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Crossed Beam Study on the F+D₂→DF+D Reaction at Hyperthermal Collision Energy of 23.84 kJ/mol†

Hei-long Wang⁠a,b, Shu Su⁠b, Sheng-rui Yu⁠c, Li Che⁠a,d*, Guo-rong Wu⁠b, Kai-jun Yuan⁠b*, Xue-ming Yang⁠b, Timothy K. Minton⁠e

a. College of Environmental Sciences and Engineering, Dalian Maritime University, Dalian 116026, China
b. State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Dalian 116023, China
c. Hangzhou Institute of Advanced Studies, Zhejiang Normal University, Hangzhou 311231, China
d. College of Science, Dalian Maritime University, Dalian 116026, China
e. Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717, USA

(Dated: Received on January 10, 2019; Accepted on January 21, 2019)

We presented an experimental apparatus combining the H-atom Rydberg tagging time-of-flight technique and the laser detonation source for studying crossed beam reactions at hyperthermal collision energies. The preliminary study of the F+D₂→DF+D reaction at hyperthermal collision energy of 23.84 kJ/mol was performed. Two beam sources were used in this study: one is the hyperthermal F beam source produced by a laser detonation process, and the other is D₂ beam source generated by liquid-N² cooled pulsed valve. Vibrational state-resolved differential cross sections (DCSs) of product for the title reaction were determined. From the product vibrational state-resolved DCS, it can be concluded that products DF(ν′=0, 1, 2, 3) are predominantly distributed in the sideway and backward scattering directions at this collision energy. However, the highest vibrational excited product DF(ν′=4), is clearly peaked in the forward direction. The probable dynamical origins for these forward scattering products were analyzed and discussed.

Key words: Crossed molecular beam, Hyperthermal collision energy, Rydberg tagging, laser detonation

I. INTRODUCTION

Due to the important application to chemical lasers, the reactions of F with H₂ and its isotopomers have played a central role in the reaction dynamics, and have been studied extensively [1–10]. With the development of high resolution experimental detection technology and accurate theoretical calculation methods, some vitally and fundamentally dynamical phenomena for this reaction system have been explored and explained, such as dynamical resonances in the F+H₂/HD reactions. The forward scattered HF(ν′=3) product was first observed by Neumark et al. in 1984 [1]. Due to less accurate theoretical calculation results, the assignment of such forward scattered products to the dynamical resonances was questionable. Recently, with the implementation of the high resolution experiment of F+H₂ at low collision energy of 0.52 kcal/mol by Qiu et al. in 2006, dynamical resonance phenomena in the F+H₂ reaction system were illustrated thoroughly [11]. Products HF(ν′=2) were evidently observed in the forward scattering direction. The Feshbach resonances from the ground and the first excited states, which were trapped in the peculiar HF(ν′=3)–H’ vibrationally adiabatic potential (VAP), combined with substantial enhancement of constructive interference between the two resonances, were considered as the reason for these forward products HF(ν′=2) [12].

Similarly, the F+D₂ reaction also received much attention, and exhibited fascinating dynamical process and results [3, 13–20]. The F+α-D₂(j=0) reactions at collision energies of 1.05–5.02 kJ/mol were investigated by Che et al. in 2007 [20]. The experimental results unambiguously showed the breakdown of the Born-Oppenheimer approximation in chemical reactions. At the lowest collision energy of 1.04 kJ/mol, the excited F* atom was ~1.6 times more reactive than the ground state F atom [20]. This title reaction was also investigated at collision energies of 3.30 and 7.61 kJ/mol by Neumark et al., only backward scattered DF products were obviously observed [3]. Tonnies et al.
studied this reaction at collision energy of 8.70 kJ/mol, and found an interesting bimodal rotational distribution structure of the DF\((v' = 2, 3)\) products in the backward direction in the center-of-mass (CM) frame [17]. They also investigated the title reaction at the even higher collision energies of 17.36 and 23.14 kJ/mol. Most of the products populated at the large and middle CM angles. In addition, the DF\((v' = 4)\) product was observed in the forward direction and its intensity increased as the collision energy increased [18].

