

Full Quantum State Resolved Scattering Dynamics of the $F+H_2 \rightarrow HF+H$ Reaction at 5.02 kJ/mol

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A crossed molecular beams, state-to-state scattering study was carried out on the $F+H_2 \rightarrow HF+H$ reaction at the collision energy of 5.02 kJ/mol, using the highly sensitive H atom Rydberg tagging time-of-flight method. All the peaks in the TOF spectra can be clearly assigned to the ro-vibrational structures of the HF product. The forward scattering of the HF product at $v'=3$ has been observed. The small forward scattering of the HF product at $v'=2$ has also been detected. Detailed theoretical analysis is required in order to fully understand the dynamical origin of these forward scattering products at this high collision energy.

Key words: Crossed molecular beams, Reactive scattering, State-to-state dynamics, Reaction resonance

The topic of reaction resonance in chemical reactions has attracted the attention from generations of chemical physicists over the last 30 years [1,2]. Reaction resonances are widely present in many chemical reactions, especially in reactions that the transition state is a deep well. However, due to the high density of resonances in these systems, it is normally difficult to investigate the detailed characteristics of the resonances for these systems both experimentally and theoretically. For direct chemical reactions, however, resonances are rare. Therefore, the resonances in direct reactions are isolated, thus easier to detect if they are not smeared by the direct reaction process. The most well known examples for reaction resonances for direct chemical reactions is the $F+H_2 \rightarrow HF+H$ reaction, which is also the pumping process for driving the powerful HF chemical laser. Theoretical predictions of a reaction resonance in the $F+H_2$ reaction were first made in 1970s [3,4]. Since then, great attentions have been given to this system both experimentally and theoretically [5-12] in an effort to elucidate the dynamical resonances in this reaction. However, a definitive detection of reaction resonances in the $F+H_2$ reaction in a scattering experiment remains elusive.

Very recently, we have investigated the $F+H_2(j=0)$ reaction in a high resolution molecular beam reactive scattering study [13]. A pronounced forward scattering peak at the collision energy of 2.17 kJ/mol for the $HF(v'=2)$ product was clearly observed. Full quantum scattering calculations based on a newly constructed, highly accurate PES attributed this pronounced for-

ward scattering peak to the effect of both the ground and the excited Feshbach resonance states, (003) and (103), correspondingly, that are quasi-trapped in the $HF(v'=3)-H'$ vibrational adiabatic potential (VAP) well. Theoretical analysis also shows that there is a constructive interference between the two dynamical resonances for the forward scattering at the collision energy of 2.17 kJ/mol.

In this work, we report a detailed study of the title reaction at the collision energy of 5.02 kJ/mol, which is significantly above the resonance energy region. A full quantum state resolved crossed beam scattering study on the $F+H_2$ reaction was carried out using the high resolution and highly sensitive H-atom Rydberg tagging method [14]. The experimental apparatus, designed for this experiment, has been described in Ref.[15]. Briefly, the H atom product is detected through a two-step excitation scheme to a highly excited Rydberg state. The 121.6 nm vacuum ultraviolet (VUV) light used in the first step excitation is generated using a two-photon resonant ($2\omega_1-\omega_2$) four wave mixing scheme in a Kr/Ar gas cell. After the first step VUV excitation, the H atom product is then sequentially excited to a high Rydberg state with $n \approx 50$ with 365 nm light. The neutral Rydberg H atom then flies a certain distance for the TOF measurement and reaches a rotatable microchannel plate (MCP) detector. The signal received by the MCP is then amplified by a fast pre-amplifier, and counted by a multichannel scaler. Two supersonic beams (F and H_2) were used in this experiment. The p- H_2 beam was generated by expanding the H_2 sample through a pulsed nozzle, which was cooled to liquid nitrogen temperature (~ 78 K). This cooling ensured that nearly all the p- H_2 molecules were in the $j=0$ state [16]. The velocity of the H_2 beam was determined to be 1385 m/s with a speed ratio ($v/\Delta v$) of about 28. The

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F-atom beam, which is rotatable around the crossing region, was generated using pulsed discharge beam expansion. A double stage pulsed discharge beam source was developed in an effort to increase the F atom beam intensity [17], which uses two discharge regions: a preionization region and a main discharge region. A separate preionization region was added in an effort to increase the efficiency of the main discharge for the flowing gas mixture (5% F₂ seeded in He at 798 kPa.). The addition of the preionization stage discharge not only stabilizes the main discharge, but also enhances the main discharge current significantly. With this arrangement, the F atom beam intensity was increased by at least an order of magnitude in comparison with a single stage discharge F-atom source with similar main discharge conditions. This remarkable increase of the F atom beam intensity makes the current experiment significantly easier. In the pulsed detection window, the F atom velocity spread is quite narrow ($v/\Delta v \approx 10$), which makes extremely high resolution studies of this benchmark system possible. Because the F* atom in the first electronic excited state $^2P_{1/2}$ is about 400 cm⁻¹ higher in energy than the ground state F($^2P_{3/2}$), the resolution (about 1% in energy, or roughly 20 cm⁻¹ at $E_t=2000$ cm⁻¹) in this work can easily distinguish the F($^2P_{3/2}$) and F*($^2P_{1/2}$) reactions. All the main signals observed and analyzed here were attributed to the ground state F atom reaction.

