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A Slow and Clean Fluorine Atom Beam Source Based on Ultraviolet Laser Photolysis

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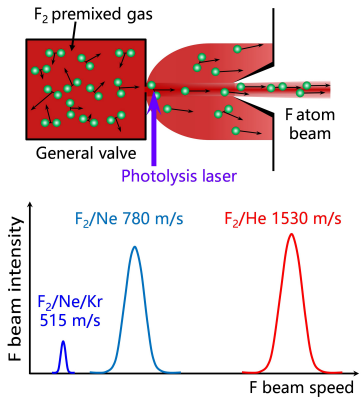
A slow and clean fluorine atom beam source is one of the essential components for the low-collision energy scattering experiment involving fluorine atom. In this work, we describe a simple but effective photolysis fluorine atom beam source based on ultraviolet laser photolysis, the performance of which was demonstrated by high-resolution time-of-flight spectra from the reactive scattering of F+HD. This beam source paved the way for studies of low energy collisions with fluorine atoms.

Key words: Photolysis, Molecular beam scattering, Fluorine atom beam



I. INTRODUCTION

A huge leap forward in our understanding of chemical reactions have been witnessed in the past few decades [1–3]. In recent years, more and more attentions have been paid to reactions at temperatures below 10 K [4–7]. One of the main reasons to investigate "colder" reactions originates from the fact that quantum effects, which are expected to be ubiquitous in chemical reactions, tend to be washed out as the temperature increases. As the temperature decreases, fewer partial waves participate in the reaction. At the same time, the de Broglie wavelength of reactants approaches to or even exceeds the dimension of the interaction range of the reaction. Consequently, reactions at low temperatures provide better chances to study quantum effects, including resonances [8, 9], quantum tunnelling [5], geometric phase effects [10], and quantum interferences [11]. Moreover, the investigation on low-temperature reactions is essential to understanding the evolution of the interstellar medium.

Molecular beam scattering experiments are among the most important methods to study chemical reactions at the scale of atom and molecule. In a scattering experiment, the collision energy E_c, a direct manifestation of temperature, can be expressed as:

$$E_c = \frac{1}{2}\mu\left({v_A}^2 + {v_B}^2 - 2v_A v_B \cos\theta\right) \quad (1)$$

here μ is the reduced mass of the collision system, v_A and v_B are velocities of reactant A and B in the laboratory frame, and θ is the crossing angle of the two reactants [12]. For a given reaction system, to realize a colder collision, which means collision at a lower E_c, it is necessary to prepare slow reactants and make them collide at a shallow angle.

Many variants of molecular scattering experiments have been developed to investigate collisions at low temperatures, such as, the supersonic expansion in a single beam [13], the merged beam scattering [14], the

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near-copropagating crossed beam experiment [15], and crossed molecular beam experiments employing Stark or Zeeman decelerators [16]. We have recently built a crossed beam apparatus with multi-channel Rydberg tagging time-of-flight detection and a minimum crossing angle of 15° [17]. It has been employed to investigate the reactive scattering of F+H_2 system, which is the benchmark reaction for dynamical resonances. In recent theoretical researches, orbiting resonances in the F+D_2/HD/H_2 reaction, trapped in van de Waals well in the entrance valley, have been theoretically predicted at collision energies below 2 meV [18–20]. In order to experimentally probe the orbiting resonances, it is necessary to achieve lower collision energy for the F+H_2 reactive scattering experiment.

A robust fluorine atom beam source with a sufficiently slow velocity is the key to realize low-collision energy scattering experiments for the F+H_2 system. In previous studies, a double-stage pulsed discharge F atom beam source was developed. The generation of charged particles by the pre-ionization stage efficiently stabilizes the discharge [21, 22]. Consequently, this beam source works stably, producing a beam of fluorine atom with speed larger than 1.5 km/s at room temperature, which cannot satisfy the requirement of low-energy collision. In order to reduce the speed, a copper channel cooled by liquid nitrogen is attached to the last discharge electrode. The hot gas stream produced by the discharge is confined in the channel and collides with the cold wall before supersonic expansion into the vacuum. So the gas stream is efficiently cooled down by the cold copper channel, resulting in a speed of about 0.8 km/s. This beam is adequately slow for F+H_2 reactive scattering experiments below the collision energy of 2 meV. However, the intensity of the fluorine atom beam, which is crucial to the scattering experiment, is significantly attenuated by the additional cooling channel due to recombination of fluorine atoms. Moreover, the reactive scattering signal is extremely small at low collision energy, and any reactive impurity in the beam may bring serious background noises to blur the signal. So a clean beam, which contains negligible impurities that may contaminate the signal, is especially crucial for low energy reactive scattering experiments. We have recently developed a slow and clean fluorine atom beam source based on ultraviolet (UV) laser photolysis. It is an ideal beam source for molecular beam scattering experiments involving the fluorine atom as one of the reactants.

