Crossed Molecular Beam Study of the F+D$_2$(v=1, j=0) Reaction

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The reaction dynamics of the fluorine atom with vibrationally excited D$_2$(v=1, j=0) was investigated using the crossed beam method. The scheme of stimulated Raman pumping was employed for preparation of vibrationally excited D$_2$ molecules. Contribution from the reaction of spin-orbit excited F*(2P$_{1/2}$) with vibrationally excited D$_2$ was not found. Reaction of spin-orbit ground F(2P$_{3/2}$) with vibrationally excited D$_2$ was measured and DF products populated in v' = 2, 3, 4, 5 were observed. Compared with the vibrationally ground reaction, DF products from the vibrationally excited reaction of F*(2P$_{3/2}$)+D$_2$(v=1, j=0) are rotationally “hotter”. Differential cross sections at four collision energies, ranging from 0.32 kcal/mol to 2.62 kcal/mol, were obtained. Backward scattering dominates for DF products in all vibrational levels at the lowest collision energy of 0.32 kcal/mol. As the collision energy increases, angular distribution of DF products gradually shifts from backward to sideway. The collision-energy dependence of differential cross section of DF(v' = 5) at forward direction was also measured. Forward-scattered signal of DF(v' = 5) appears at the collision energy of 1.0 kcal/mol, and becomes dominated at 2.62 kcal/mol.

Key words: Stimulated Raman pumping, D$_2$, vibrational excitation, Molecular beam, Forward scattering

I. INTRODUCTION

The reactions of fluorine atom with hydrogen molecule and its isotopic variants played a central role in the development of experimental and theoretical chemical dynamics and kinetics during the past decades and have been considered as benchmark reactions in the field of reaction dynamics. They have also been extensively studied because of the importance in chemical laser. The vibrational distribution of HF/DF products from these reactions is highly inverted, which is crucial for chemical laser.

The reaction of F+D$_2$→DF+D has been extensively investigated by scattering experiments. In 1970, Lee and coworkers reported a crossed beam study of this reaction in which vibrational states of the DF product were identified directly from angular distributions [1]. In 1984, using the universal crossed molecular beam method, Lee and coworkers conducted a scattering experiment on the title reaction. They observed some forward scattered DF(v=4) signals at the collision energy of 3.32 kcal/mol, and tentatively attributed them to be a signature of dynamical resonances in the transition state [2]. In 1990s, Toennies and coworkers measured the absolute reactive cross sections and product rotational distribution [3, 4]. They also found that the vibrational product state distributions of DF depended strongly on the initial rotational state of D$_2$ reactants [5, 6]. In 2007, Yang and coworkers measured relative integral and differential cross sections for reaction of the ground F*(2P$_{1/2}$) and excited F*(2P$_{1/2}$) spin-orbit state with ortho-D$_2$. They found that the reactivity of the Born-Oppenheimer (BO)-forbidden F* becomes increasingly more efficient at low collision energy, relative to the BO-allowed F reaction of the ground spin-orbit state, which is in excellent agreement with quantum calculations [7].

Vibrational excitation of reactant molecules has profound effects on a chemical reaction. Early studies on triatomic reactions led to the establishment of the well-known Polanyi rules, which explain and predict the relative effectiveness of translational and vibrational energy in driving the atom-diatom reactions [8]. In 1990s, Crim and coworkers showed that the mode-selective re-
reactant excitation has huge effects on the outcomes of chemical reactions. For example, in the H+HOD reaction, 4 quanta of initial excitation in the H−OD stretch led to H₂+OD products, while 5 quanta in the HO−D stretch led to HD+OH products [9]. Zare and coworkers also observed the mode-selectivity after comparing the effects of reactant stretch and bend excitation in the H+D₂O reaction [10]. More recently, the pursuit of a rule for polyatomic reaction that goes beyond the Polanyi rules for triatomic reaction, has attracted extensive attention, with the reaction of halogen atom with CH₄ and its isotopically substituted analogs as the model reaction. Most notably, a series of crossed beam experiments conducted by Liu and coworkers have provided in-depth insights for understanding the dynamics of polyatomic reactions, and posed great challenges to theory [11, 12]. Liu and coworkers also are pioneers in the studies of stereodynamics in the reaction of state-selected and aligned CHD₃ molecules prepared by polarized infrared laser [13, 14].

