Laser-induced reactions between a Ca\(^+\) Coulomb crystal and polar molecules

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Abstract. We have studied laser-induced reactions between a Ca\(^+\) