A study of cold molecular ion–polar molecule reactions using a Stark velocity filter combined cryogenic ion trap apparatus

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1. Introduction

Cold ion-molecule reactions play important roles in synthesis of interstellar molecules [1]. In particular, cold ion-polar molecule reactions are important for the chemical evolution in interstellar clouds [2]. Therefore, databases of rate constants have been developed for studying astrochemistry [3, 4]. However, most of the rate constants stored in the databases were measured only at room temperature or at a restricted range of temperatures near room temperature, even though the reactions occur at low temperature in interstellar clouds. Especially, cold ion-polar molecule reactions have not been studied extensively in the laboratory owing to experimental difficulties, such as condensation of polar gases at low temperatures.

Recently, a new method to directly measure cold ion-polar molecule reactions was demonstrated by combining a laser-cooling technique with a Stark velocity filter [5]. In the experiment, the reaction rate between a Ca^+ Coulomb crystal and velocity-selected CH_3F molecules was measured at about 1 K under ultra-high vacuum conditions.

In this work, we extended this kind of experiment to reaction-rate measurements between stored sympathetically cooled molecular ions and velocity-selected slow polar molecules. In a first experiment, the Stark velocity filter was connected to a cryogenic linear Paul trap and the reaction-rate measurements between laser-cooled Ca^+ Coulomb crystals and the velocity-selected polar molecules were carried out. In addition, we measured the reaction-rate constants between slow polar molecules (ND_3, CH_3CN) and sympathetically cooled molecular ions (N_2^+, N_2H^+) for the first time. A comparison between experimental rate constants and theoretical values has been carried out.

2. Experimental setup

Figure 1 shows a schematic drawing of our experimental setup. The slow polar molecules are produced by a Stark velocity filter (left section in Fig.1). The chamber containing the Stark velocity filter is divided into two parts for differential pumping. The background pressures of the first and second chambers are kept at about 10^{-4} Pa and 10^{-6} Pa during reaction-rate measurements. The molecular beam guide consists of four stainless steel rods with a diameter of 2 mm and the distance between the rods is designed to be 1 mm. The radii of the curvature of the first and second bent sections are 12.5 mm and 25 mm, respectively. The total length of the beam guide is 942 mm. In the present setup, the maximum guiding voltages applied to the quadrupole electrodes is ±3.0 kV, which corresponds to the nominal electric field of 60 kV/cm.
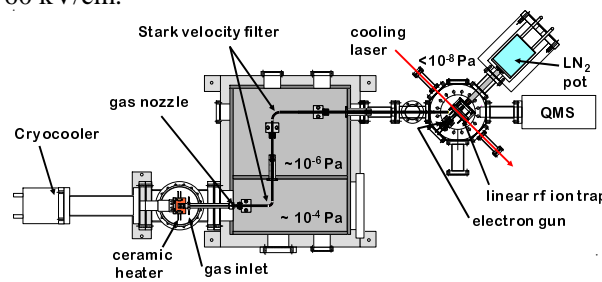

Fig. 1 Experimental setup

We confirmed the generation of slow ND_3, H_2CO, and CH_3CN molecules having thermal energies of a few Kelvin. In addition, the number densities of the slow velocity-filtered polar molecules were determined to be in the range of $n = 10^4 \sim 10^6$ cm^{-3}.

As shown in Fig. 1, a liner Paul ion trap is located in front of the exit of the Stark velocity filter. The linear Paul trap consists of four segmented rods with a diameter of 8 mm. The inner radius of the quadrupole electrodes is 3.5 mm. The base plate of the linear ion trap is cooled by a liquid nitrogen pot. This cryogenic linear trap is necessary to avoid undesirable reactions between cold molecular ions and room-temperature polar molecules.

For sympathetic laser cooling of molecular ions, Ca^+ ions are produced and trapped by the laser-ablation method, and laser-cooled. Ca^+ ions are cooled by two laser beams (wave length λ = 397 and 866 nm) and form an ion Coulomb crystal as shown in Fig. 2. Laser induced fluorescence (LIF) is observed with a cooled CCD camera at a right angle to the trap axis. After the preparation of a Ca^+ Coulomb crystal

molecular ions are produced by electron impact ionization. The molecular ions are cooled to a very low temperature by elastic Coulomb collisions with cold Ca^+ ions, i.e. sympathetic cooling effect.
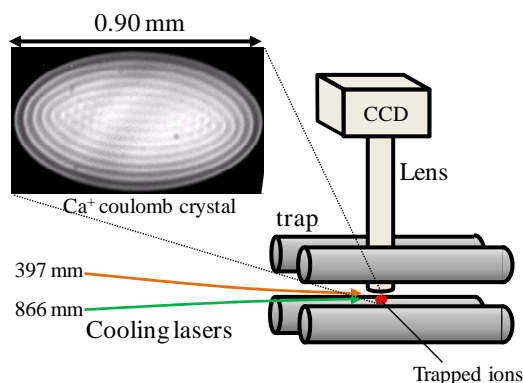

Fig. 2 A sketch of the ion trap. Ca^+ ions are cooled by two laser beams (wave length λ = 397 and 866 nm). A Ca^+ Coulomb crystal is observed using a cooled CCD camera via a telecentric lens system (upper left image).

