

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

Cite as: Rev. Sci. Instrum. **76**, 083107 (2005); <https://doi.org/10.1063/1.1960718>

Submitted: 27 February 2005 . Accepted: 28 May 2005 . Published Online: 21 July 2005

Minghui Qiu, Li Che, Zefeng Ren, Dongxu Dai, Xiuyan Wang, and Xueming Yang



View Online



Export Citation

ARTICLES YOU MAY BE INTERESTED IN

[Velocity map imaging of ions and electrons using electrostatic lenses: Application in photoelectron and photofragment ion imaging of molecular oxygen](#)

Review of Scientific Instruments **68**, 3477 (1997); <https://doi.org/10.1063/1.1148310>

[Application of time-sliced ion velocity imaging to crossed molecular beam experiments](#)

Review of Scientific Instruments **74**, 2495 (2003); <https://doi.org/10.1063/1.1561604>

[Molecular Beam Reactive Scattering Apparatus with Electron Bombardment Detector](#)

Review of Scientific Instruments **40**, 1402 (1969); <https://doi.org/10.1063/1.1683809>

Lock-in Amplifiers

Find out more today



Zurich
Instruments

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

Minghui Qiu,^{a)} Li Che, Zefeng Ren, Dongxu Dai, Xiuyan Wang, and Xueming Yang^{b)}
*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics,
Chinese Academy of Sciences, Dalian, Liaoning 116023, People's Republic of China*

(Received 27 February 2005; accepted 28 May 2005; published online 21 July 2005)

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 H₂ 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,¹ 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.²⁻⁶ 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 devel-

opments 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)⁷ 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+D₂→HD+H recently⁸ and many important unimolecular dissociation processes.⁹

Recent studies on the H₂O photochemistry,¹⁰ the O(¹D)+H₂ reaction¹¹ and the OH+D₂ reaction¹² 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

^{a)}Also with the Department of Physics, Dalian Jiaotong University, Dalian, Liaoning, P. R. China.

^{b)}Author to whom all correspondence should be addressed; electronic mail: xmyang@dicp.ac.cn

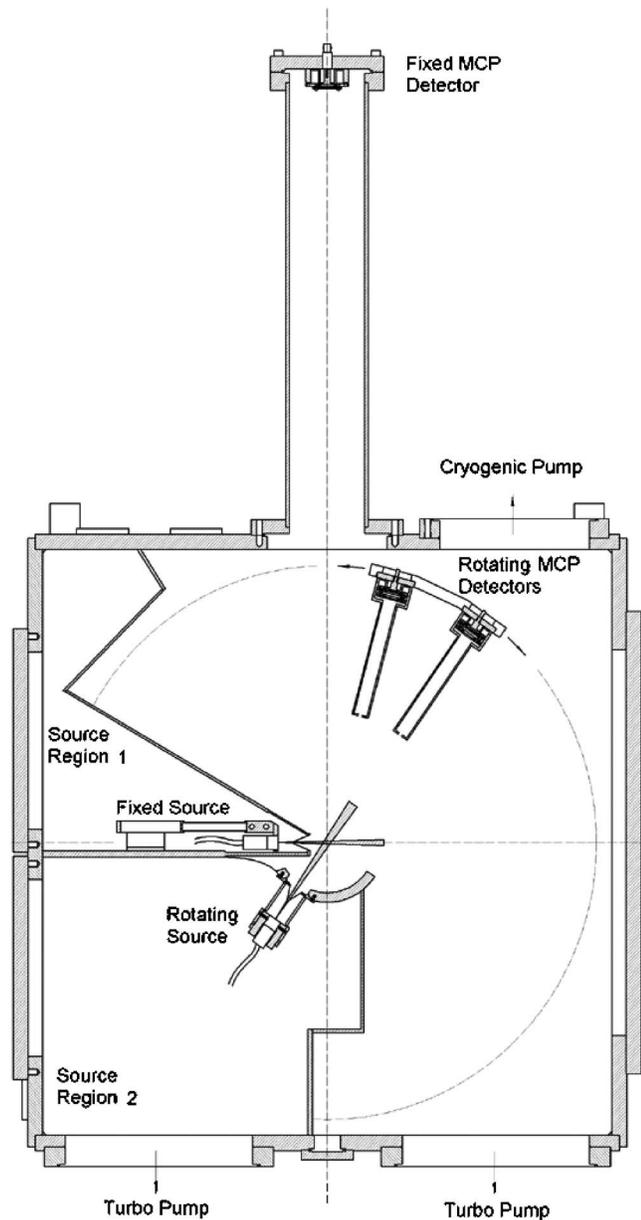


FIG. 2. The vertical cut view of the instrument that shows the arrangement of the main components of the instrument.

