

## Dynamical Resonances in the Fluorine Atom Reaction with the Hydrogen Molecule

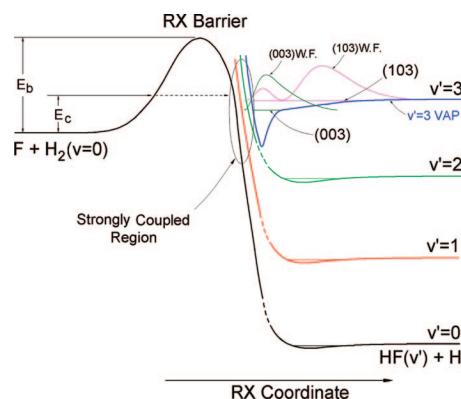
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### CONSPECTUS

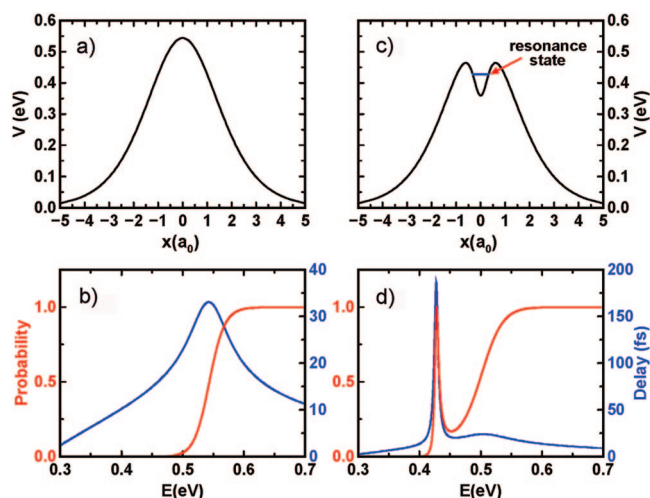
The concept of transition state has played a crucial role in the field of chemical kinetics and reaction dynamics. Resonances in the transition state region are important in many chemical reactions at reaction energies near the thresholds. Detecting and characterizing isolated reaction resonances, however, have been a major challenge in both experiment and theory. In this Account, we review the most recent developments in the study of reaction resonances in the benchmark  $F + H_2 \rightarrow HF + H$  reaction. Crossed molecular beam scattering experiments on the  $F + H_2$  reaction have been carried out recently using the high-resolution, highly sensitive H-atom Rydberg tagging technique with HF rovibrational states almost fully resolved. Pronounced forward scattering for the HF ( $\nu' = 2$ ) product has been observed at the collision energy of 0.52 kcal/mol in the  $F + H_2$  ( $j = 0$ ) reaction. Quantum dynamical calculations based on two new potential energy surfaces, the Xu–Xie–Zhang (XXZ) surface and the Fu–Xu–Zhang (FXZ) surface, show that the observed forward scattering of HF ( $\nu' = 2$ ) in the  $F + H_2$  reaction is caused by two Feshbach resonances (the ground resonance and first excited resonance). More interestingly, the pronounced forward scattering of HF ( $\nu' = 2$ ) at 0.52 kcal/mol is enhanced considerably by the constructive interference between the two resonances. In order to probe the resonance potential more accurately, the isotope substituted  $F + HD \rightarrow HF + D$  reaction has been studied using the D-atom Rydberg tagging technique. A remarkable and fast changing dynamical picture has been mapped out in the collision energy range of 0.3–1.2 kcal/mol for this reaction. Quantum dynamical calculations based on the XXZ surface suggest that the ground resonance on this potential is too high in comparison with the experimental results of the  $F + HD$  reaction. However, quantum scattering calculations on the FXZ surface can reproduce nearly quantitatively the resonance picture of the  $F + HD$  reaction observed in the experiment. It is clear that the dynamics of the  $F + HD$  reaction below the threshold was dominated by the ground resonance state. Furthermore, the forward scattering HF ( $\nu' = 3$ ) channel from the  $F + H_2$  ( $j = 0$ ) reaction was investigated and was attributed mainly to a slow-down mechanism over the centrifugal exit barrier, with small contributions from a shape resonance mechanism in a narrow collision energy range. A striking effect of the reagent rotational excitation on resonance was also observed in  $F + H_2$  ( $j = 1$ ), in comparison with  $F + H_2$  ( $j = 0$ ). From these concerted experimental and theoretical studies, a clear physical picture of the reaction resonances in this benchmark reaction has emerged, providing a textbook example of dynamical resonances in elementary chemical reactions.



