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Effect of Reagent Rotational Excitation on Dynamics of $F+H_2 \rightarrow HF+H^\dagger$

Tian-gang Yang^{a,b}, Long Huang^b, Yu-run Xie^b, Tao Wang^{b,c,d}, Chun-lei Xiao^b, Zhi-gang Sun^{b,c*}, Dong-xu Dai^b, Mao-du Chen^{a*}, Dong H. Zhang^{b,c}, Xue-ming Yang^{b,c*}

a. Key Laboratory of Materials Modification by Laser, Electron, and Ion Beams (Ministry of Education), School of Physics and Optoelectronic Technology, Dalian University of Technology, Dalian 116024, China

b. State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116023, China

c. Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei 230026, China

d. Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

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The dynamics of the $F+H_2(v=0, j=0, 1)$ reactions have been studied at the collision energy of 1.27 kcal/mol using a high-resolution crossed molecular beam apparatus. HF product rotational state resolved differential cross sections have been obtained at the $v'=1, 2, 3$ levels. The product HF($v'=2$) angular distributions are predominantly backward scattered for both $H_2(j=0, 1)$ reagents. However, the distributions of product HF($v'=2$) rotational states for the $F+H_2(v=0, j=0)$ reaction are significantly different from those for the $F+H_2(v=0, j=1)$ reaction. Experimental results show that the rotational excitation of H_2 produces rotationally 'hotter' HF($v'=2$) product. In addition, the HF($v'=3$) product is more likely scattered into the forward direction when the H_2 reagent is populated at $j=0$ state, which could be attributed to a slow-down mechanism.

Key words: Crossed molecular beam, Rydberg tagging, Differential cross sections

I. INTRODUCTION

The $F+H_2 \rightarrow HF+H$ reaction is a benchmark system in the field of reaction dynamics that has been extensively studied over the past decades [1]. It is one of the simplest reactions which involve resonance and attract much attention from both theoreticians and experimentalists. In 1970s, Schatz and Wu predicted the reaction resonances in the $F+H_2$ system for the first time with a two-dimensional numerical model [2, 3]. In 1984, Lee and co-workers carried out a landmark experiment on the $F+H_2$ reaction using a universal crossed molecular beam apparatus [4, 5]. They observed a forward scattered HF($v'=3$) product, which was interpreted as a result of reaction resonances. However, full quantum mechanical (QM) [6] and quasi-classical trajectory (QCT) [7] calculations carried out on the Stark-Werner potential energy surfaces (SW-PES) [8] disagreed with the conjecture of dynamics resonances causing the HF($v'=3$) forward scattering signal. In 2000, a step in the excitation function around

0.5 kcal/mol was observed in the $F+HD \rightarrow HF+D$ reaction which was attributed to a Feshbach resonance in this reaction [9]. The undisputed evidence of reaction resonances in the $F+H_2$ system remained elusive until 2006 when Qiu and co-workers observed an enhanced forward scattering peak of HF($v'=2$) at the collision energy of 0.52 kcal/mol, which was attributed to quantum interference between two Feshbach resonance states by accurate quantum dynamics calculation on a newly developed PES [10]. Further study indicated that the forward peak of HF($v'=3$) in the $F+H_2$ reaction at higher collision energy was due to slow-down mechanism instead of resonances [11].

The influence of reagent rotation on the chemical reactions has also been one of the most concerned issues in the $F+H_2$ reaction [12]. The $F+H_2$ reaction has attracted much interest in the field of chemical laser [13] due to the significant inverted vibrational distribution towards the $v'=2, 3$ states in the HF product [11]. The effect of excitation of the reagent rotation on the final state distributions was investigated using infrared chemiluminescence [14, 15]. These investigations concluded that para- H_2 (p - H_2) produced more vibrational excitation of HF product than normal- H_2 . Similarly, the crossed molecular beam experiment carried out by Lee and co-workers found a decrease in the scattering signal intensity of product HF($v'=1$ and $v'=2$) and an

[†]Dedicated to Professor Qing-shi Zhu on the occasion of his 70th birthday.