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

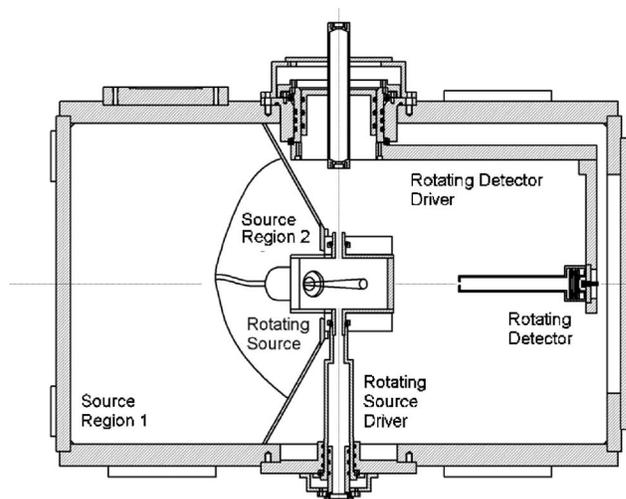


FIG. 3. The horizontal cut view of the instrument that shows the driving mechanisms for the rotating detector and the rotating source.

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.^{16–25} 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

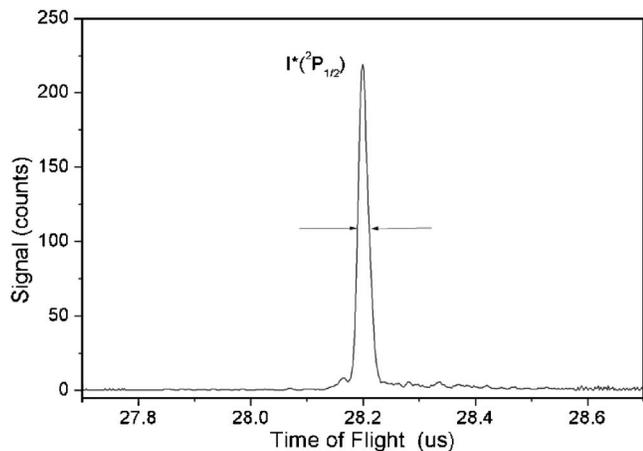


FIG. 4. The time-of-flight spectrum of the H atom product from the HI photodissociation at 121.6 nm. The main structure in the spectrum corresponds to the $I^*(P_{1/2})$ product.

$I^*(P_{1/2})$ 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. $F(^2P)$ atom reaction with H_2

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_2 . The reactions of $F(^2P)$ with H_2 and its isotope variants have played a central role in the development of gas phase reaction dynamics.²⁶ 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.^{27,28} Recently, Liu and co-workers have studied the same system experimentally using the Doppler selected TOF methods.²⁹ The F+HD system is the most clearly defined example for reaction resonances.³⁰ 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 $F(^2P)$ 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 $F(^2P)$ reaction with H_2 and other isoto-

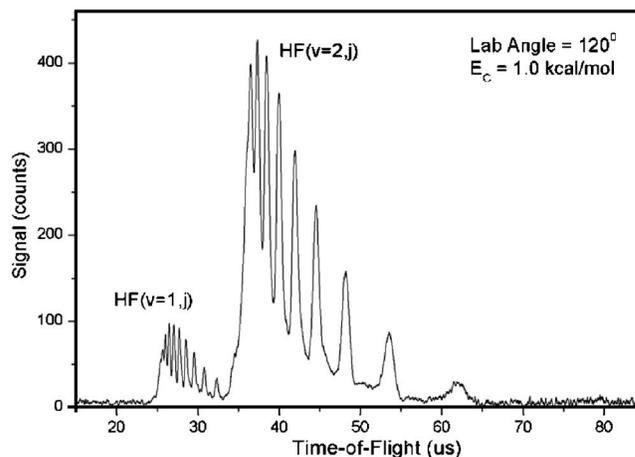


FIG. 5. The H atom time-of-flight spectrum at the laboratory angle of 120° from the $F(^2P)$ reaction with H_2 at the collision energy of 1.0 kcal/mol.

mers 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.

ACKNOWLEDGMENTS

This work was mainly funded by an instrument equipment fund from the Chinese Academy of Sciences, and also partly by the Ministry of Science and Technology of China and the Dalian Institute of Chemical Physics, CAS.

¹ Y. T. Lee, J. D. MacDonald, P. R. Lebreton, and D. R. Herschbach, *Rev. Sci. Instrum.* **40**, 1402 (1969).

² Y. T. Lee, *Science* **236**, 793 (1987).

³ P. Casavecchia, *Rep. Prog. Phys.* **63**, 355 (2000).