### 1. Introduction

Chemical reactions occur when one reactant collides with another and some rearrangements among reactants take place along a path connecting reactants to products. This path is called the reaction coordinate for a chemical reaction, along

which the reactants will go through a reaction intermediate region to reach the product side. This intermediate region is defined as the transition state for a chemical reaction, an important concept introduced by Eyring<sup>1</sup> and Polanyi<sup>2</sup> in 1935. Direct observation of the transition state has been regarded as a "Holy Grail" of chemistry.<sup>3</sup> In a typ-



**FIGURE 1.** One-dimensional views of two model reactions, a reaction with a simple barrier and a typical reaction with a dynamical resonance: (a) the potential energy curve along the reaction coordinate for a model reaction with a simple barrier; (b) the calculated reaction probability and time delay for the model reaction in panel a; (c) the potential energy curve along the reaction coordinate for a model reaction with a dynamical resonance; (d) the calculated reaction probability and time delay for the model reaction in panel c. The two reaction models were adapted from ref 4.

ical chemical reaction with an energetic barrier (Figure 1a), no discrete quantum structure exists in the transition state region along the reaction coordinate, and the reaction probability simply increases as the reaction energy goes above the barrier (Figure 1b).<sup>4</sup> In certain cases, however, quantized states can be transiently trapped in the transition state region along the reaction coordinate (Figure 1c).<sup>4</sup> These transiently trapped quantum states are often called dynamical resonances, or reaction resonances, which enhance the reaction probability dramatically through resonance-mediated tunneling (Figure 1d). The lifetimes of these transiently trapped states are typically on the order of a few hundred femtoseconds (Figure 1d). Since reaction resonances are extremely sensitive to the potential energy surface governing a chemical reaction, they provide possible direct and delicate probes to the critical region of the potential energy surface. As a result, the reaction resonance has been a central topic in the study of chemical reaction dynamics in the last few decades.<sup>5–11</sup> However, because of the averaging effect due to orientations, impact parameters, and collision energies in chemical reactions, probing the structure and dynamics of such resonances experimentally has been a great challenge in modern reaction dynamics.

Significant efforts have been devoted to investigating the structures and dynamics of reaction resonances in elementary chemical reactions during the last few decades. Experi-

mentally, the negative ion photodetachment technique<sup>12</sup> and the crossed-molecular-beams reactive scattering method<sup>6</sup> have been the two primary tools to detect reaction resonances in elementary chemical reactions. Theoretical predictions of the reaction resonances in the H + H<sub>2</sub><sup>13–16</sup> and F + H<sub>2</sub> reaction<sup>17–19</sup> were made in the early 1970s, when quantum dynamical calculations on model potential energy surfaces became possible. The search and characterization of reaction resonances in these two reactions represent a significant part of the efforts to understand the dynamics of reaction resonances in chemical reactions. It was only recently that the physical pictures of the reaction resonances in these two benchmark systems became gradually clear due to concerted theoretical and experimental efforts at the quantum state-to-state level. Recent studies have revealed the interesting dynamics of the quantized bottleneck states in the H + H<sub>2</sub> reaction.<sup>20–22</sup> However, no reaction resonance, that is, transiently trapped resonance state along the reaction coordinate, has been identified in this system thus far. In contrast, the F + H<sub>2</sub> reaction has proven to be a truly benchmark system for dynamical resonances.

Since the first theoretical prediction of reaction resonances in the F + H<sub>2</sub> reaction in the early 1970s by Schatz et al.<sup>17,18</sup> and Wu et al.,<sup>19</sup> the search for evidence of such resonances in this reaction has attracted much attention from many top research groups in this field. In 1984, Neumark et al. performed a landmark crossed-beams experiment on the F + H<sub>2</sub> reaction using a universal crossed molecular beams apparatus.<sup>23,24</sup> A clear forward scattering peak was observed for the HF ( $\nu' = 3$ ) product, which was attributed to reaction resonances in this reaction. Furthermore, forward scattering for the DF ( $\nu' = 4$ ) product from F + D<sub>2</sub> as well as the HF ( $\nu' = 3$ ) product from F + HD were observed,<sup>25</sup> consistent with the F + H<sub>2</sub> experiment.<sup>23</sup> However, the full quantum mechanical (QM) scattering calculations of the F + H<sub>2</sub> reaction<sup>26</sup> on the Stark–Werner PES (SW-PES)<sup>27</sup> did not support this resonance conjecture. Quasi-classical trajectory (QCT) calculations on the same surface by Aoiz et al. also exhibit forward scattering of HF ( $\nu' = 3$ ) in the same reaction.<sup>28</sup> The SW-PES is reasonably accurate in describing the transition state region for the F + H<sub>2</sub> reaction as revealed in the negative ion photodetachment study of the FH<sub>2</sub><sup>−</sup> system.<sup>12</sup> Observation of forward scattered HF ( $\nu' = 3$ ) product from QCT calculations based on classical mechanics on the SW-PES implies that the HF ( $\nu' = 3$ ) forward scattering observed in the experiment might be due to mechanisms other than resonances, because resonance is a quantum phenomenon, which cannot be described properly by classical mechanics.