In recent years, we have developed a high-energy, single longitudinal mode stimulated Raman pumping laser system, with which highly effective preparation of H₂ and its isotopic variants in a specific rovibrationally excited state was achieved [15−17]. Based on this laser system, reactions of vibrationally excited HD with fluorine and chlorine atom were investigated. Oscillations in the dependence of backward-scattered signal on collision energy were observed, which were attributed to resonances by quantum theory [18, 19]. We also investigated the effect of reagent vibrational excitation on the dynamics of F+H₂(v=1, j=0) reaction [20].

Reported here is a systematic crossed beam study on the reaction of fluorine atom with vibrationally excited D₂(v=1, j=0).

II. EXPERIMENTAL SETUP

The experimental apparatus used in this crossed beam study has been described previously [21]. A beam of fluorine atom was generated by a double-stage discharge source [22], which produced both ground F(2P₃/₂) and spin-orbit excited F⁺(2P₁/₂) atoms. In an attempt to find the contribution from the reaction of F⁺ with vibrationally excited D₂, two kinds of pre-mixed gases were used for discharge. The first one is 5% F₂ seeded in helium. The second one was a mixture of F₂, He, and NF₃, with the volume fraction of 2.5%, 47.5%, and 50%, respectively. According to the previous experiment, a fluorine atom beam with a higher ratio of spin-orbit excited F⁺ (F⁺F⁺ ratio is 4.8) would be generated by discharge of the second premixed gas [7]. A D₂ beam was generated by a supersonic expansion of pure ortho-D₂ gas through a nozzle cooled to liquid nitrogen temperature, which ensured that almost all D₂ molecules in the beam were populated in the lowest rovibrational state (ν=0, j=0). The ortho-D₂ sample was prepared by passing normal D₂ slowly through a copper tube filled with ferro-magnetic catalyst cooled by a cryogenic pump, and then stored in an aluminum tank can. The velocity of the D₂ molecules was measured to be 1030 m/s, with a speed ratio better than 20. The F beam and D₂ beam intersected each other at the crossing region. The F beam was rotatable around the crossing point so we were able to tune the collision energy by changing the crossing angle.

The vibrationally excited D₂ was prepared by the scheme of simulated Raman pumping (SRP) [18, 19] with a pump laser at 532 nm and a Stokes laser at 633 nm. About 300 mJ of 532 nm was generated directly from a Nd:YAG laser (Continuum Inc. PL8000 OPO) with injection seeding. The 633 nm single-longitudinal mode Stokes laser was generated by a home-built narrow bandwidth optical parameter oscillator/amplifier (OPO/OPA), which was pumped by another injection-seeding Nd:YAG laser. The Stokes laser had a pulse energy of 40 mJ and a pulse duration of about 6 ns (FWHM). The pump and Stokes laser were combined collinearly and focused onto the D₂ beam with a diameter of 0.7 nm near the nozzle tip. A computer program was used to lock the frequency difference of the pump and Stokes lasers for stable excitation. The vibrational excitation efficiency of D₂ molecules was estimated to be about 8%.

The D atoms produced from the crossing region, as a result of the reactive scattering of F⁺+D₂→DF⁺+D, were detected by the D-atom Rydberg tagging technique. D atoms were firstly excited from n=1 to n=2 by 121.6 nm radiation generated by four-wave mixing of 212 and 845 nm in a Kr/Ar gas cell. As the second step, a 365 nm laser excited D atoms in n=2 to a high Rydberg state (n≈50). These two excitation laser pulses were well overlapped both in time and space in the crossing region. The neutral Rydberg D atoms then flew about 318 mm before reaching a micro-channel plate (MCP) detector with a fine metal mesh (grounded) in the front. After passing the mesh, the Rydberg D atoms were immediately field-ionized by the electric field applied between the MCP and the mesh, and then detected by the MCP detector. The signal received by the MCP was then amplified by a fast preamplifier and counted by a multichannel scaler (MCS).

The two molecular beams, the detection laser and the data acquisition system worked at 30 Hz, while the stimulated Raman pumping laser system worked at 15 Hz. So TOF spectra with and without vibrational excitation of D₂ were acquired in a shot-to-shot mode.

