 1.21 and 35 meV, in an effort to determine accurately the energy of the reaction resonance state in the low collision energy region (Fig. 2a). A peak at ~5 meV is clearly observed in the QSSBSS, which can be assigned to the lowest resonance state in terms of collision energy. This resonance feature in the QSSBSS not as clear as the lowest resonance state. The energy of the lowest resonance state was determined to be 4.9 ± 0.5 meV. The feature at a collision energy of ~20 meV is related to the first excited resonance state of this reaction, but mixed with signals from the direct reaction via regular quantum tunnelling through the energy barrier, thus making the resonance feature in the QSSBSS not as clear as the lowest resonance state. In addition to the QSSBSS measurement, the full DCSs at collision energies of 1.56, 6.93 and 9.97 meV were also experimentally measured and are shown in Fig. 3. As pointed out in the Methods, the uncertainty of collision energy in this experiment is ~10%, that is, 0.5 meV at a collision energy of 5 meV.

Anion photoelectron spectroscopy has been used to probe the transition-state resonances in the F + H₂ reaction. Recently, the high-resolution anion photoelectron spectrum for FH⁻ has been measured using the cryo-SEVI (slow-electron velocity-map imaging with cryogenic ion cooling) technique, a high-resolution photoelectron spectroscopy method, to detect the transition-state resonances of the F + H₂ reaction. Figure 2b presents a plot of the photoelectron spectrum of FH⁻, with the collision energy on the x axis, which can be compared directly with the QSSBSS results in Fig. 2a. Conversion of the photoelectron energy to the collision energy is carried out using the relationship described in Supplementary Section A. The main resonance peak (peak A) position was determined to be at 5.4 meV in the cryo-SEVI spectrum in terms of the collision energy in this experiment. Here, we use the most recent theoretical value for the dissociation energy of FH⁻, D₀(FH⁻) = 2.028 eV (ref. 38), obtained using a highly accurate ab initio method, and the electronic affinity energy of the F atom from experiment, EΑ(F) = 3.4012 eV (ref. 39), to rescale the cryo-SEVI spectrum for comparison with the QSSBSS result (Supplementary Fig. 1). The resonance state energy in the rescaled cryo-SEVI spectrum is in excellent agreement with the resonance energy (4.9 ± 0.5 meV) obtained in the QSSBSS measurements (Fig. 2a). The small disagreement between the two numbers could come from the uncertainty of the theoretical value of D₀(FH⁻) and the experimental measurement errors. Thus, the position of the lowest resonance state in terms of collision energy is accurately determined to within 0.5 meV from these two accurate experimental methods, which allows us to benchmark the resonance picture of the F + H₂ reaction with high accuracy. Furthermore, the width of
HF($v=2$) product from the F$^-$H$_2$ photodetachment spectra of the adiabatic iCSZ PES, and the red line was calculated using the diabatic PESs. The magenta line is the Lorentzian fit to the lowest peak. The olive line was calculated using the diabatic PESs, see Supplementary Section B. The adiabatic ground-state iCSZ PES (see the following subsection), the diabatic PESs and the spin–orbit non-adiabatic coupling effects, were also compared below the collision energy zero (from accurate energy characterizations in the QSSBSS experiment) and thus should not play a significant role in the F$^-$H$_2$ reaction in the low-temperature interstellar medium.

**Mechanism investigation by quantum reaction dynamics theory.** To understand the role of the observed resonances in the chemical reactivity of F$^-$H$_2$ in the low-temperature region, an improved adiabatic PES for the ground electronic state based on the CSZ PES was constructed, because the CSZ PES does not provide a sufficiently accurate description of the long-range interaction potential in the reactant channel, which is a crucial part of the surface for determining the reactivity at low temperatures. A total of 6,118 ab initio points at the UCCSD(T)/AVQZ level were applied to the CSZ PES to improve its accuracy in the long-range part of the surface. For a more detailed description of this improved CSZ PES (iCSZ PES) for the ground state, see Supplementary Section B.