*Authors to whom correspondence should be addressed. E-mail: zsun@dicp.ac.cn, mdchen@dlut.edu.cn, xmyang@dicp.ac.cn

increase in the forward product HF($v'=3$) of F+*p*-H₂ at the collision energy of 1.84 kcal/mol [4]. Although the previous crossed beam experiment supplied a large number of details of the title reaction, the rotational state resolved DCSs have not been reported yet.

Using a Rydberg tagging machine, high resolution experiment was carried out to study the dynamics of the D+H₂($v=0, j=0, 1$)→HD+D, which discovered that the H₂ rotation had a great influence on the reaction dynamics due to the selection of quantum bottleneck states [16]. The effect of the H₂ reagent rotational excitation on the O(¹D) reaction with H₂ was also investigated by the same method [17]. Most recently, the title reaction was carried out at the collision energies of 0.19 and 0.56 kcal/mol in our laboratory, where the effect of rotational excitation of H₂ reagent on the Feibash resonance was investigated [18]. However, there was no high resolution experiment measurement on the effect of reagent rotation in the F+H₂($j=0, 1$)→HF+H reactions at higher collision energies.

In this work, we carried out crossed molecular beam study on the effect of reagent rotation in the F+H₂($j=0, 1$)→HF+H reactions using high resolution time-of-flight (TOF) H-atom Rydberg tagging technique at the collision energy of 1.27 kcal/mol. Product vibrational state as well as rotational state-resolved DCSs were obtained. Product rotational state distributions of HF($v'=2$) are shown for H₂ samples of both rotational state $j=0$ and 1 in this work.

II. EXPERIMENTS

The crossed beam scattering study on the title reaction has been carried out using the H-atom Rydberg tagging TOF technique [19]. The experimental apparatus in our laboratory has been described in detail previously [20–25], only a brief description is given here.

In the experiment, the H atom product of the reaction F+H₂($j=0, 1$)→HF+H was first excited from $n=1$ to $n=2$ by the 121.6 nm VUV light which was generated by a two-photon resonance ($2\omega_1-\omega_2$) of 212.5 nm light and 845 nm light using four-wave mixing scheme in a Kr/Ar gas cell. Then the H-atom of $n=2$ was sequentially excited to a high Rydberg state by the 365 nm light. The Rydberg H-atoms were prepared in the crossed region then flew about 317 mm to reach the micro channel plate (MCP) Z-stack detectors. Just prior to reaching the MCP, the neutral Rydberg H-atoms were field-ionized. The TOF signal reflects the ro-vibrational character of the HF product via the conservation of energy and momentum, where a greater scattering velocity, shorter flight time, is generally inversely proportional to the internal energy of the species. The 212.5 nm (ω_1) laser light was produced by doubling a 425 nm dye laser (Sirah, PESC-G-24) pumped by a Nd:yttrium-aluminum-garnet (YAG) (355 nm) laser, while ω_2 (845 nm) was the direct output of a dye

laser (Continuum ND6000) pumped by the same YAG (532 nm) laser. The 365 nm laser was also generated by doubling a dye laser (Sirah, PESC-G-24) pumped by the same YAG (532 nm) laser.

III. RESULTS AND DISCUSSION

A. Experimental time-of-flight spectra

The F atom beam was produced by double-stage pulse discharge of F₂ (5% F₂ seeded in 95% He) [26]. About 90% of F atoms were found in their ground state (²P_{3/2}), as previously determined by VUV synchrotron ionization [27]. The H₂ beam was cooled to the liquid nitrogen temperature to populate only the lowest rotational states, providing the opportunity to study the effect of the H₂ rotation on the dynamics of the F+H₂ reaction. Two different H₂ samples were used in the experiment, *p*-H₂ populated only in the $j=0$ state through ferro-magnetic catalyst at low temperature (~ 20 K) and expanding from a liquid nitrogen cooled valve, while normal H₂ is populated in both $j=0$ and $j=1$ with a ratio of 1:3. TOF spectra at eleven laboratory (LAB) scattering angles from 120° to -30° were measured for both H₂ sample with exactly the same experiment conditions. These spectra were measured back and forth 16 times to reduce the systematic errors in the experiment. The TOF spectra of H₂ at $j=0$ and $j=1$ can then be constructed by subtracting TOFS with the two H₂ sample using the following equations:

$$\text{TOFS}(p\text{-H}_2) = \text{TOFS}(j = 0) \quad (1)$$

$$\text{TOFS}(n\text{-H}_2) = \frac{3}{4}\text{TOFS}(j = 1) + \frac{1}{4}\text{TOFS}(j = 0) \quad (2)$$

$$\text{TOFS}(j = 0) = \text{TOFS}(p\text{-H}_2) \quad (3)$$

$$\text{TOFS}(j = 1) = \frac{4}{3} \left[\text{TOFS}(n\text{-H}_2) - \frac{1}{4}\text{TOFS}(p\text{-H}_2) \right] \quad (4)$$

Figure 1 shows the TOF spectra of the H atom product from the F(²P_{3/2})+H₂($j=0, 1$)→HF+H reaction at the collision energy of 1.27 kcal/mol. The three laboratory angles correspond roughly to the HF($v'=2$) product at the backward, sideways, and HF($v'=3$) product at the forward scattering directions, relative to the F atom beam direction in the center of mass (CM) frame. It is clear that the distributions of product HF($v'=2$) rotational states are much hotter in the F(²P_{3/2})+H₂($j=1$)→HF+H reaction than the F(²P_{3/2})+H₂($j=0$)→HF+H reaction at the backward direction in Fig.1(a). The product of HF($v'=3$) is also shown in Fig.1(b) for both H₂ samples in the sideways direction. The H₂($j=1$) reagents produce less HF($v'=3$) populations and more HF($v'=2$) populations. For the forward scattering direction in Fig.1(c), the product HF($v'=3$) has much less intensity for H₂ ($j=1$) reagents. Little HF($v'=1, 2$) signal was displayed for both H₂

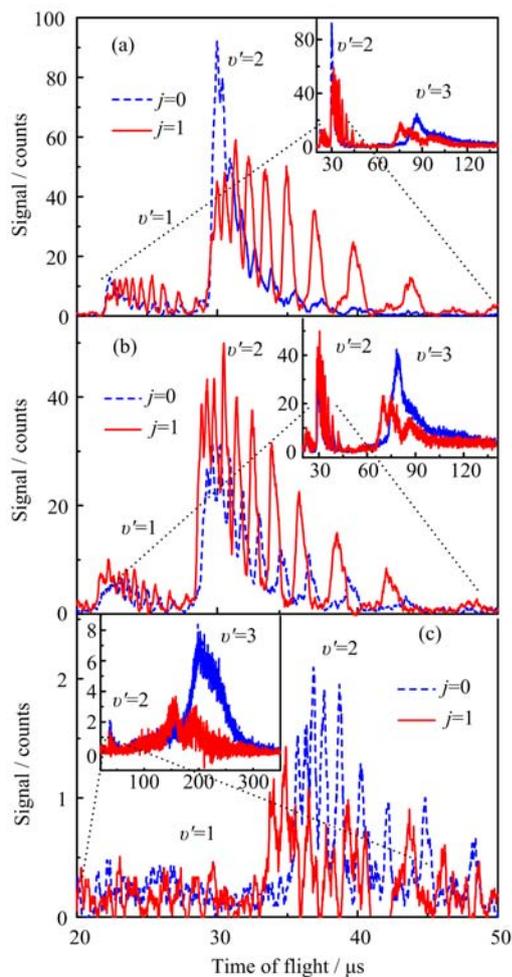


FIG. 1 TOF spectra of the H atom product from the $F(^2P_{3/2})+H_2(v=0, j=0, 1) \rightarrow HF+H$ reaction at the collision energy of 1.27 kcal/mol at the different laboratory angles: (a) $\theta_L=120^\circ$, (b) $\theta_L=50^\circ$, (c) $\theta_L=-10^\circ$. The three laboratory angles correspond roughly to the $HF(v'=2)$ product at the backward, sideways, and $HF(v'=3)$ product at the forward scattering directions in the CM frame respectively.

samples at this direction, which is quite different from the previous study of this reaction at the collision energy around 0.52 kcal/mol [10, 18].

