

# A study on cold ion-molecule reactions between sympathetically cooled ions and rotationally cooled polar molecules

Atomic Physics Laboratory B1578511 Yusuke Takada

## 1. Introduction

Cold ion-molecules reactions play important roles in synthesis of interstellar molecules and chemical evolution in interstellar clouds [1, 2]. In astrochemistry the time evolution of the chemical composition in interstellar molecular clouds is numerically calculated using astrochemical reaction networks and databases, such as the UMIST database for better understanding of the chemical evolution [3]. Since most of the reaction-rate constants compiled in the database were measured at near room temperature, the reaction-rate constants at low temperatures were estimated by extrapolated values [3]. Actually most of experimental reaction-rate constants were measured by a conventional ion-cyclotron resonance (ICR) technique and swarm techniques, such as selected ion-flow tube and flowing afterglow. In particular the experimental reaction-rate constants between molecular ions and polar molecules (PMs) at low temperatures are insufficient owing to experimental difficulties, such as condensation and sublimation of polar gases at low temperatures. Thus, the scaling formula obtained by numerical simulations is often used to estimate the reaction-rate constants in astrochemistry [4]. However, these estimated values should be tested by experiments.

In the above contexts, the reaction-rate constants of some cold ion-PM reactions have been measured in our laboratory using a new experimental technique, which combines sympathetic laser cooling in a linear Paul trap for generating cold molecular ions with a Stark velocity filter for producing cold PMs [5]. Unfortunately the measurements were performed only at restricted translational and rotational temperatures of PMs. Actually the translational temperatures were lower than 10 K, which was limited by a curvature radius of a Stark velocity filter. The rotational temperature of velocity-selected PMs was a constant because the input polar gas was fixed to room temperature.

In this work, we have improved the original experimental setup in order to expand rotational and translational temperatures of velocity-selected PMs. Specifically, we have introduced a temperature

variable gas nozzle and buffer gas cell as a source of polar gases, and developed a new linear Stark velocity filter to change the translational temperature of PMs over the temperature range of molecular clouds without changing a beam position. We have performed time-of-flight measurements for velocity selected  $\text{ND}_3$  and  $\text{CH}_3\text{CN}$ , and determined the translational temperature range that could be varied. On the other hand, the rotational temperatures were evaluated by comparing the experimental results with numerical simulations.

Finally, we measured the reaction-rate constants between rotationally cooled  $\text{CH}_3\text{CN}$  and sympathetically cooled  $\text{Ne}^+$  and  $\text{N}_2\text{H}^+$  using the temperature variable gas nozzle. The effective rotational temperature dependence on the reaction-rate constants was studied.

## 2. Experimental Setup

Figure 1 shows a schematic drawing of our experimental setup. A linear Paul trap (LPT) is located in front of the exit of the Stark velocity filter. The LPT consists of four segmented SUS304 rods with a diameter of 8 mm. The inner radius of the LPT is 3.5 mm. The base plate of the LPT is cooled by a liquid-nitrogen in order to evacuate background polar gases.  $\text{Ca}^+$  ions are trapped by the laser-ablation method and are laser cooled for sympathetic laser cooling of molecular ions [5]. The diode lasers with oscillation wavelength of 397 nm and 866 nm are used for laser cooling of  $\text{Ca}^+$ . The laser induced fluorescence (LIF) from  $\text{Ca}^+$  is observed with a cooled CCD camera.

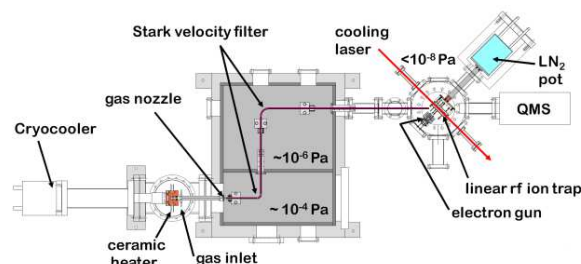


Fig.1 Experiment setup

The slow PMs are produced by a Stark velocity filter as shown in the left side of Fig.1. The chamber

containing the Stark velocity filter is divided into two parts for differential pumping. The molecular beam guide consists of four stainless steel rods with a 2 mm diameter and the distance between the adjacent rods is 1 mm. The total length of guide is about 942 mm. Maximum and minimum voltages applied to the Stark electrodes are  $\pm 3.0$  kV. The minimum curvature radius of the deflection sections of the Stark velocity filter is 12.5 mm, which limits the maximum translational temperatures of velocity-selected polar molecules to the temperature lower than 10 K. Figure 2 shows a schematic drawing of a newly developed linear Stark velocity filter to significantly change translational temperatures of PMs. The apparatus consists of three sections, i.e., gas introduction section, deflection section for velocity selection, and molecule detection section. The translational temperature can be significantly changed without changing a beam position by replacing the deflection section with a different curvature and deflection angle. On the other hand, a temperature variable gas cell is attached to a cryocooler for generation of rotationally cooled PMs. Actually the temperature of the gas cell can be varied from  $\sim 27$  K to 300 K by simultaneously driving the cryocooler and a ceramic heater.

