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# High resolution time-of-flight spectrometer for crossed molecular beam study of elementary chemical reactions

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In this article, we describe an apparatus in our laboratory for investigating elementary chemical reactions using the high resolution time-of-flight Rydberg tagging method. In this apparatus, we have adopted a rotating source design so that collision energy can be changed for crossed beam studies of chemical reactions. Preliminary results on the HI photodissociation and the F atom reaction with  $H_2$  are reported here. These results suggest that the experimental apparatus is potentially a powerful tool for investigating state-to-state dynamics of elementary chemical reactions. © 2005 American Institute of Physics. [DOI: 10.1063/1.1960718]

#### I. INTRODUCTION

Significant advances have been made on the experimental studies of the dynamics of elementary chemical reactions during the last few decades. Nascent product quantum state distribution in chemical reactions can be routinely measured using many advanced laser techniques, such as laser-induced fluorescence, resonance-enhanced multiphoton ionization, etc. In an elementary chemical reaction, quantum state distribution of nascent chemical products, however, only carries part of the product information in a molecular beam scattering experiment. Likewise, information on the angular distributions of reactive scattering products is at least as important as the product quantum state distribution to the understanding of the whole picture of chemical reactions. The development of various techniques for reactive scattering measurement, especially the universal crossed molecular beam method in the early days,<sup>1</sup> has been instrumental in the understanding of bimolecular and unimolecular chemical reactions over the last few decades. Important information has been derived on primary mechanisms of elementary chemical processes.<sup>2-6</sup> Ideally, quantum state resolved differential cross section measurements would provide the most detailed mechanistic information on an elementary chemical reaction, and also the most stringent test for a quantitatively accurate theoretical picture for the reaction. However, measuring the quantum-state resolved differential cross sections is difficult, to say the least. This is largely due to the limited translational energy resolution of various translational spectroscopic techniques and poor molecular beam condition under which molecular beam experiments are routinely carried out. Recent developments in experimental techniques for molecular dynamics studies have greatly enhanced our ability to measure quantum-state resolved differential cross sections. The advancement of the ion imaging techniques, especially developments of the velocity mapping and slicing methods, have made a significant impact in this research field. The development of the H atom Rydberg "tagging" time-of-flight technique (HRTOF)<sup>7</sup> has also provided us with an extremely powerful tool for measurement of state resolved differential cross sections for both unimolecular and bimolecular reactions with unprecedented translational energy resolution and extremely high sensitivity. This technique has been applied successfully to the studies of the important benchmark reaction  $H+D_2 \rightarrow HD+H$  recently<sup>8</sup> and many important unimolecular dissociation processes.<sup>9</sup>

Recent studies on the  $H_2O$  photochemistry,<sup>10</sup> the  $O(^1D)+H_2$  reaction<sup>11</sup> and the  $OH+D_2$  reaction<sup>12</sup> using this technique have further demonstrated the powerfulness of this method in obtaining experimentally the most detailed dynamics of these benchmark systems.

In investigating crossed beam reactions, collision energy dependence studies of various dynamics quantities are essential for the understanding of the reaction mechanism, which is similar to the temperature dependence measurement of chemical kinetic rate constants in a gas cell experiment. In all previous crossed beam studies on elementary chemical reactions using the HRTOF technique, collision energy dependence studies are achieved by generating variable energy atomic beams with tunable frequency photolysis of diatomic precursors, such as H atom from HI. When the velocities of two atomic/molecular beams are comparable, collision energy dependence studies can be achieved more efficiently by varying the crossing angle of the two beams using a rotating source design. Therefore, adopting a rotating source design with the HRTOF technique could significantly enhance our ability to investigate the detailed state-to-state dynamics of interesting elementary chemical reactions by basically adding another degree of freedom with the technique. In this article, we will describe a crossed beam apparatus using the HRTOF method to study elementary chemical reactions at variable collision energies. Preliminary results of photodissociation and crossed beam reactive scattering experiments using this apparatus will be described. The development of

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this apparatus provides a unique tool to investigate many interesting phenomena in chemical reactions, such as rotational and vibrational excitation effects on the reactive resonances and quantized bottleneck state dynamics, as well as nonadiabatic effects on the reaction dynamics such as the effects of spin-orbit couplings and conical intersections.

#### **II. NEW APPARATUS**

#### A. H atom Rydberg tagging technique

The H-atom Rydberg tagging time-of-flight technique (HRTOF) was developed in the early 1990s by Welge and co-workers.<sup>7</sup> The detailed experimental methods used to study the crossed beam  $H+D_2 \rightarrow HD+H$  reaction have been described in great detail previously.<sup>8</sup> A detailed description of this technique used for studying molecular photodissociation can also be found in Ref. 9. The central scheme of this technique is the two-step efficient excitation of the H atom from its ground state to its high Rydberg levels (n=35-90)without ionizing the H atom product as in the (1+1') multiphoton ionization scheme used earlier. The high-n Rydberg H atoms are known to be long lived to millisecond time scale in a small electric field ( $\sim 20 \text{ V/cm}$ ). The enhancement of Rydberg H atom lifetime in a small electric field is likely caused by the mixing of the  $\ell$  quantum number in the high*n* Rydberg H atom.<sup>13,14</sup> These long-lived neutral H atoms are suitable for long distance time-of-flight measurement. The neutral Rydberg H atoms can be easily detected using field ionization. Very high TOF resolution can be achieved by minimizing the physical sizes of the tagging region and the field ionization region.