III. RESULTS AND DISCUSSION

A. Time-of-flight spectra

FIG. 1(a) shows TOF spectrum at 0.32 kcal/mol in the backward scattering direction. The “off” spectrum contains contribution from D₂(ν=0, j=0). When stimulated Raman pumping laser is on, some portion of D₂
molecules is pumped from \((v=0, j=0)\) to \((v=1, j=0)\), and in the TOF spectrum it is obvious that many new peaks appear, which could be attributed to the reaction of \(D_2(v=1, j=0)\). Using conservation of energy and momentum, the main structures in the TOF spectrum could be attributed to different vibrational states of DF products, as marked in the figure. Due to that the vibrational constants of \(D_2\) and DF are approximately the same \((\omega_{D_2}=3115\ \text{cm}^{-1}, \omega_{D^2F}=2998\ \text{cm}^{-1})\), the DF products from \(D_2(v=1, j=0)\) and \(D_2(v=0, j=0)\) are overlapped in the TOF spectrum. For the vibrationally ground reaction, DF products in \(v'=2\) and \(v'=3\) are dominated, while for the vibrationally excited reaction, most of DF products are populated in \(v'=3\), \(v'=4\) and \(v'=5\) states, indicating that the vibration energy of \(D_2(v=1)\) reactant is reserved in the vibration of DF products, instead of going into translation energy of the product. Because the potential energy surface (PES) of this reaction has an “early” barrier, this behavior is in agreement with Polanyi rules, which predicts that the available energy of the reaction with an “early” barrier prefers to go into vibrational excitation of the products. The “on” spectrum contains contribution from reaction from both \(D_2(v=0, j=0)\) and \(D_2(v=1, j=0)\). So the relation of TOF spectrum and vibrational excitation could be expressed as follows:

\[
\begin{align*}
\text{TOF (off)} &= \text{TOF (v=0)} \\
\text{TOF (on)} &= \text{TOF (v=0)} \cdot (1 - \text{EE}) + \text{TOF (v=1)} \cdot \text{EE}
\end{align*}
\]

In previous experiments, the excitation efficiency can be obtained by calculating the depletion of the area of a specific peak contributed only from the vibrationally ground reaction \([18, 20]\). While in this experiment, this method is not applicable due to the lack of a separate peak originated only from the reaction of \(D_2(v=0, j=0)\). We estimated the excitation efficiency to be 8%. Using the formula (Eq.(3)), TOF spectrum of the reaction \(F(2P_{3/2})+D_2(v=1, j=0)\) is obtained, as shown in FIG. 1(b). The main structure in the spectrum can be attributed to different vibrational states of DF products. Most of DF products are populated in the \(v'=4\) and \(v'=5\) states. The rotational states of \(DF(v'=4)\) products from the reaction of \(F+D_2(v=1, j=0)\) are also well resolved. It is interesting that, compared with DF products from the vibrationally ground reaction, DF products from vibrationally excited reaction are rotationally “hotter”, probably indicating higher partial waves also contribute in the vibrationally excited reaction.

In order to investigate the reactivity of the spin-orbit excited F* with vibrationally excited D2, TOF spectrum was obtained with F atom beam generated by discharge of the second premixed gas, as shown in FIG. 2. It is obvious that in the TOF spectrum with stimulated Raman pumping laser off, there is a little peak at 47 ms, which can be attributed to \(DF(v'=3)\) products from the reaction of spin-orbit excited F* with vibrationally ground state of \(D_2\), as reported in Ref.[7], indicating that a significant amount of F* is contained in the F atom beam. While with Raman pumping laser on, only the contribution from the reaction of spin-orbit ground F with \(D_2(v=1, j=0)\) is found in the TOF spectrum, and no obvious contribution from the reaction of spin-orbit excited F* with \(D_2(v=1, j=0)\) is found. FIG. 2 is a typical TOF spectrum at 0.54 kcal/mol in the backward-scattered direction, and we also carried out scattering experiment at a lower collision energy of 0.37 kcal/mol and still no signal was found from the reaction of \(F^*+D_2(v=1, j=0)\), indicating that the vibrationally
FIG. 2 (a) Raw TOF spectra with stimulated Raman pumping lasers on (red solid line) and off (blue solid line) at the collision energy of 0.54 kcal/mol in the backward scattering direction. Contributions from F* are obvious and marked in the figure. (b) TOF subtracted from the two raw TOF spectra, contained contribution only from the vibrationally excited reaction F+D$_2$($v=1$, $j=0$). Rovibrational state of DF products are indicated by the labels. No contribution from F*+D$_2$($v=1$, $j=0$) is found.

excited reaction obeys the BO approximation at the collision energies investigated.