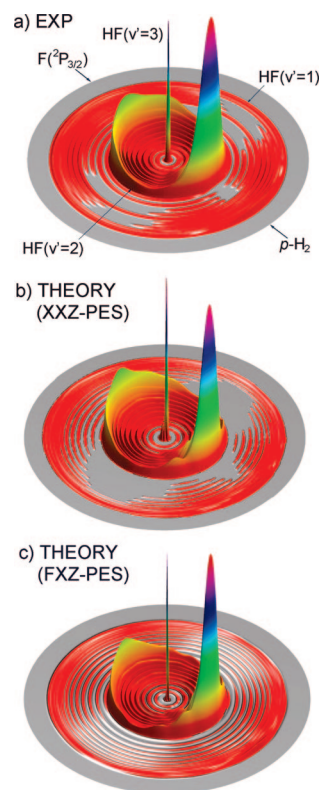
In a more recent crossed beam experiment, Skodje et al. unambiguously observed a step in the total excitation function at about 0.5 kcal/mol collision energy in the F + HD → HF + D reaction.<sup>29</sup> Theoretical analysis based on the SW-PES attributed this step to a single reaction resonance in the F + HD reaction. Differential cross sections for this reaction measured at various collision energies also revealed a resonance signature in the reaction.<sup>30</sup> However, no step in the excitation function similar to that for the F + HD reaction was observed for the F + H<sub>2</sub> reaction,<sup>31</sup> suggesting the dynamics for these two systems are considerably different. Theoretical study on the SW-PES also found that resonance in the F + HD reaction has a profound effect on the reactive cross section and thus the reaction rate constant at collision energies below and above the reaction barrier.<sup>32</sup>

In the past few years, we have studied extensively the F + H<sub>2</sub>(HD) reaction in an effort to understand the dynamics of reaction resonances in this important system, using the high-resolution crossed molecular beams (CMB) technique in combination with full quantum scattering calculation based on accurate potential energy surfaces. The advances made in these studies have provided a clear physical picture of reaction resonances in this benchmark system that has eluded us for decades.

## 2. Feshbach Resonances in F + H<sub>2</sub> (*j* = 0)

Crossed molecular beam scattering studies of the F + H<sub>2</sub> reaction were performed using the high-resolution and highly sensitive H-atom Rydberg tagging time-of-flight (TOF) method.<sup>33,34</sup> The technique was developed in the early 1990s<sup>35</sup> and has been applied to the study of many important elementary chemical reactions.<sup>20,21,36,37</sup> A special double stage discharged beam source of F atoms,<sup>38</sup> mostly in the <sup>2</sup>P<sub>3/2</sub> state, was used with a H<sub>2</sub> beam source that was cooled to liquid nitrogen temperature. This puts nearly all para-H<sub>2</sub> molecules in the beam in the *j* = 0 state and allows us to measure the H atom product TOF spectra at extremely high resolution that resolves nearly all rovibrational states of the HF product.

TOF spectra of the H atom products from the F + H<sub>2</sub> reaction were measured at different scattering angles at the collision energy of 0.52 kcal/mol. These spectra were then converted to product kinetic energy (KE) distributions. By simulating the experimental kinetic energy distributions, we determined fully rovibrational state resolved differential cross sections (DCS) (Figure 2a). One of the most intriguing obser-



**FIGURE 2.** The experimental and theoretical three-dimensional (3D) contour plots for the HF product for the F(<sup>2</sup>P<sub>3/2</sub>) + H<sub>2</sub> (*j* = 0) reaction at the collision energy of 0.52 kcal/mol: (a) experimental results; (b) theoretical results on the XXZ-PES; (c) theoretical results on the FXZ-PES. The different circles represent different HF product rovibrational states. The forward scattering direction for HF is defined along the F atom beam direction.

vations in this study is the pronounced forward scattering peak for the HF (*v*' = 2) product.<sup>33</sup> Forward scattered product is an important indication of reaction resonances, even though it is not necessarily caused by resonances.<sup>20</sup> Furthermore, careful measurements were carried out to obtain the collision energy dependent DCS for HF (*v*' = 2) in the forward scattering direction. The experimental data in the collision energy range of 0.2–0.9 kcal/mol show a clear peak for the forward scattering HF (*v*' = 2) product at the collision energy of about 0.52 kcal/mol.

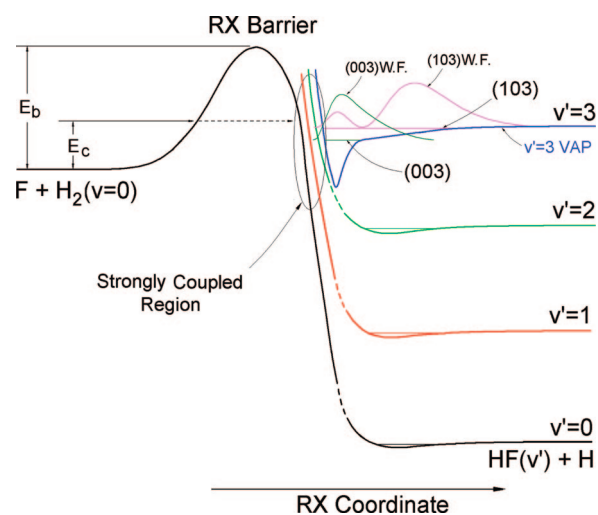
To understand these experimental observations, two new potential energy surfaces were constructed recently. The Xu–Xie–Zhang potential energy surface (XXZ-PES) was constructed for the F (P<sub>3/2</sub>) + H<sub>2</sub> reaction, using the internally contracted multireference configuration interaction method<sup>39,40</sup> with the Davidson correction (icMRCI+Q)<sup>41</sup> with the augmented correlation-consistent valence 5-zeta (aug-cc-pv5z) basis set of Dunning.<sup>42</sup> More recently, to interpret the F + HD experimental result, which will be discussed later in this Account, the Fu–Xu–Zhang potential energy surface (FXZ-PES) for this system was also constructed<sup>43</sup> based upon the