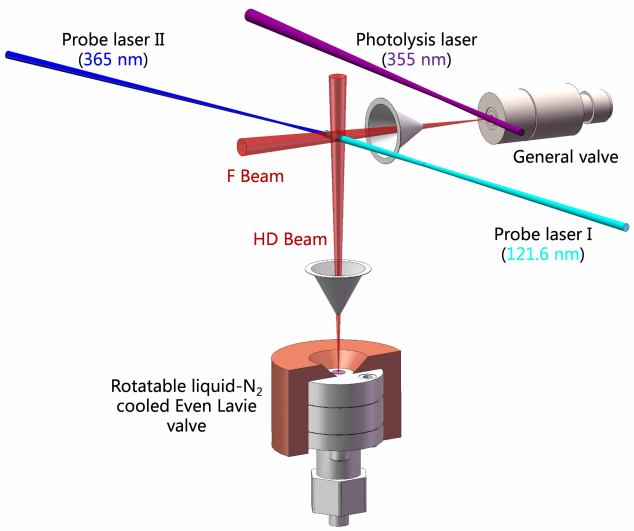

FIG. 1 A schematic of the experimental setup.

II. EXPERIMENTS

A schematic of the experimental setup is shown in FIG. 1. A pulsed valve (General valve, serial 9, Parker Hannifin Corp.) was employed to produce the molecular beam by the supersonic expansion of a premixed gas containing F_2 as the precursor. An ultraviolet (UV) laser, acting as the photolysis laser, intersected the molecular beam as close as possible to the nozzle tip and dissociated molecular fluorine to produce atomic fluorine. The photolysis laser was generated from the third harmonic of an Nd:YAG laser (Beamtech Optronics Co., Ltd., Model Nimma Extra) with a pulse energy of 185 mJ at 355 nm. The spot diameter of the photolysis laser was about 1.5 mm at the intersection region. To evaluate the quality of the fluorine atom, we carried out crossed molecular beam experiments of F+HD→HF+D and F+HD→DF+H. A beam of HD molecules was generated from another pulsed valve (LAMID Ltd., Model EL-5-C-SS-HRR-2014) cooled by liquid nitrogen at a speed of 1240 m/s and a speed-ratio of 35. After passing through skimmers, the F beam and the HD beam intersected each other at the crossing region. The D (or H) atoms produced from the reaction were excited to a high-lying Rydberg state via a two-step excitation by absorption of a 121.6-nm photon and a 365-nm photon. The D (or H) atoms in the Rydberg state maintained their nascent velocity and flight a certain distance until detected by the micro-channel plate (MCP) detector, in

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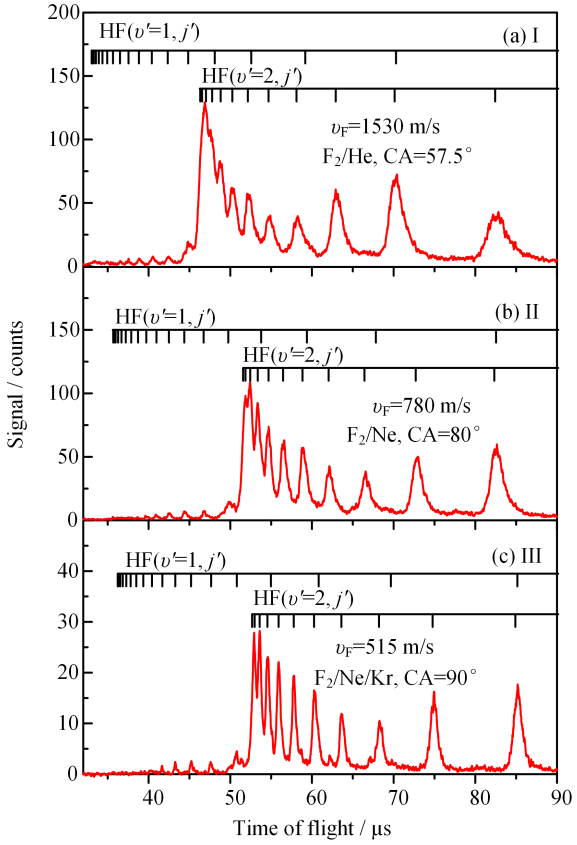