Using the time-independent reactive scattering ABC code, a converged DCS calculation was carried out on the new adiabatic iCSZ PES using the parameters listed in Supplementary Section D. The calculated QSSBSS for the HF($v'=2$) product is presented in Fig. 2a as the olive line. The agreement between theoretical and experimental results is quite good. A small difference in peak position is clearly seen. In addition, in the lowest collision energy region, the theoretical result seems to go up slightly with the collision energy approaching zero, while the experimental result goes down. To test if this difference is due to the spin–orbit non-adiabatic effect, we carried out time-dependent wavepacket calculations (for details see Supplementary Section C), which include the spin–orbit coupling in the reaction, based on the new diabatic PESs (iCSZ-LWAL PESs), which are constructed from the iCSZ PES and the diabatic LWAL PESs (for a detailed description of these new diabatic PESs see Supplementary Section B). The adiabatic ground state of the new diabatic PESs uses the iCSZ PES, but the non-adiabatic couplings and excited surfaces of the new diabatic PESs use those of the LWAL PESs.

The QSSBSS data below 20 meV are then calculated using the new diabatic PESs. The calculated QSSBSS for the HF($v'=2$) product is shown in Fig. 2a as the red line; this seems to be in better agreement with the experimental result than the adiabatic calculation based on the iCSZ PES in the low collision energy region. The calculated peak position for the lowest resonance using the diabatic iCSZ-LWAL PESs is ~6.1 meV, which is 1.2 meV off the QSSBSS experimental value and 0.7 meV off the cryo-SEVI result. The calculated peak width is also in very good agreement with both experimental results. This is clearly a remarkable achievement of the theory, which has reached far beyond chemical accuracy (1 kcal mol$^{-1}$). The high accuracy of the PESs also allows us to analyze how the resonance state would affect chemical reactivity in the very low temperature regime.

The DCSs calculated in the entire scattering angular range (0–360°) using the new diabatic iCSZ-LWAL PESs, which include the spin–orbit non-adiabatic coupling effects, were also compared with the experimentally measured DCSs at collision energies of 1.56, 6.93 and 9.97 meV (Fig. 3). The agreement between experiment and theory is quite good. These results suggest that the new diabatic PESs are highly accurate and the inclusion of the spin–orbit coupling seems to have a non-negligible effect in the reaction dynamics of F($P_{v=2}$) + H$_2$($j=0$), especially in the collision-energy-dependent DCS in the very low collision energy regime.

**Reaction rate constant calculations by quantum dynamics theory.** Using the diabatic iCSZ-LWAL PESs, we also investigated the effect of resonance on the reaction rate constants for the $F+P-H_2$ reaction in the low temperature region of interstellar chemistry of interest (see Methods and Supplementary Sections C and D), down to 1 K. In particular, reaction rate constant calculations for the $F+P-H_2$ reaction were carried out by taking out the first resonance state peak in the reaction probability in each partial wave (for details see Supplementary Section H), to see how the ground resonance state affects the reaction rate in the low temperature region. Figure 5 shows the calculated rate constants of the $F+P-H_2$ reaction with and without the ground resonance in the low temperature region. From this figure, we conclude that the $F+P-H_2$ reaction in the low temperature region (below 40 K) is mostly due to the ground reaction resonance state. Similarly, the ICS for the $F+P-H_2$ reaction in the low collision energy region is also predominantly due to the ground resonance state (Supplementary Section E and Supplementary Fig. 9).

Because of the difference between the effect of resonances on the reaction rate constants of the $F+P-H_2(j=0)$ reaction and those of the $F+o-H_2(j=1)$ reaction, the effect of reaction resonances in the interstellar medium with different ortho–para ratios should also be quite different\(^\text{15}\). In Fig. 6, we show the results of calculations of the reaction rate constants for the $F+\eta-H_2$ reaction (ortho–para ratio of 3:1), and with ortho and para $H_2$ in the local thermal equilibrium condition in the low temperature instellar medium. The calculated reaction rate constants were compared with previously measured rate constants for the $F+\eta-H_2$ reaction\(^\text{14}\). The agreement is quite