spin unrestricted, coupled cluster method, including single and double excitations with perturbative accounts of triple excitations, using the same basis set as the XXZ-PES. Spin-orbit effect is included in both surfaces.<sup>43</sup>

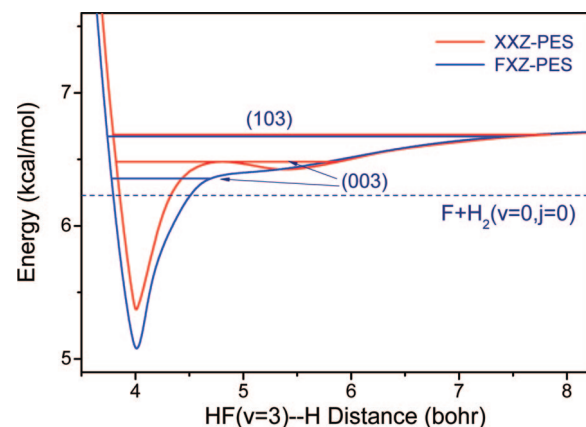
Fully converged quantum scattering calculations were carried out on these two new surfaces for the F ( $P_{3/2}$ ) + H<sub>2</sub> ( $j = 0$ ) reaction at collision energies up to 1.5 kcal/mol using the ABC code.<sup>44</sup> The calculated DCSs at 0.52 kcal/mol from the two potential surfaces were shown in Figure 2b,c, in direct comparison with the experimental result. The agreement between the experimental data and the theoretical results from both potential energy surfaces are quite remarkable. The collision energy dependence for the forward scattering HF ( $\nu' = 2$ ) product was also calculated for both surfaces and the results agree fairly well with the experimental data. This demonstrates that the theoretical pictures of this reaction described by both the XXZ-PES and the FXZ-PES are quite reasonable.

Further analysis based on the two potential surfaces shows that the pronounced forward scattering of HF ( $\nu' = 2$ ) at the collision energy of 0.52 kcal/mol is caused by two Feshbach resonances, which constructively interfere with each other at this energy. The ground resonance on both surfaces can be assigned to the (003) state trapped in the HF ( $\nu' = 3$ )–H' vibrational adiabatic potential (VAP) well with zero quantum vibration on both the reaction coordinate and the bending motion and three quanta vibration on the HF stretching. The excited reaction resonance can be assigned to the (103) state with an additional quantum vibration along the reaction coordinate compared with the (003) state.

Figure 3 shows the resonance-mediated reaction mechanism in a one-dimension (1D) vibrational adiabatic picture on the FXZ-PES. The resonance states in this case clearly lie in the postbarrier regime. The HF ( $\nu' = 3$ )–H' VAP on the FXZ-PES is quite peculiar with a deep vibrationally adiabatic well close to the reaction barrier and a van der Waals (vdW) part of the potential, which is quite different from that on the SW-PES<sup>27</sup> and more similar to that on the SWMHS-PES.<sup>45</sup> The one dimension wave function for the ground resonance state in Figure 3 shows that this state is mainly trapped in the inner deeper well of the HF ( $\nu' = 3$ )–H' VAP with a little bit of vdW character, while the excited state is mainly a vdW resonance. Since the resonance states are trapped in the HF ( $\nu' = 3$ )–H' adiabatic potential and may decay to the HF ( $\nu' = 1,2$ ) channels via couplings between the HF ( $\nu' = 3$ )–H' adiabatic potential and the HF ( $\nu' = 1,2$ )–H' adiabatic potentials, it is obvious that the HF ( $\nu' = 1,2$ ) product channels proceed via a typical Feshbach resonance mechanism.