Recently, a review paper concerning chemical reactions at hyperthermal collision energies pointed out that evident changes happened in product scattering direction when reaction collision energies located far above the transition-state barrier, and angular momentum effects took primary responsibility [21]. For example, in the H\(^+\)D\(_2\)\(\rightarrow\)HD\(^+\)+D reaction [22] at hyperthermal collision energy, it was found that the HD products shifted from the sideway scattering to the forward scattering. It was considered that as the collisions energy increased, more reactive collision with larger impact parameters or higher orbital angular momentum occurred, leading to the forward scattered HD products. To shed more light in chemical reactions at hyperthermal collision energies, we herein investigated the reaction of F\(^+\)D\(_2\)\(\rightarrow\)DF\(^+\)+D at hyperthermal collision energies.

For a conventional crossed beam apparatus, the reaction collision energies were mainly affected by the beam velocities and crossed angles. In order to obtain higher collision energies, one usually changed the crossed angles, seeded inert gas with smaller mass, and heated the general valve [18, 20, 23]. Another effective method to improve the collision energy is to use the laser detonation to produce high-speed (around several km/s) beam sources, which was first introduced by Caledonia et al. [24]. The laser detonation producing method was further developed by Minton et al. [25, 26], and the hyperthermal beam sources of Ar, O and F atoms were produced and used in various areas [27–34]. The combination of the high resolution H-atom Rydberg tagging time-of-flight (HRTOF) technique and the laser detonation source is a novel way to investigate chemical reactions at hyperthermal collision energies [35–38]. In this work, we would like to describe a design to use the laser detonation source and the HRTOF technique to study the title reaction at hyperthermal collision energies. Preliminary results of the F\(^+\)D\(_2\)\(\rightarrow\)DF\(^+\)+D reaction at collision energy of 23.84 kJ/mol will be presented.

II. EXPERIMENTS

The study was carried out on a newly constructed crossed beam apparatus. The schematic diagram is shown in FIG. 1. This machine includes the laser detonation beam source chamber, the H\(_2\)/D\(_2\) molecular beam source chamber, a mass spectrometer, and a H/D-atom Rydberg tagging time-of-flight detection system. The hyperthermal F beam used in this work was produced by the laser detonation. Details of this source have been described elsewhere [28, 31, 32, 39–43]. Briefly, pure SF\(_6\) gas (99.9%) with a pressure of 230 psi, was introduced into the source nozzle through a piezoelectric ceramic valve. About 330–340 \(\mu\)s after the valve was triggered, 10.6 \(\mu\)m laser pulse (7.5 J/pulse) produced by a CO\(_2\) laser was introduced to the laser detonation source chamber and focused into the nozzle apex using a gold-coated mirror which was mounted 50 cm from the nozzle. The laser pulse initiated a breakdown of the SF\(_6\) gas and heated F and F related fragment plasma beam source to a quite high temperature (~20000 K). Following the detonation, the high-temperature, high-density plasma expanded rapidly into the diverging cone, and engulfed the remaining cold gas. The local densities in the nozzle were sufficient to permit efficient electron-ion recombination. With these processes of the formation of the F related plasma, as well as acceleration, expansion, and neutralization, the hyperthermal beam source including the neutral F beam and some residual fragments, with a high speed around 3–4 km/s, was formed eventually. The F atom beam then flowed to the main chamber and its velocity distribution was monitored in real time by

![FIG. 1 The schematic diagram of the experimental apparatus used in this study.](image-url)
using of a mass spectrometry. In order to obtain F atom beam with better speed ratio, a chopper wheel was used to select a small portion of the F atom beam with a certain speed for different collision energies. The chopper wheel was mounted near the skimmer (which was mounted between the hyperthermal F beam source chamber and the main chamber), with the thickness of 0.15 mm, and the rotation speed of 210 rps. Four 1 mm slits were evenly distributed near its edge. The velocity distributions of the unchopped F beam pulse and the chopped F beam pulse are shown in FIG. 2. The speed ratio of the chopped F beam pulse was 13, and that of the unchopped F beam pulse was 4.5. The central velocity of the chopped F beam pulse used in this work was 3.68 km/s.