B. State-resolved differential cross sections

The TOF spectra at various LAB scattering angles were converted to the product kinetic energy (KE) distributions using a standard Jacobian transformation. The KE distributions in the LAB frame were then simulated by adjusting the relative populations of the rovibrational states of the DF product to obtain relative population distributions of the DF product at each rovibrational state at the LAB angles measured. By fitting the rovibrational population distributions of DF products at all the LAB angles, quantum-state resolved DCSs of the DF product in the CM frame are then determined, as shown in FIG. 3. Different circles in the figure correspond to different rovibrational states of DF products. At the four collision energies measured, the DF products in the $v'=2$, 3, 4, 5 states were detected. At the lowest collision energy of 0.32 kcal/mol, DF products in all vibrational states are distributed in the backward hemisphere, with the maximum at the backward scattering direction $\theta_{cm}=180^\circ$. As collision energy increases, the angular distribution of DF products gradually shifts from backward to sideway direction, and the rotational distribution becomes hotter. This behavior indicates the vibrationally excited reaction F($^2P_1/2$)+D$_2$($v=1$, $j=0$) probably happens via a direct D-abstraction mechanism. At the lowest collision energy, only the lowest partial waves contribute to the reaction, so backward-scattered products are dominated and rotationally “cold”. With increased collision energy, higher partial waves contribute to the reaction, so the angular distribution of products shifts gradually to sideway, and the rotational temperature of DF products becomes hotter. At the collision energy of 1.00 kcal/mol, forward-scattered DF($v'=5$) is observed. The forward-scattered signal becomes dominated at 2.62 kcal/mol.

C. Collision-energy dependence of forward differential cross sections of DF($v'=5$)

Forward scattering signals are considered to be a signature of time delay caused by dynamical resonances, although there are many other mechanisms that also lead to time delay [23]. In this work, we measured the collision-energy dependent differential cross sections for the reaction F+D$_2$($v=1$, $j=0$)$\rightarrow$DF($v'=5$)+D at the forward scattering direction. The result is shown in FIG. 4, which was done by connecting two separated measurements, covering a range of collision energy from 0.81 kcal/mol to 3.92 kcal/mol. The forward scattering signal of DF($v'=5$) appears at around 1.0 kcal/mol and monotonically increases to the highest collision energy measured. In previous work, forward-scattered sig-
FIG. 4 Collision-energy dependence of forward differential cross sections of DF($v' = 5$) products from F+D$_2$(v=1, j=0) reaction. This curve was finished in two separate measurements, and then were connected by multiplying a factor.

nal of DF($v' = 4$) from vibrationally ground reaction of F+D$_2$(v=0) has been reported by Lee and coworkers at the collision energy of 3.32 kcal/mol. Similar forward scattering of HF($v' = 3$) products from F+H$_2$(v=0) reaction was observed and explained by slow-down mechanism over the centrifugal barrier and shape resonance mechanism by tunneling through the centrifugal barrier [23, 25]. The mechanism for the forward scattering DF($v' = 5$) products from vibrationally excited reaction of F+D$_2$(v=1, j=0) is believed to be similar to that of F+H$_2$(v=0, j=0). But further theoretical simulations are needed to clarify the origin of the DF($v' = 5$) forward scattering peak.

IV. CONCLUSION

The vibrationally excited reaction of F+D$_2$(v=1, j=0) was investigated with crossed beam method. Contribution from the reaction of spin-orbit excited F$^+$($^2P_{3/2}$) with vibrationally excited D$_2$ was not found at collision energies of 0.37 and 0.54 kcal/mol, as predicted by BO approximation. Differential cross sections at four collision energies were measured. DF products in $v' = 2$, 3, 4, 5 were observed. At lowest collision energy of 0.32 kcal/mol, the DF products at all vibrational levels are backward-scattered. As the collision energy increases, the angular distribution of $v' = 2$, 3, 4 changes to sideway. Forward-scattered signal of DF($v' = 5$) appears at 1.0 kcal/mol, and becomes dominated at 2.62 kcal/mol. Collision-energy dependence of forward differential cross sections of DF($v' = 5$) is measured and found to increase monotonically from 1.0 kcal/mol to the highest collision energy measured.

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