Time-of-flight (TOF) spectra of the H atom products from the F+H₂ reaction were measured at many laboratory (LAB) angles at 10° intervals, with the collision energy fixed at 5.02 kJ/mol (Fig.1). The main structures in these TOF spectra can be clearly assigned to the HF product ro-vibrational states from the ground state F($^2P_{3/2}$) reaction with H₂($j=0$). The spectra were then converted to the center-of-mass (CM) frame using a standard Jacobian transformation to obtain the product kinetic energy (KE) distributions. In this conversion, detection efficiencies of the H atom product at different LAB angles and different velocities were simulated and included. The KE distributions obtained experimentally in the LAB frame were fitted by simply adjusting the relative populations of the ro-vibrational states of the HF product. From these fittings, relative population distributions of the HF product at each ro-vibrational state were determined at 16 LAB angles at the collision energy of 5.02 kJ/mol. Quantum-state distributions of HF product in the CM frame ($\Theta_{CM}=0^\circ$ to 180°) were then determined by a polynomial fit to the above results, and from these distributions, full ro-vibrational state resolved differential cross section (DCS) values were determined (Fig.2).

At this collision energy, all HF($v'=1,2,3$) products were observed. Clearly, HF($v'=1,2$) products are dominantly backward scattered, while the HF($v'=3$) is primarily forward scattered. In addition, there is also some forward scattering for HF($v'=1,2$), about 10% of

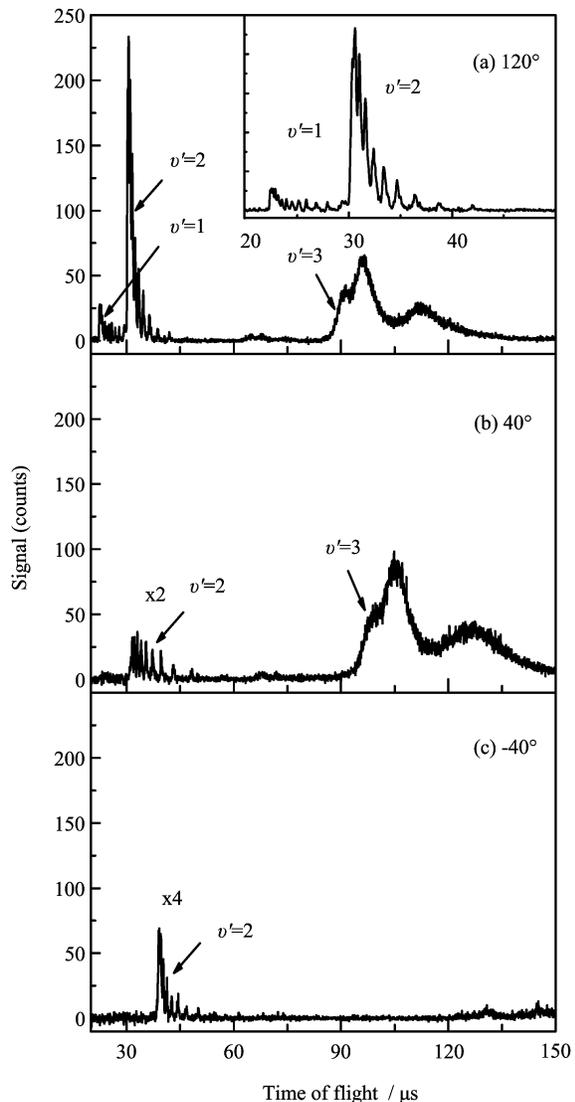


FIG. 1 TOF spectra of the H atom product from the F($^2P_{3/2}$)+H₂($j=0$) reaction at the collision energy of 5.02 kJ/mol. TOF spectra at three laboratory angles are shown, (a) $\Theta_L=120^\circ$, (b) $\Theta_L=40^\circ$ and (c) $\Theta_L=-40^\circ$, which correspond roughly to the forward, sideways, and backward scattering directions for the HF($v'=2$) product in the center-of-mass frame, respectively. Only HF($v'=1,2,3$) products are observed here. The insert in (a) $\Theta_L=120^\circ$ also shows the formation of HF($v'=1,2$).