B. State-resolved differential cross sections

TOF spectra were measured at eleven laboratory scattering angles from 120° to -30° which covered from 180° to 0° in the CM frame. All the TOF spectra were converted to the CM frame with a standard Jacobian transformation to obtain product kinetic energy distributions. Then the product kinetic energy distributions were fitted using a computer simulation program by adjusting the relative populations of the ro-vibrational state of the HF product. From these simulations, relative population distributions of the HF product at

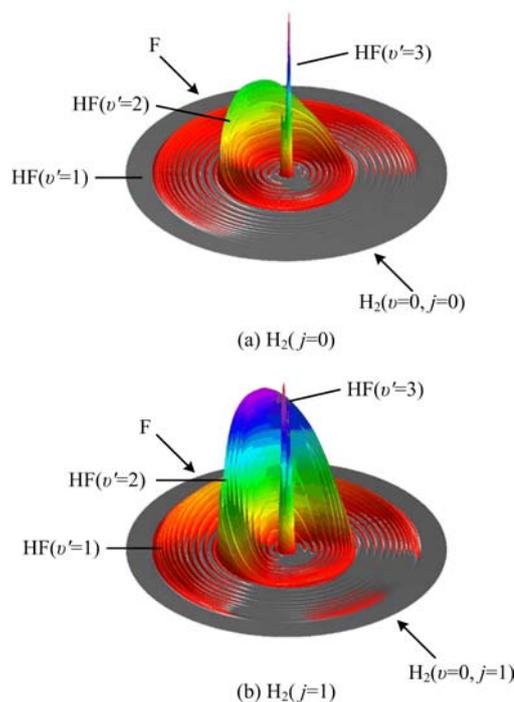


FIG. 2 The experimental three-dimensional DCS contour plots for the $F+H_2(j=0, 1)$ reactions at the collision energy of 1.27 kcal/mol.

each ro-vibrational state were determined in the LAB frame. With the conversion of these distributions from the LAB frame to the CM frame, full ro-vibrational state resolved differential cross sections (DCSs) were obtained. Figure 2 shows the experimental three-dimensional DCSs contour plots for the $F+H_2(j=0, 1)$ reactions at the collision energy of 1.27 kcal/mol. The DCS maps show the $HF(v'=2)$ product are scattered predominantly in the backward hemisphere. Little signal of the $HF(v'=2)$ product are observed in the forward direction. This is because that the collision energy is far away from Feshbach resonances (~ 0.52 kcal/mol) that produce the forward $HF(v'=2)$ product [10]. However, the $HF(v'=3)$ product are scattered mostly into the forward direction, which is likely due to the slow-down mechanism as the reaction intermediate passed over the exit centrifugal barrier [11]. According to previous studies, it is reasonable to conclude that there is no reaction resonance at this collision energy.

Comparing Fig.2 (a) with (b), it is clear that the relative ratio of $v'=3$ at the forward direction decreases with the H_2 reagent rotational excitation. And there are significant differences at the backward direction of the $HF(v'=2)$ product for the F reactions with $H_2(j=0)$ and $H_2(j=1)$. Actually, the seeming difference between the reaction of F with $H_2(j=1)$ and $H_2(j=0)$ comes from the total energy difference with the same translational energy. With a shifting of a translational energy of the rotational energy difference $H_2(j=1)-H_2(j=0)$, the reactions of these two rotational reactants are essentially