The D$_2$ beam used in the study was obtained by expanding neat D$_2$ gas through a general pulsed valve cooled by liquid-N$_2$. The velocity distribution of the D$_2$ beam is shown in FIG. 3, with a center value of 0.99 km/s, and speed ratio of 14. The D$_2$ beam and the chopped hyperthermal F beam crossed with each other perpendicularly in the main chamber, leading to the collision energy of 23.84 kJ/mol in this work.

The HRTOF technique used in this work was described in detail elsewhere [44-48]. The D atom products from the crossing region were excited from $n$=1 to $n$=2 state by a VUV photon excitation at the Lyman-$\alpha$ wavelength (121.6 nm), and were further excited from $n$=2 to a high-$n$ Rydberg state by a UV photon excitation at about 365 nm. The 121.6 nm VUV light was produced by difference four-wave mixing process, in which two 212.5 nm photons and one 845 nm photon were introduced to a Kr/Ar (ratio 1:3) gas cell synchronously and one 121.6 nm photon was produced. The 212.5 nm laser was obtained by doubling 425 nm, which was produced by a tunable dye laser pumped by 845 nm (the third harmonic output of a Nd:YAG laser). And the 845 nm laser was the direct output of another dye laser pumped by part of the 532 nm (second harmonic output from the same Nd:YAG laser). The 365 nm laser was produced through doubling the output of a tunable dye laser operated at about 730 nm, which was pumped by the other part of 532 nm of the Nd:YAG laser. The three laser beams (212.5, 845, and 365 nm) involved in this work overlapped not only in space but also in time in the reaction region.

Charged species generated by the laser beams at the tagging region were extracted away through a small electric field with an intensity of ~75 V/cm. Then, the neutral products of D atoms, after flying a distance about 28 cm, were ionized by a strong electric field with an intensity around ~4 kV/cm, and then detected by a Z-stack microchannel plate (MCP) detector. Finally, the signal was amplified by a fast preamplifier and counted by a multichannel scaler. The MCP detector can sweep from $-55^\circ$ to $100^\circ$, and the time-of-flight spectra of D atom product were collected at intervals of 10°.

III. RESULTS AND DISCUSSION

A. Product velocity distributions

The D atom TOF spectra were collected at 16 laboratory angles with the collision energy fixed at 23.84 kJ/mol from $-50^\circ$ to $+100^\circ$ at 10° intervals. The TOF spectra were then converted into the velocity distributions for further analysis. The velocity spectra collected at laboratory angles $-50^\circ$, $40^\circ$, and $100^\circ$ are shown in FIG. 4, corresponding to forward, sideway, and backward scattering direction in the CM frame, respectively. In this work, the forward direction is the initial direction of the D$_2$ beam.

It can be seen clearly from FIG. 4 that the angular distribution of the product DF($v'$=4) is different from that of the DF($v'$=0, 1, 2, 3) products. The DF($v'$=0, 1, 2, 3) products are mostly scattered in the sideway and backward direction, while DF($v'$=4) product is mainly peaked in the forward direction. It is worth noting that DF($v'$=0) products are clearly observed in the sideway
FIG. 4 Velocity spectra of the D-atom product from the F+D$_2$→DF+D reaction at the collision energy of 23.84 kJ/mol. Velocity spectra at three laboratory angles are shown: (top panel) $\theta_L=50^\circ$, (middle panel) $\theta_L=40^\circ$, (bottom panel) $\theta_L=100^\circ$, which correspond roughly to the forward-, sideway-, and backward-scattering directions for the DF product in the center-of-mass frame, respectively. DF($v'=0, 1, 2, 3, 4$) products are observed here.

B. Product differential cross sections

The vibrational state specific DCSs were obtained by fitting the DF product velocity distributions using a program developed in our laboratory. Then we drew out the three dimensional DCSs (3D DCSs) for the F+D$_2$→DF+D reaction, which are showed in FIG. 5. The peaks in the picture can be assigned, from the outermost one, to DF($v'=0, 1, 2, 3, 4$). It is noted that the DF($v'=0, 1, 2, 3$) products are mainly dominated in the backward and sideway scattering direction, and the relative proportion of sideway scattering gradually increases with the vibrational quantum number from $v'=0$ to $v'=3$. Furthermore, a portion of the DF($v'=3$) product is observed in the forward direction. Interestingly, the DF($v'=4$) product is forward-scattered, which is quite different from the DF product with lower vibrational excitation. These results are similar to that observed by Faubel et al. at the collision energy of 23 kJ/mol [15].