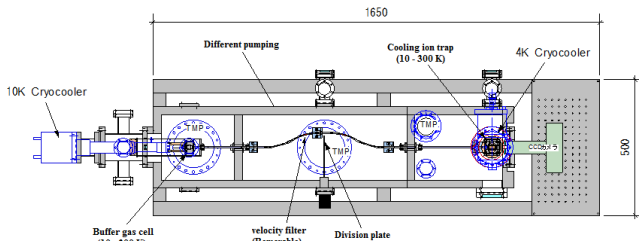


Fig.2 Schematic drawing of a linear Stark velocity filter

### 3. Results and Discussion

Figure 3 shows snapshots of the LIF images of two-species Coulomb crystal containing  $\text{Ca}^+$  and  $\text{Ne}^+$  ions before/after  $\text{Ne}^+ + \text{CH}_3\text{CN} \rightarrow$  products reactions. The dark area occupied with  $\text{Ne}^+$  ions progressively decreases with increasing the reaction time mainly due to the progress of the  $\text{Ne}^+ + \text{CH}_3\text{CN} \rightarrow \text{Ne} + \text{CH}_3\text{CN}^+$  reaction. The relative number of  $\text{Ne}^+$  ( $N_{\text{rel}}$ ) is obtained by calculating the volume of dark area in the LIF images by assuming the cylindrical column distribution of  $\text{Ne}^+$  ions as well as the constant number density, which are reasonable assumptions in our experimental conditions [5].

Figure 4 shows plots of  $N_{\text{rel}}$  as a function of the reaction time at different nozzle temperatures. The

reaction rate obviously increased for the cooled gas nozzle. There are two possible reasons why the reaction rate becomes faster at the lower nozzle temperature. First, the number density of slow  $\text{CH}_3\text{CN}$  increases because the velocity distribution shifts to the low velocity side. The second reason is that the ion-dipole capture rate between  $\text{Ne}^+$  and  $\text{CH}_3\text{CN}$  possibly increases as the rotational temperature of  $\text{CH}_3\text{CN}$  decreases.

In this presentation we will discuss the rotational cooling effect on reaction-rate constants by comparing the results between  $\text{CH}_3\text{CN}-\text{Ne}^+$  and  $\text{CH}_3\text{CN}-\text{N}_2\text{H}^+$  reaction systems. The experimental results of performance evaluation of a linear Stark velocity filter will also be presented and discussed.

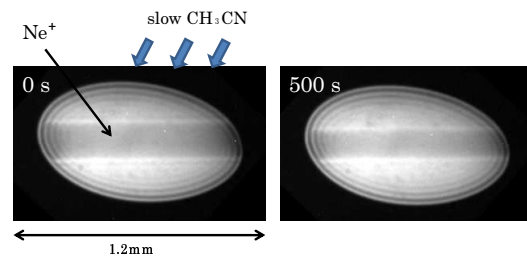


Fig.3 LIF images of two-species Coulomb crystal containing  $\text{Ca}^+$  (bright area) and  $\text{Ne}^+$  ions before/after introducing slow  $\text{CH}_3\text{CN}$  molecules.

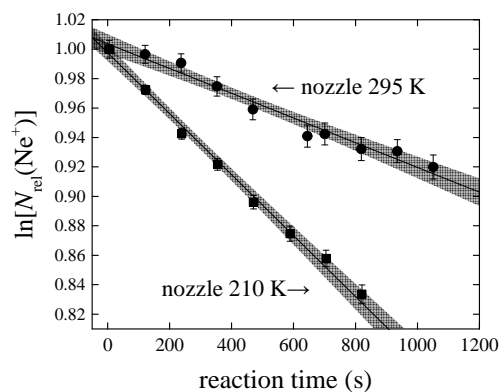


Fig.4 Plots of the relative number of sympathetically cooled  $\text{Ne}^+$  ions during  $\text{CH}_3\text{CN} + \text{Ne}^+ \rightarrow$  products reactions at different nozzle temperatures.

### Reference

- [1] E. Herbst and W. Klempler, *ApJ* **185**, 505 (1973).
- [2] V. Wakelam *et al.*, *Space Sci. Rev.* **156**, 13 (2010).
- [3] D. McElroy *et al.*, *A&A* **550**, A36 (2013).
- [4] T. Su *et al.*, *JCP* **76**, 5183 (1982).
- [5] K. Okada *et al.*, *Phys. Rev. A* **87**, 043427 (2013); *Phys. Rev. Appl.* **4**, 054009 (2015).