FIG. 2 Three typical TOF spectra of D atoms from the F+HD→HF+D reaction at collision energy around 0.56 kcal/mol in the backward scattering direction using three different F beams (v_F: the speed of the fluorine atom beam. CA: crossing angle of the two reactant beams).

the form of time-of-flight (TOF) spectra.

FIG. 2 shows three typical TOF spectra of D atoms of the F+HD→HF+D reaction at collision energy around 0.56 kcal/mol in the backward scattering direction. The prominent peaks can be attributed to HF products in the v'=2 state. A series of smaller peaks can be attributed to HF products in the v'=1 state. All these peaks are very sharp, and notably, even the HF (v'=2, j'=2) is clearly separated from other peaks, indicating the very high quality of the fluorine atom beam. No apparent background is observed in the TOF spectra, implying that the beam is very clean. Based on the conservation of momentum and energy, the velocity of the fluorine atom beam can be obtained by fitting the TOF spectra. The detailed parameters of the fluorine atom beam source are listed in Table I. By changing the carrier gas, the speed of the fluorine atom beam can be tuned in a very wide range, with a minimum speed of 515 m/s. In order to estimate the relative intensity of

TABLE I Detailed parameters (composition of the premixed gas, F atom speed v_F, and relative beam intensity) of the fluorine atom beam source (v_F in m/s).

F beam	Composition	v_F	Intensity
(I)	5%F_2/95%He	1530	5.3
(II)	5%F_2/95%Ne	780	4.8
(III)	2.4%F_2/45.6%Ne/52%Kr	515	1

the fluorine beam, the signals in three TOF spectra in FIG. 2 were summed up respectively and then divided by the sum of signal in FIG.2(c). The beam intensity of (I) and (II) is similar, while the intensity of (III) is about one-fifth of (I) or (II). The concentration of F_2 in (III), which is about half of (I) or (II), partly explains the attenuation of the beam intensity. In beam (III), krypton, which is much heavier than the fluorine atom, is used as the carrier gas. During the formation of a molecular beam, the lighter species tend to be "kicked out" of the flow axis [23]. We believe this is another reason for the attenuation of the beam.

FIG. 3 shows a TOF spectrum of H atoms from the F+HD→DF+H reaction at collision energy around 0.46 kcal/mol in the backward scattering direction, using neon as the carrier gas. Besides contribution from the ground reaction of F+HD→DF+H, the contribution from the reaction of HD with the spin-orbit excited F atom (denoted as F*), F*+HD→DF+H, is clearly observed. So the photolysis source yields fluorine atoms not only in the ground spin-orbit state but also in the excited spin-orbit state, making it a potential beam source for investigating the scattering of F* [22, 24].

III. DISCUSSION

In a discharge atomic beam source, violent collisions between molecules and atoms in the gas stream introduced by the discharge are essential to dissociate molecular precursors into atoms. Consequently, both the precursor molecules and the carrier gas are unavoidably heated in the gas stream. Subsequently, to achieve a low velocity, it is necessary to remove the heat in the gas stream through the additional cooling channel, resulting in the attenuation of the beam intensity. In contrast, in a photolysis beam source, only precursor molecules absorb photon energy and dissociate into atoms, while the carrier gas (in most case noble gas) does not absorb the photon energy. In most case, the precursor