3.   Result and discussion

Figure 3 shows fluorescence images of two-species Coulomb crystal containing Ca^+ and N_2H^+ ions during the $CH_3CN + N_2H^+ \rightarrow CH_3CNH^+ + N_2$ reaction. The sympathetically cooled N_2H^+ ions exist in a dark region in the center of the crystals. In this work, we determine the relative number of molecular ions from the LIF images by assuming the following conditions. First, we assumed the constant number density of cold trapped ions in a linear Paul trap. Actually, the number density at 0 Kelvin can be derived by Poisson's equation under the pseudopotential approximation [6]. Moreover, we assume the cylindrical symmetry of the spatial distribution of N_2H^+ ions. Since the number of ions contained in the edge of the ion crystal is expected to be very small, it can be ignored as a first approximation. Thus, the relative number of N_2H^+ ions can be determined from the volume of the shadowed area of the LIF images. Figure 4 shows a plot of the relative number of N_2H^+ as a function of reaction time. The deduced reaction rate is 2.4(0.4) $\times$ 10^{-3} /s. We repeated the same measurements eight times and obtained the averaged reaction rate of 1.9(0.1) $\times 10^{-3}$ /s. Using the number density of CH_3CN, the reaction-rate constant is determined to be k_{exp} = 1.6(0.5) $\times 10^{-8}$ cm^3/s. Since the average kinetic energy of sympathetically cooled N_2H^+ ions is estimated to be lower than 1 K from the molecular dynamics simulation [7], the average collision energy of this reaction system is estimated to be lower than 3.0 K.

For comparison, we estimate a realistic ion-polar neutral capture rate by using the trajectory scaling formula, which is often used in astrochemistry [8].

The calculated value is k_{ts} = 3.8×10^{-8} cm^3/s. On the other hand, the experimental reaction-rate constant was measured at room temperature [9] and the value (k_{RT} = 4.1 $\times$ 10^{-9} cm^3 / s) is stored in the UMIST database. In astrochemistry, k_{RT} is extrapolated to low temperature using $k_{UD} = k_{RT} (T/300)^{1/2}$ [3]. The rate constant at 3.0 K is calculated to be $k_{UD} = 4.1 \times 10^{-8}$ cm^3/s. Compared to the present experimental value of k_{exp}, these speculated reaction-rate constants seem to be overestimated by a factor of 2. The detailed discussions and the other results will be presented at the oral presentation and the master thesis.
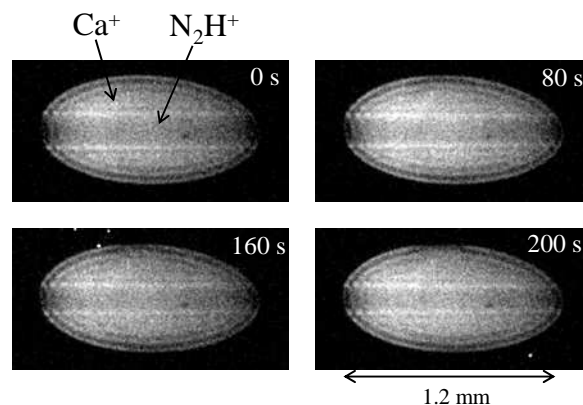

Fig. 3 Fluorescence images of two-species Coulomb crystal including Ca^+ and N_2H^+ during the $CH_3CN + N_2H^+ \rightarrow CH_3CNH^+ + N_2$ reaction.
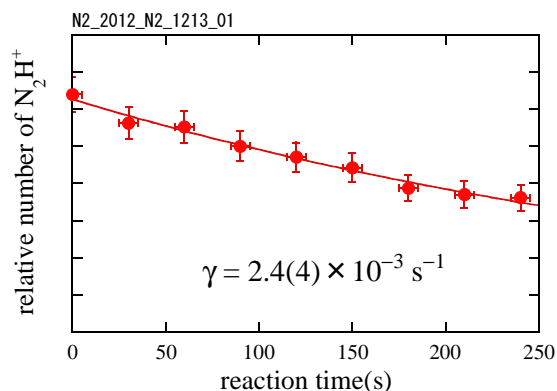
Fig. 4 A plot of relative number of N_2H^+ as a function of reaction time in $CH_3CN + N_2H^+ \rightarrow CH_3CNH^+ + N_2$ reaction.

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