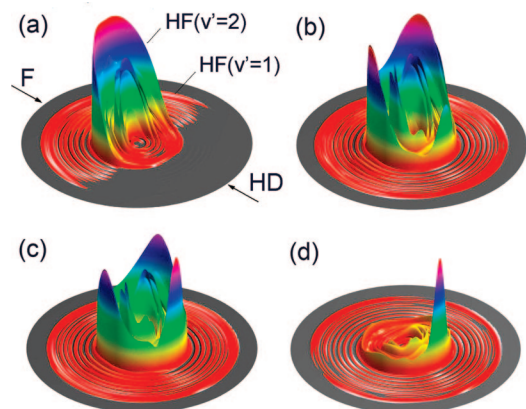


**FIGURE 3.** Schematic diagram for the resonance-mediated reaction mechanism for the F + H<sub>2</sub> reaction with two resonance states trapped in the peculiar HF ( $\nu' = 3$ )–H' VAP well. The one-dimensional wave functions of the two resonance states are also shown. The (003) state is the ground resonance state, while the (103) resonance is the first excited resonance state. This diagram was made based on the FXZ-PES.



**FIGURE 4.** The one-dimensional adiabatic resonance potentials of HF ( $\nu' = 3$ )–H for the F + H<sub>2</sub> reaction traced out from the XXZ-PES and the FXZ-PES.

It is interesting to note that the two potential energy surfaces actually have some noticeable differences in the resonance region although the dynamics described by both potential surfaces are in rather good agreement with the experimental observations for the F + H<sub>2</sub> reaction. Figure 4 compares the 1D HF ( $\nu' = 3$ )–H' VAPs for the two potential surfaces for the F + H<sub>2</sub> reaction. The shapes of the two VAPs are quite different. The 1D VAP for the XXZ-PES exhibits two wells: a deeper inner well and a shallow van der Waals well with a bump near 4.8 bohr. This bump on the 1D VAP from the XXZ-PES, however, disappears on the FXZ-PES. More importantly, the inner resonance well on the FXZ-PES is obviously deeper than that on the XXZ-PES. As a result, the ground resonance (003) on the FXZ-PES is shifted to lower energy by



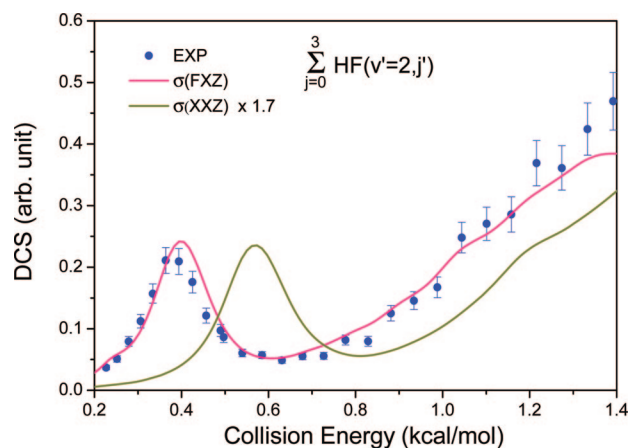
**FIGURE 5.** The experimental three-dimensional (3D) contour plots for the HF product from the F ( $^2P_{3/2}$ ) + HD ( $j = 0$ ) reaction at the collision energies of (a) 0.43, (b) 0.48, (c) 0.52, and (d) 0.71 kcal/mol.

about 0.12 kcal/mol from that on the XXZ-PES, while the (103) resonance state on the FXZ-PES merely shifts down by 0.01 kcal/mol. This is because the (103) resonance state is mainly determined by the long-range vdW potential, which is very similar for the two surfaces. The dynamics of the F + H<sub>2</sub> reaction at 0.52 kcal/mol is largely determined by the excited resonance state and quite insensitive to the position of the ground resonance. As a result of this picture, both potential energy surfaces can describe rather well the observed dynamics for the F + H<sub>2</sub> reaction even though the energies of the ground resonance states on the two surfaces are somewhat different. Based on the F + H<sub>2</sub> dynamical observations at 0.52 kcal/mol, it is obviously hard to judge which potential surface is more accurate in describing the resonance picture in the F + H<sub>2</sub> reaction.

### 3. Feshbach Resonances in the F + HD Reaction: Isotope Effect on Reaction Resonances

Hoping to probe the resonance picture of this benchmark reaction more accurately, we carried out a full quantum state resolved scattering study on the isotope substituted reaction, F + HD ( $j = 0$ ) → HF + D, using the D-atom Rydberg tagging TOF method.<sup>43</sup> TOF spectra of the D-atom product from the F + HD reaction were measured at different scattering angles in the collision energy range from 0.3 to 1.2 kcal/mol, and full rovibrational state resolved differential cross sections (DCS) were determined as for the F + H<sub>2</sub> reaction. Figure 5 shows four experimental DCS contour plots in three dimensions for the F + HD reaction at four collision energies: 0.43, 0.48, 0.52, and 0.71 kcal/mol.