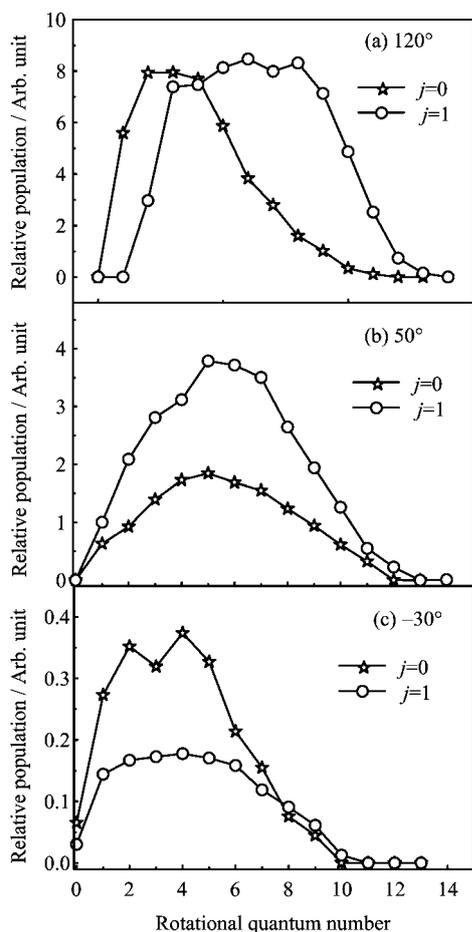


FIG. 3 Comparisons of the rotational state distributions obtained from the $F+H_2$ at the $j=0$ and $j=1$ levels at the backward, sideways, and forward scattering angles in the CM frame relative to the $HF(v'=2)$ product. (a) 120° , (b) 50° , and (c) -30° .

the same. More rotational states of $HF(v'=2)$ are observed at the backward scattering for the $H_2(j=1)$ reaction, as suggested by Fig.2(b). This is due to the higher total energy of the reagents of the reaction with $H_2(j=1)$, which is about 0.34 kcal/mol higher than that with $H_2(j=0)$. We note that the $HF(v'=1)$ product is only observed in the backward direction, and the signal of this state is much smaller than that of the other states.

C. Product vibrational and rotational state distributions

In order to understand the reaction in more detail, the product $HF(v'=2)$ rotational state distributions from the $F+H_2(j=0, 1)$ reaction are shown in Fig.3. From the state distributions obtained, it is clear that one quantum rotational excitation in the H_2 reagent has a significant effect on the $HF(v'=2)$ product, especially in the backward direction. The excitation of

the H_2 rotational state produces higher rotationally excited $HF(v'=2)$ product, due to more available energy to deposit in the product. For the sideways scattering, the rotational state distributions of $HF(v'=2)$ are similar from $j'=0$ to $j'=12$, except that the integral cross section these rotational states produced by the H_2 diatomic reagent at $j=1$ is two times larger than those with H_2 at $j=0$. Similarly, the H_2 molecule at $j=0$ reacts with F atom with more product in the forward direction, due to the lower available energy that is closer to the resonance states.

IV. CONCLUSION

In this work, we have carried out a high resolution crossed molecular beam study on the $F+H_2(j=0, 1)\rightarrow HF+H$ reactions using H-atom Rydberg tagging technique. Full quantum state resolved DCSs were obtained at the collision energy of 1.27 kcal/mol. The DCSs show a predominantly backward scattering peak for the product $HF(v'=1, 2)$, which are consistent with the previous study that the Feshbach forward resonances peak appeared at around the collision energy of 0.52 kcal/mol. The distribution of product $HF(v'=2)$ rotational states becomes much hotter when the H_2 reagent is rotationally excited. The $HF(v'=3)$ product is more likely scattered into the forward directions with $H_2(j=0)$ reagent, which is likely due to a slow-down mechanism. From the experimental work, it is suggested that there is no clear signature of reaction resonances at collision energy of 1.27 kcal/mol in the $F+H_2$ reaction, and single quantum H_2 -rotation does have a large dynamical effect on the chemical reactions, due to large energy for the rotational excitation of H_2 reagent.

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