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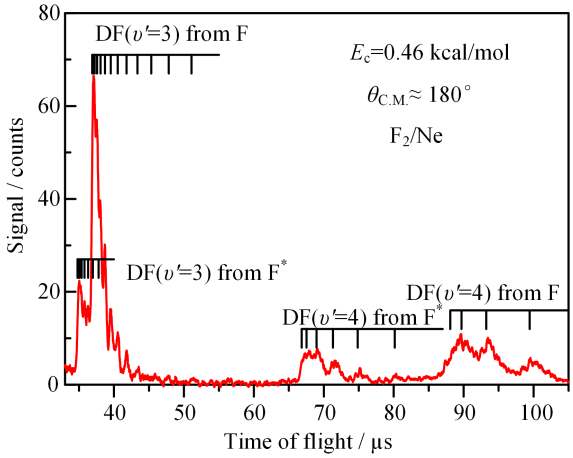

FIG. 3 A typical TOF spectrum of H atoms from the F/F*+HD→DF+H reaction at the collision energy of 0.46 kcal/mol in the backward scattering direction using F atom beam source.

gas makes up only a small portion of the gas stream, so the heating effect in the photolysis beam source is minimal. Consequently, no subsequent cooling of the gas stream before the supersonic expansion is required for achieving a slow beam velocity.

This photolysis fluorine atom beam source has many advantages. Firstly, its structure is straightforward. Compared with the discharge source, the photolysis source needs neither electrodes nor further modification of the pulsed valve for vacuum sealing at cryogenic temperature. Secondly, for the discharge source, the corrosion of electrodes sets a limit for the lifetime of stable discharge, while no such limit exists for the photolysis source. As a result, the photolysis source can work for a very long time stably. Thirdly, before the supersonic expansion in the discharge source, the gas stream from the pulsed valve has to go through the discharge region and the cooling channel, which brings serious disturbance to the gas stream, leading to degradation of the beam quality. In contrast, in the photolysis source, the supersonic expansion happens immediately at the nozzle tip, so the beam quality is much better.

The UV photolysis laser should be focused onto a region as close to the nozzle as possible, ensuring F atoms are generated before the supersonic expansion is finished. Although F atoms produced from the UV photolysis possess nascent velocity and angular distributions, sufficient collisions experienced by F atoms during the free jet expansion at the nozzle tip will translationally cool the F atoms, resulting in only one velocity component of the beam, which is weakly related with the photolysis wavelength but determined by the nozzle temperature. In order to avoid the generation of active species from laser ablation, it should be noted that the irradiation of the UV laser on the nozzle must be avoided.

In this work, a photolysis laser at 355 nm was employed to dissociate the F_2 molecules. However, we should note that the absorption coefficient of F_2 in the UV range has a maximum at about 280 nm, and the absorption at 355 nm is considerably weak [25]. So an effective photolysis beam source of fluorine atoms based on UV photolysis of F_2 at 355 nm is quite unexpected. If a different wavelength is used for photolysis, for example, 266 nm, where the absorption of F_2 is much stronger than that at 355 nm, the intensity of the fluorine atom beam is expected to be significantly enhanced. Another possible way to enhance the beam intensity is to boost the concentration of F_2 in the premixed gas. It should be noted that the pulsed valve worked at room temperature in this work. In order to generate a slower fluorine atom beam, the nozzle of the pulsed valve could be cooled down, ensuring that the supersonic expansion of the premixed gas begins at a lower temperature.

This work demonstrates the attractiveness of atomic beam sources based on laser photolysis over those based on discharge. For the most small molecules, the photon absorption in the vacuum ultraviolet (VUV) spectrum range is very strong [26]. So the generation of atomic beams with small molecules as the precursor by the VUV photolysis is expected to be a general method. Further attempts of the generation of high-quality atomic beam sources will be carried out using the newly constructed Dalian Coherent Light Source (DCLS), which is capable of producing the VUV laser pulse with unprecedented brightness in the range of 50−150 nm.

IV. CONCLUSION

In this work, we describe a robust beam source of fluorine atom based on photolysis of molecular fluorine by a UV laser. The quality of the beam was demonstrated by crossed molecular beam experiments of F+HD→HF+D. The beam was found to be very clean, and the speed can be tuned in a wide range at a minimum speed of 515 m/s. Further improvements, including enhancement of beam intensity and the further slowdown of the speed, could be expected. This simple

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but effective fluorine atom beam source paves the way for low energy collisions involving fluorine atoms.

V. ACKNOWLEDGEMENTS

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