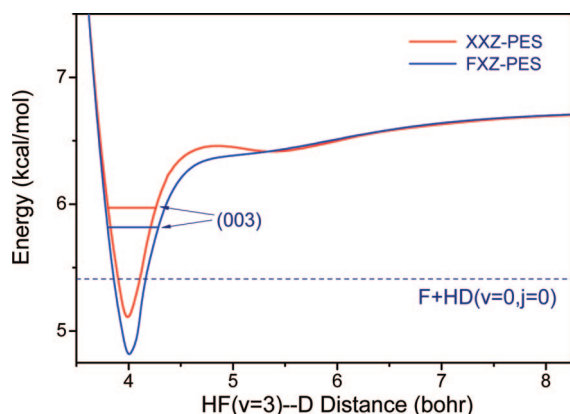
The most striking observation in the experimental DCS is the drastic changes of the three-dimensional DCS at the col-



**FIGURE 6.** Collision energy dependent DCS for the backward scattering HF ( $\nu' = 2$ ) products summed over at  $j' = 0-3$ . A resonance-like peak is clearly present at the collision energy of about 0.39 kcal/mol. The solid circles are the experimental data, and the solid lines are the calculated theoretical results based on the XXZ surface and the FXZ surface.

lision energy around 0.5 kcal/mol. Within an energy range of 0.28 kcal/mol, or 98 cm<sup>-1</sup>, the DCS goes through a series of remarkable changes. One may note that there exist some substantial differences between the 3D DCS contour plots from this work and that reported in ref 30 at the collision energy near 0.5 kcal/mol. The experimental conditions, especially the HD beams, are quite different in the two experiments and would likely cause some differences in the DCS. It is not known, however, whether differences in the experimental conditions can explain all the dynamical differences observed in the two experiments. In ref 43, the scattering signal at the backward scattering direction for HF ( $\nu' = 2$ ) was also measured in the collision energy range between 0.2 and 1.2 kcal/mol. Figure 6 shows the summed signal of HF ( $\nu' = 2$ ,  $j' = 0-3$ ) as a function of collision energy, with a peak around 0.39 kcal/mol. The peak is obviously related to the resonance in the reaction. In addition, a peculiar trimodal rotational distribution of the HF ( $\nu' = 2$ ) product from the F + HD reaction has been observed.

Quantum dynamical calculations on both the XXZ-PES and the FXZ-PES for the F + HD → HF + D reaction have also been performed in order to explain the experimental results. The predicted peak for the backward scattered HF ( $\nu' = 2$ ,  $j' = 0$  to 3) product obtained on the XXZ-PES falls at an incorrect collision energy as shown in Figure 6, suggesting that the resonance state on the XXZ-PES is also too high for the F + HD reaction. Because of this problem, the calculated DCSs on the XXZ-PES do not agree with the experimental results when they are compared at the same collision energy. In contrast, the predicted peak on the FXZ-PES is clearly in better agreement with the experimental data than the XXZ-PES as shown

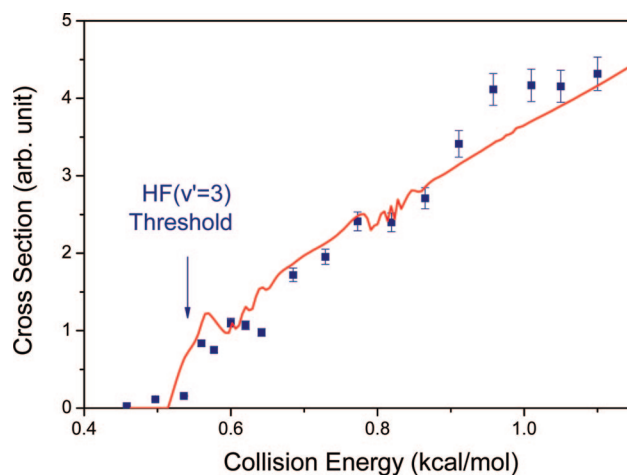


**FIGURE 7.** The one-dimensional adiabatic resonance potentials of HF ( $\nu' = 3$ )-D for the F + HD reaction traced out from the XXZ-PES and the FXZ-PES.

in Figure 6. More remarkably, the theoretical results obtained on the FXZ-PES can reproduce very well the dramatic variations in experimental DCS shown in Figure 5, as well as the observed intriguing trimodal structures in the HF ( $\nu' = 2$ ) rotational distribution.<sup>43</sup>

Theoretical analysis reveals that the fascinating experimental observations at low collision energy for the F + HD reaction are due exclusively to the ground resonance state trapped in the HF ( $\nu' = 3$ )-D adiabatic well. The well depth on the FXZ-PES is deeper by about 0.3 kcal/mol than that on the XXZ-PES; consequently the ground resonance on the FXZ-PES is lower in energy by 0.16 kcal/mol for the F + HD reaction as shown Figure 7, resulting in a better agreement between experiment and theory. The good agreement between the experimental results and dynamical calculations on the FXZ-PES for both the F + H<sub>2</sub> and F + HD reactions strongly suggests that the FXZ-PES is more accurate in describing the dynamical resonances in the reactions. It is also interesting to note that isotope substitution appears to be an extremely sensitive probe of the resonance potential in the reactions as it is often used to probe the molecular potentials in spectroscopic studies.