⁴ P. Casavecchia, N. Balucani, M. Alagia, L. Cartechini, and G. G. Volpi, *Acc. Chem. Res.* **32**, 503 (1999).

⁵ K. Liu, *Annu. Rev. Phys. Chem.* **52**, 139 (2001).

⁶ J. Helpburn, in *Atomic and Molecular Beam Methods*, edited by G. Scoles (Cambridge University Press, Cambridge).

⁷ L. Schnieder, W. Meier, K. H. Welge, M. N. R. Ashfold, and C. M. Western, *J. Chem. Phys.* **92**, 7027 (1990).

⁸ L. Schnieder, K. Seekamp-Rahn, J. Borkowski, E. Wrede, K. H. Welge, F. J. Aoz, L. Banares, M. J. D'Mello, V. J. Herrero, V. Saez Rabanos, and R. E. Wyatt, *Science* **269**, 207 (1995); L. Schnieder, K. Seekamp-Rahn, E. Wrede, and K. H. Welge, *J. Chem. Phys.* **107**, 6175 (1997).

⁹ M. N. R. Ashfold, D. H. Mordaunt, and S. H. S. Wilson, *Advances in Photochemistry*, edited by D. C. Neckers, D. H. Volman, and G. v. Bunau (Wiley, New York, 1996, Vol. 21, p. 217).

¹⁰ R. N. Dixon, D. W. Huang, X. F. Yang, S. Harich, J. J. Lin, and X. Yang, *Science* **285**, 1249 (1999).

- ¹¹X. Liu, J. J. Lin, S. A. Harich, G. C. Schatz, and X. Yang, *Science* **289**, 1536 (2000).
- ¹²B. R. Strazisar, C. Lin, and H. F. Davis, *Science* **290**, 958 (2000).
- ¹³W. A. Chupka, *J. Chem. Phys.* **98**, 4520 (1993).
- ¹⁴A. ten Wolde, L. D. Noordam, A. Lagendij, and H. B. van Linden van den Heuvell, *Phys. Rev. A* **40**, 485 (1989).
- ¹⁵J. P. Marangos, N. Shen, H. Ma, M. H. R. Hutchinson, and J. P. Connerade, *J. Opt. Soc. Am. B* **7**, 1254 (1990).
- ¹⁶R. D. Clear, S. J. Riley, and K. R. Wilson, *J. Chem. Phys.* **63**, 1340 (1975).
- ¹⁷R. Schmiedl, H. Dugan, W. Meier, and K. H. Welge, *Z. Phys. A* **304**, 137 (1982).
- ¹⁸P. Brewer, P. Das, and R. Bersohn, *J. Chem. Phys.* **79**, 720 (1983).
- ¹⁹C. A. Wight and S. R. Leone, *J. Chem. Phys.* **79**, 4823 (1983).
- ²⁰G. N. A. Van Veen, K. A. Mohamed, T. Baller, and A. E. de Vries, *Chem. Phys.* **80**, 113 (1983).
- ²¹I. Levy and M. Shapiro, *J. Chem. Phys.* **89**, 2900 (1988).
- ²²Z. Xu, B. Koplitz, and C. Wittig, *J. Phys. Chem.* **92**, 5518 (1988).
- ²³T. N. Kitsopoulos, M. A. Buntine, D. P. Baldwin, R. N. Zare, and D. W. Chandler, *Proc. SPIE* **1858**, 2 (1993).
- ²⁴S. R. Langford, P. M. Regan, A. J. Orr-Ewing, and M. N. R. Ashfold, *Chem. Phys.* **231**, 245 (1998).
- ²⁵D. J. Gendron and J. W. Hepburn, *J. Chem. Phys.* **109**, 7205 (1998).
- ²⁶R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford University Press, Oxford, 1987).
- ²⁷D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, and Y. T. Lee, *J. Chem. Phys.* **82**, 3045 (1985).
- ²⁸D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden, K. Shobatake, R. K. Sparks, T. P. Schafer, and Y. T. Lee, *J. Chem. Phys.* **82**, 3067 (1985).
- ²⁹S.-H. Lee, F. Dong, and K. Liu, *J. Chem. Phys.* **116**, 7839 (2002); F. Dong, S.-H. Lee, and K. Liu, *J. Chem. Phys.* **113**, 3633 (2000).
- ³⁰R. T. Skodje, D. Skouteris, D. E. Manolopoulos, S.-H. Lee, F. Dong, and K. Liu, *J. Chem. Phys.* **112**, 4536 (2000); R. T. Skodje, D. Skouteris, D. E. Manolopoulos, S.-H. Lee, F. Dong, and K. Liu, *Phys. Rev. Lett.* **85**, 1206 (2000).