The excitation of the ground state H atom product (n = 1) was made by the following two-step excitation scheme via the n=2 level:

 $H(n = 1) + hv(121.6 \text{ nm}) \rightarrow H(n = 2)$ 

and

 $H(n = 2) + hv(365 \text{ nm}) \rightarrow H^*(n \sim 50).$ 

The detection laser system for the two-step excitation was arranged as in Fig. 1. The 121.6 nm vacuum ultraviolet (VUV) light used in the first step excitation was generated using a two photon resonant  $(2\omega_1 - \omega_2)$  four wave mixing scheme in the Kr gas cell. The  $2\omega_1$  (212.5 nm) is resonant with the Kr (4*p*-5*p*) transition.<sup>15</sup> The  $\omega_1$  was generated by doubling a dye laser pumped by a Nd:yttrium-aluminumgarnet (YAG) (355 nm) laser, while  $\omega_2$  (845 nm) was the direct output of a dye laser pumped by the second harmonic of the same YAG laser. During the experiment, about 2 mJ of 212.5 nm and 5 mJ of 845 nm laser light were generally used. The 121.6 nm light generated in an optimized overlapping condition of the two laser beams is sufficient to saturate the first step excitation since this transition has a very large cross section  $(3.0 \times 10^{-13} \text{ cm}^2)$ . We used an optimized mixture of Ar/Kr (3/1) at ~80 Torr in the four-wave mixing cell, which is somewhat different from the condition used in Ref. 15. Following the first step VUV excitation, the H atom product was then sequentially excited to a high Rydberg state with  $n \approx 50$  using a 365 nm light in near saturation, which



FIG. 1. The arrangement of the H atom Rydberg tagging laser system for the present instrument.

was generated by doubling a dye laser pumped by the same YAG laser. This two-step excitation scheme allowed us to pump the H atom to a high Rydberg state in nearly unity efficiency. These two excitation laser pulses have to be overlapped exactly both in space and time. The neutral Rydberg H atoms prepared in the crossed region flied a certain TOF distance to reach a microchannel plate (MCP) *Z*-stack detector with a fine metal grid (grounded) in the front. After passing through the grid, the Rydberg tagged H atoms were then immediately field ionized by the electric filed applied between the front plate of the *Z*-stack MCP detector and the fine metal grid. The signal detected by the MCP was then amplified by a fast preamplifier, and counted by a multichannel scaler.

#### B. Vacuum system of the apparatus

The crossed beam apparatus was designed with the following three goals: (1) introducing a rotating source that allows one to study chemical reactions at different collision energy; (2) significantly broadening the detectable angle range so that reactions with more extreme kinematics can be investigated in the whole scattering angle; (3) detecting the H atom reaction products using multiple MCP detectors at different angles that can enhance the measurement efficiency.

Figure 2 shows the schematics of the instrument. The apparatus has two source chambers and a main chamber. Both source chambers are differentially pumped with a BOC Edwards 2000 1/s magnetically levitated turbo-molecular pump; a base vacuum of about  $1 \times 10^{-8}$  Torr can be reached for both regions. The main chamber is pumped with a BOC Edwards 2000 1/s magnetically levitated turbo-molecular pump, with a cryogenic pump. The source turbo pumps are backed by a normal mechanic pump and a molecular sieve trap, while the main chamber turbo is backed with a pump station. This arrangement allows us to obtain an oil free vacuum environment. Residual hydrocarbons in the main chamber are maintained below  $10^{-10}$  Torr range. This allows





Turbo Pump

Source

Region 2

Turbo Pump

us to detect a hydrogen atom with almost no background. Most of the H atom background in our experiment is beam related.

Two molecular beam sources can be used in this apparatus. One is a fixed beam source, and the other is a rotatable beam source. Two types of experiments can be carried out on this apparatus: unimolecular photodissociation and bimolecular reaction. When a photodissociation experiment is performed, only a single beam is used. For a crossed beam experiment, both molecular beam sources have to be used. The fixed source was mounted in the source region 1, while the rotating source was mounted in the source region 2 and was rotatable around the center of the beam crossing region through a mechanism shown in Fig. 3. The crossing angle of the two beam sources can be varied from 40° to 150°. Small changes are needed for the source wall for studies with larger beam crossing angles. In the apparatus, a room temperature



FIG. 3. The horizontal cut view of the instrument that shows the driving mechanisms for the rotating detector and the rotating source.

beam source and a liquid nitrogen cooled beam source are available for the fixed source. The rotating source is equipped with a pulsed dc discharge source to generate atomic and radical beams.