By integrating the rotational population for each vibrational state of the DF product at specific scattering angles, we can determine the angular distribution of the DF product on $v'=0, 1, 2, 3, 4$ vibrational states. FIG. 6 shows the angular distributions of the vibrational state specific DF products at the title reaction. From these distributions, it is interesting that the DF($v'=4$) product has a peak in the forward direction within the CM angle of $20^\circ-40^\circ$, while DF($v'=0, 1, 2, 3$) products are mainly distributed in the sideway and backward directions.

In addition, we obtained the relative vibrational
state branchings of DF products, which is presented in FIG. 7. Except the DF(v′=0) product, the DF(v′=1, 2, 3, 4) products have similar population at the collision energy of 23.84 kJ/mol. This phenomenon is obviously different from the results at lower collision energies, in which the DF products at v′=2 and 3 are always dominant [35].

We now seek to reveal the origin of the forward scattering DF(v′=4) product. Neumark et al. observed the forward scattering peak of DF(v′=4) in DCS from the corresponding reaction F+D₂ previously [2, 3], and the phenomenon was initially considered as reaction resonance. The forward scattering peak was also obtained from the quasi-classical trajectory (QCT) calculations which were based on different semi-empirical and ab initio potential energy surfaces [4, 8, 13, 49]. As reaction resonances should be quantum mechanical phenomena, the QCT calculation results forced researchers to question the origin of the forward scattering products [50]. Recently, Wang et al. observed the forward scattering HF(v′=3) product in the reaction of F+H₂→HF(v′=3)+H, with collision energies threshold about ~2.17 kJ/mol, and the theoretical analysis suggested that the forward scattering HF(v′=3) product was induced mainly by the slow-down mechanism over the centrifugal barrier in the exit channel. Besides, the shape resonance mechanism also had contribution, which was dominant in a very small collision energy regime slightly above the HF(v′=3) threshold [37]. However, for the forward scattering DF(v′=4) product from the reaction of F+D₂ at collision energies of 5.10–14.89 kJ/mol, quantum mechanical calculations by Sun et al. pointed out that, it mainly came from those reaction processes, in which the F atom reacts with D₂ with large collision parameters along the direction perpendicular to the D₂ molecular axis [38, 51]. The mechanism of the forward scattering DF(v′=4) product observed in this experiment is possibly similar to that reported by Sun et al., but the relative vibrational state branching of DF products is obviously different from that observed at collision energies of 5.10–14.89 kJ/mol, therefore further calculations are needed to reveal the detailed reaction mechanism.

From the above results, it is clear that the new constructed apparatus can be used to study the F+D₂→DF+D reaction at hyperthermal collision energies, and more results for this reaction at higher collision energies will be discussed in the future. This experimental setup is also applicable to other reaction systems, such as O(3P)+H₂ reactions at hyperthermal collision energies.

IV. CONCLUSION

In summary, we have demonstrated a new experimental setup in our laboratory for studying chemical reactions at hyperthermal collision energies using the high resolution H-atom Rydberg tagging time-of-flight technique combined with a laser detonation source. The F+D₂→DF+D reaction at the hyperthermal collision energy of 23.84 kJ/mol has been performed and shown in this work. From the product DCSs, DF(v′=0, 1, 2, 3) products mainly populated in the sideways and backward scattering direction, while DF(v′=4) product was distributed in the forward direction. Possible mechanism for this forward scattering DF(v′=4) product has been discussed.

V. ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No.21473015, No.21203016, No.41574101, No.21673232, No.21773213). Li Che thanks the Foundation for the Author of National Excellent Doctoral Dissertation of China (No.201222).


FIG. 7 DF product vibrational state branching at collision energy of 23.84 kJ/mol.

DOI:10.1063/1674-0068/cjcp1901005 ©2019 Chinese Physical Society