It appears that the FXZ-PES (CCSD(T)) in this case is clearly better to describe the resonances in the F + H<sub>2</sub> reaction than the XXZ-PES (MRCI). MRCI is generally better than CCSD(T) in electronic energy calculations when there are excited electronic states nearby. However, the resonance region in the F + H<sub>2</sub> reaction is located in the postbarrier zone where the electronic excited states are far above the ground electronic state. Therefore, it is reasonable to argue that the single-reference CCSD(T) method be more accurate than the MRCI method for calculating the part of potential important to the resonance states in the reactions. The results presented above clearly support such argument.



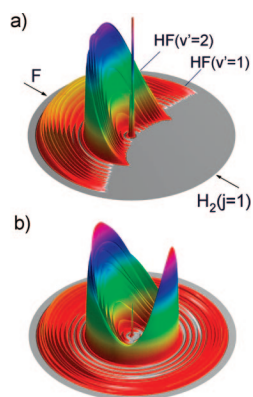
**FIGURE 8.** The total excitation function for the HF ( $\nu' = 3$ ) channel from the F (<sup>2</sup>P<sub>3/2</sub>) + H<sub>2</sub> ( $j = 0$ ) reaction. The squares are the experimental data, and the error bars are the measurement errors. The solid line is the theoretical excitation function using the full quantum dynamics calculations based on the FXZ-PES.

#### 4. The HF ( $\nu' = 3$ ) Forward Scattering

In order to determine the exact threshold of the HF ( $\nu' = 3$ ) channel, the excitation function of the HF ( $\nu' = 3$ ) channel was determined between 0.40 and 1.2 kcal/mol as shown in Figure 8.<sup>46</sup> The HF ( $\nu' = 3$ ) signal appears right at the threshold of this reaction channel around 0.52 kcal/mol, suggesting that the HF ( $\nu' = 3$ ) channel has little or no exit barrier.

DCSs in the center-of-mass frame (CM) have also been measured from 0.4 to 1.2 kcal/mol for the HF ( $\nu' = 3$ ) channel with pronounced forward scattering product observed. This is consistent with the experimental observation at higher collision energies by Neumark et al.<sup>23</sup> In order to trace the dynamical origin of the HF ( $\nu' = 3$ ) forward scattering, quantum dynamics calculations for the HF ( $\nu' = 3$ ) channel were also performed on the accurate FXZ-PES. The calculated excitation function for the HF ( $\nu' = 3$ ) channel in the F + H<sub>2</sub> reaction is in good agreement with the experimental results as shown in Figure 8. The calculated DCS at collision energy of 0.94 kcal/mol for the HF ( $\nu' = 3$ ) channel also agrees with the experimental result,<sup>46</sup> providing a solid foundation for theoretical interpretation of the interesting dynamics of the forward scattering peak for the HF ( $\nu' = 3$ ) product.

As pointed out above, there are two resonance states trapped in the HF ( $\nu' = 3$ )-H' VAP for the total angular momentum  $J = 0$  (see Figure 3) for the F + H<sub>2</sub> ( $j = 0$ ) reaction. The formation of the HF ( $\nu' = 1, 2$ ) products at low collision energy occurs via the Feshbach resonance mechanism, as has been pointed out above. For the HF ( $\nu' = 3$ ) channel, the resonance states cannot play any role since the energy of this channel is simply above the two resonance states for small  $J$  numbers. For  $J$  larger than 6, the ground



**FIGURE 9.** The experimental three-dimensional (3D) contour plots for the HF product from the F ( $^2P_{3/2}$ ) + H<sub>2</sub> ( $j = 1$ ) reaction at the collision energies of (a) 0.56 and (b) 0.19 kcal/mol.

resonance state trapped in the well of the HF ( $\nu' = 3$ )–H VAP actually forms the HF ( $\nu' = 3$ ) product via tunneling through the centrifugal barrier in the exit region. This is a clear case of shape resonance.<sup>47</sup> For  $J$  larger than 10, no resonance can be supported any longer on the effective potential with the centrifugal term. However, time delay in the formation of HF ( $\nu' = 3$ ) can still happen due to slow-down over the exit barrier,<sup>46</sup> similar to the time-delay mechanism in the H + HD reaction.<sup>20</sup> This type of time-delay mechanism in the reaction intermediate can also cause forward scattering as the shape resonance mechanism for the HF ( $\nu' = 3$ ) channel. Based on these analyses, the forward scattering of HF ( $\nu' = 3$ ) observed at higher collision energies by Lee et al.<sup>23–25</sup> is likely caused by the slow-down mechanism over the centrifugal barrier in the exit channel, not by the transiently trapped reaction resonances.