The apparatus is also equipped with three Z-stack MCP detectors. One is a fixed MCP detector with an active area of 40-mm-diam MCP (see Fig. 2). This detector is about 1 m away from the beam crossing region, and is used for photodissociation experiment with the highest time-of-flight resolution. In addition, there are two MCP detectors 20° apart that are mounted on a rotating arm (see Fig. 2). If the detector mount arm is slightly modified, a total of four detectors can be easily put on the mount. The two detectors were made of MCP with an active area of 18 mm diameter and can be operated simultaneously. This will help us to significantly shorten the data measurement duration. The two detectors are about 330 mm away from the beam crossing region. The source region 1 was also specially designed so that the rotating detector can detect reaction products from the beam crossing region with a detectable angle range of  $-70^{\circ} - 150^{\circ}$ . The rotating mechanism of the detector is shown in Fig. 3. Such design allows us to easily measure scattering products in the whole scattering range for chemical reactions with extreme kinematic arrangements.

#### III. PRELIMINARY RESULTS

## A. Unimolecular dissociation of HI

Photochemistry of hydrogen halides has long served as the prototypical systems for molecular photodissociation. The dynamics of HI photodissociation following at various wavelengths has been investigated previously using various experimental methods.<sup>16–25</sup> In order to characterize the apparatus, photodissociation of HI at 121.6 nm has been carried out. The purpose of the experiment is to characterize the detection laser system and the fixed long distance MCP detector. Figure 4 shows the time-of-flight spectrum of the H atom product from HI photodissociation at 121.6 nm. The observed H atom peak in the spectrum corresponds to the



FIG. 4. The time-of-flight spectrum of the H atom product from the HI photodissociation at 121.6 nm. The main structure in the spectrum corresponds to the  $I^{*}(^{2}P_{1/2})$  product.

 $I^*(P_{1/2})$  product. From the measurement of this peak, the time-of-flight resolution of this apparatus using the fixed detector is determined to be about 0.06%. This result indicates that the apparatus is now in a good condition for photochemistry investigations.

### B. $F(^{2}P)$ atom reaction with H<sub>2</sub>

The primary goal of setting up the apparatus is to study reactive scatterings of elementary chemical reactions. One of the benchmark elementary chemical reactions is the F atom reaction with H<sub>2</sub>. The reactions of  $F(^{2}P)$  with H<sub>2</sub> and its isotope variants have played a central role in the development of gas phase reaction dynamics.<sup>26</sup> These reactions have been extensively studied using a variety of experimental techniques. A major milestone on the experimental front was the crossed beam study of the reactions by Lee and co-workers.<sup>27,28</sup> Recently, Liu and co-workers have studied the same system experimentally using the Doppler selected TOF methods.<sup>29</sup> The F+HD system is the most clearly defined example for reaction resonances.<sup>30</sup> However, these previous experimental studies were carried out without full quantum state resolution. Many interesting questions regarding this reaction remain to be answered. One of the most interesting questions is the effect of the spin orbit and the reagent rotational excitation on the reaction dynamics.

In this article, we report some preliminary results on the F atom reaction with  $H_2$ . The F atom beam (rotatable) was generated using pulsed discharge, and  $H_2$  beam was generated using a room temperature expansion of a high purity  $H_2$  sample. Figure 5 shows the TOF spectrum of the H atom product at a lab angle of 120° from the F(<sup>2</sup>P) reaction with  $H_2$  at the collision energy of 1.0 kcal/mol measured using the apparatus described here. The 120° lab angle corresponds to roughly the backward scattering direction in the center-of-mass frame. There are clearly two main structures in the TOF spectrum that correspond to the HF(v=1) and HF(v=2) products. The fine peaks correspond to the HF products at different rotational states. From this figure, it is now clearly possible to study F(<sup>2</sup>P) reaction with H<sub>2</sub> and other isoto-



FIG. 5. The H atom time-of-flight spectrum at the laboratory angle of  $120^{\circ}$  from the F(<sup>2</sup>P) reaction with H<sub>2</sub> at the collision energy of 1.0 kcal/mol.

pomers at full quantum state resolution with the instrument described here. This will greatly help our understanding of this important reaction.

#### **IV. SUMMARY**

We have constructed a crossed beam apparatus in our laboratory for studying elementary chemical reactions using the high resolution time-of-flight Rydberg tagging method. Preliminary results on the HI photodissociation and the F atom reaction with  $H_2$  are reported here. The HI photodissociation experiment shows that TOF resolution of 0.06% can be achieved using this instrument. Full quantum state resolved reactive scattering measurements have been carried out on the F atom reaction with  $H_2$ . These encouraging results also suggest that the instrument is a powerful tool to investigate state-to-state dynamics of elementary chemical reactions in great detail.

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