![Fig. 3 | Three-dimensional product contour plots as a function of product velocity for the $F+H_2(\nu=0, j=0)\to HF+H$ reaction.](image)

**Fig. 4** | Schematic explaining the roles of the two resonances states (003) and (103) in the product channel in the reaction of $F+H_2(j=0)$ and $F+H_2(j=1)$. The ground resonance state in the exit channel (post-barrier) is mainly responsible for the $F+H_2(j=0)$ reaction at very low temperature, while the excited resonance state in the exit channel should play a more important role than the ground resonance state for the $F+H_2(j=1)$ reaction in the very low temperature regime.
The calculated reaction rate constant, \( k \), for the F + p-H\(_2\) → HF + H and F + o-H\(_2\) → HF + H reactions as a function of temperature. Solid lines represent the calculated reaction rate constants including the non-adiabatic spin–orbit effect based on the diabatic iCSZ-LWAL PESs. Dash-dotted lines are the calculated rate constants by excluding the contribution of related resonances for the two reactions.

Fig. 5 | Calculated reaction rate constants. The calculated reaction rate constant, \( k \), for the F + p-H\(_2\) → HF + H and F + o-H\(_2\) → HF + H reactions as a function of temperature. Solid lines represent the calculated reaction rate constants including the non-adiabatic spin–orbit effect based on the diabatic iCSZ-LWAL PESs. Dash-dotted lines are the calculated rate constants by excluding the contribution of related resonances for the two reactions.

Fig. 6 | Calculated reaction rate constants. The calculated reaction rate constants \( k \) are shown for the F + p-H\(_2\) → HF + H reaction (blue solid line) and the F + H\(_2\) → HF + H reaction (red dash-dotted line) under the local thermal equilibrium (LTE) as a function of temperature. Filled circles are experimental results from ref. \(^1\). Lines represent the calculated rate constants including the non-adiabatic spin–orbit effect based on the diabatic iCSZ-LWAL PESs.

The F atom beam was also cooled by liquid nitrogen to slow the beam velocity and to reduce the speed ratio to achieve better energy resolution for the experiment. The F atom beam velocity could be varied from 0.8 to 1.5 km s\(^{-1}\) with a speed ratio of ~20 using this method. By slowing both the F atom and H\(_2\) beams using liquid-nitrogen-cooled pulsed valves and optimizing the rotating beam source design, a minimum crossing angle as low as 26° between the two beams was reached, allowing a reaction collision energy as low as 1.21 meV to be achieved. The energy spread of the collision energy was estimated to be ~10% of the collision energy.

Theory. A time-dependent wavepacket method for describing the coupled states’ reactive scattering processes was applied in the quantum dynamics calculations to obtain the product quantum state-resolved \( S \) matrices, for which we only applied the reactant Jacobi coordinate during the wavepacket propagation. The fourth-order split operator was applied to propagate the wavepacket. The numerical parameters used in the calculations were capable of giving converged DCSs. For more details of the theory describing the dynamics of triatomic reactions, see refs. \(^{64,65}\). For the adiabatic reactive scattering model we used the ABC code, which uses the time-independent hyperspherical coordinate method, to calculate the product quantum state-resolved \( S \) matrices. The parameters for the ABC code adopted in this work are similar to those in our previous work\(^8\).

Data availability
Data supporting the findings of this study are available from the corresponding authors on request.

Code availability
The accurate iCSZ and iCSZ-LWAL PESs developed in this work are available from the corresponding authors on request.

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Author contributions
X.Y., D.H.Z., C.X., D.M.N. and M.H.A. conceived and supervised the research. The experiments were carried out by T.Y., L.H., T.W., D.D. and C.X. Data analysis and interpretation were performed by T.Y., L.H., T.W., D.D. and C.X. Theoretical calculations were performed by Z.S., J.C., F.L., M.H.A. and D.H.Z. The manuscript was written by X.Y., Z.S., M.H.A., D.Z. and D.M.N., with contributions from all authors. All authors contributed to discussions about the content of the paper.

Competing interests
The authors declare no competing interests.

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