## 5. Effect of H<sub>2</sub> Rotational Excitation on Resonances in F + H<sub>2</sub>

Ren et al. have also investigated the effect of a single quantum rotational excitation of H<sub>2</sub> on the dynamics of the F + H<sub>2</sub> reaction in the low collision energy region.<sup>48</sup> The experimental technique used in this work is similar to the above experiments. In this work, two different H<sub>2</sub> samples were used in the experiment: a normal H<sub>2</sub> sample and a pure para-H<sub>2</sub> sample.<sup>49,50</sup> Since the H<sub>2</sub> beam is produced by expanding the H<sub>2</sub> sample via a cooled nozzle at the liquid nitrogen temperature, the H<sub>2</sub> molecules in the beam are only populating the lowest rotational states:  $j = 0$  (100%) for  $p$ -H<sub>2</sub>,  $j = 0$  (25%) and  $j = 1$  (75%) for  $n$ -H<sub>2</sub>. By measuring the relative H atom TOF signals for the F atom reactions with  $p$ -H<sub>2</sub> and  $n$ -H<sub>2</sub>, the relative TOF signals can be determined for both the F + H<sub>2</sub> ( $j = 0$ ) and F + H<sub>2</sub> ( $j = 1$ ) reactions.

Figure 9 shows the experimental three-dimensional (3D) contour plots for the HF product from the F + H<sub>2</sub> ( $j = 1$ ) reac-

tion at the collision energies of 0.56 and 0.19 kcal/mol. At the collision energy of 0.56 kcal/mol, the F + H<sub>2</sub> ( $j = 1$ ) reaction shows no forward scattering signal for  $\nu' = 2$  HF product, in contrast to the F + H<sub>2</sub> ( $j = 0$ ) reaction at the same energy. However, a large HF ( $\nu' = 2$ ) forward scattering peak was observed for the F + H<sub>2</sub> ( $j = 1$ ) reaction at 0.19 kcal/mol. In order to see how the forward scattering signal changes with the collision energy in the F + H<sub>2</sub> ( $j = 1$ ) reaction, collision energy dependent forward scattering signal of the HF ( $\nu' = 2$ ) product has also been measured, a peak around 0.16–0.18 kcal/mol was observed in the excitation function.<sup>46</sup> This result is somewhat similar to that of F + H<sub>2</sub> ( $j = 0$ ),<sup>33</sup> except the peak was shifted to lower energy by about 0.35 kcal/mol, which is roughly equal to the rotational energy of the H<sub>2</sub>  $j = 1$  level.

Full quantum scattering calculations<sup>48</sup> suggest that the F + H<sub>2</sub> ( $j = 1$ ) reaction at 0.56 kcal/mol proceeds predominantly via the continuum tunneling reaction mechanism, without any contribution from the two reaction resonances. Therefore, very little product of HF ( $\nu' = 2$ ) was seen at the forward direction for this reaction at this collision energy. For the F + H<sub>2</sub> ( $j = 1$ ) reaction at 0.19 kcal/mol, theoretical calculations also show strong forward scattering for the HF ( $\nu' = 2$ ) product, which is also attributed to the two reaction resonances in F + H<sub>2</sub>. Theoretical calculations also exhibit a peak around 0.17 kcal/mol in the collision energy dependent forward scattering signal of the HF ( $\nu' = 2$ ) product from the F + H<sub>2</sub> ( $j = 1$ ) reaction, in agreement with the experimental data. These results indicate that the resonance energy for the F + H<sub>2</sub> ( $j = 1$ ) reaction shifted to 0.17 kcal/mol from 0.52 kcal/mol for the F + H<sub>2</sub> ( $j = 0$ ) reaction due to the additional reagent (H<sub>2</sub>) rotational energy of 0.34 kcal/mol in the reaction.

## 6. Concluding Remarks

The F + H<sub>2</sub> and F + HD reactions have been studied using the high-resolution H-atom Rydberg tagging TOF technique in a crossed molecular beam setup under a single collision condition, in combination with full quantum dynamics calculations based on highly accurate potential energy surfaces. An explicit picture of reaction resonances has emerged for the F + H<sub>2</sub> reaction, in which two Feshbach resonances are important in this reaction at the low collision energies. More interestingly, the two Feshbach resonances interfere with each other. Through the studies of the isotope substituted F + HD → HF + D reaction, the resonance potential was probed with nearly spectroscopic accuracy. It appears that the FXZ potential energy surface obtained recently based on the CCSD(T)

method provides the most accurate account of the dynamical resonances in both the F + H<sub>2</sub> ( $j = 0$ ) and F + HD ( $j = 0$ ) reactions. The forward scattering HF ( $\nu' = 3$ ) phenomenon was observed and attributed largely to a slow-down mechanism over the exit barrier in the F + H<sub>2</sub> reaction. The shape resonance mechanism only plays a minor role in a narrow range of collision energy. The effect of the H<sub>2</sub> reagent rotational excitation on the reaction resonances in the F + H<sub>2</sub> reactions has also been investigated. Both experimental and theoretical results show that reagent rotational excitation has a profound effect on the dynamics of the resonance-mediated reaction. Through the detailed investigations, an accurate physical picture of reaction resonances in this benchmark reaction has been established, providing an excellent case of dynamical resonances in elementary chemical reactions.

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