the backward signal. This is quite interesting because 5.02 kJ/mol should be considerably above the dynamics resonance region already. Therefore, it is unlikely that the forward scattering HF($v'=1,2$) products are from the resonance mediated mechanism. Another interesting issue is the dynamics of the forward scattering HF($v'=3$) product, which remains to be unresolved in this benchmark system. Clearly, more theoretical dynamics studies are needed in order to understand the intriguing dynamical phenomena

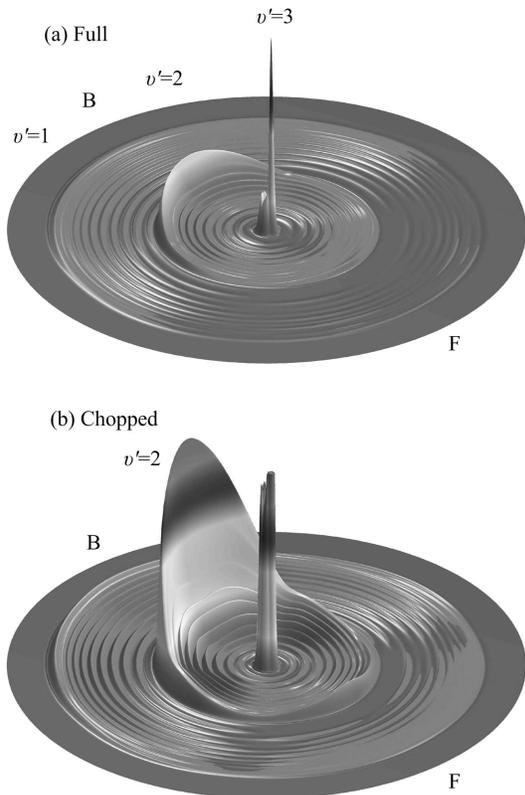


FIG. 2 The experimental overall (a) and chopped (b) three dimensional (3D) contour plots for the product translational energy and angle distributions for the $F(^2P_{3/2})+H_2(j=0)$ reaction at the collision energy of 5.02 kJ/mol. The different circles represent different HF product ro-vibrational states. The forward scattering direction for HF is defined along the F atom beam direction.

observed in this experiment.

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- [1] K. Liu, *Annu. Rev. Phys. Chem.* **52**, 139 (2001).
- [2] F. Fernandez-Alonso and R. N Zare, *Annu. Rev. Phys. Chem.* **53**, 67 (2002).
- [3] G. C. Schatz, J. M. Bowman and A. Kuppermann, *J. Chem. Phys.* **58**, 4023 (1973).
- [4] S. F. Wu, B. R. Johnson and R. D. Levine, *Mol. Phys.* **25**, 839 (1973).
- [5] D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden and Y. T. Lee, *Phys. Rev. Lett.* **53**, 226 (1984).
- [6] D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden and Y. T. Lee, *J. Chem. Phys.* **82**, 3045 (1985).
- [7] F. J. Aoiz, L. Banares, V. J. Herrero, V. Sagz Rabanos, K. Stark and H. J. Werner, *Chem. Phys.* **223**, 215 (1994).
- [8] J. F. Castillo, D. E. Manolopoulos, K. Stark and H. J. Werner, *J. Chem. Phys.* **104**, 6531 (1996).
- [9] K. Stark and H. J. Werner, *J. Chem. Phys.* **104**, 6515 (1996).
- [10] R. T. Skodje, D. Skouteris, D. E. Manolopoulos, S. H. Lee, F. Dong and K. Liu, *Phys. Rev. Lett.* **85**, 1206 (2000).
- [11] D. M. Manolopoulos, K. Stark, H. J. Werner, D. W. Arnold, S. E. Bradforth and D. M. Neumark, *Science* **262**, 1852 (1993).
- [12] L. Y. Rusin, M. B. Sevryuk and J. P. Toennies, *J. Chem. Phys.* **122**, 134314 (2005).
- [13] M. Qiu, Z. Ren, L. Che, D. Dai, S. Harich, X. Wang and X. Yang, C. Xu, D. Qian, M. Gustafsson, R. T. Skodje, Z. Sun and D. H. Zhang, *Science* **311**, 1440 (2006).
- [14] L. Schnieder, K. Seekamp-Rahn, E. Wrede and K. H. Welge, *J. Chem. Phys.* **107**, 6175 (1997).
- [15] M. Qiu, L. Che, Z. Ren, D. Dai, X. Wang and X. Yang, *Rev. Sci. Instrum.* **76**, 083107 (2005).
- [16] L. Schnieder, K. Seekamp-Rahn, E. Wrede and K. H. Welge, *J. Chem. Phys.* **107**, 6175 (1997).
- [17] Z. Ren, M. Qiu, L. Che, D. Dai, X. Wang and X. Yang, *Rev. Sci. Instrum.* **77**, 016102 (2006).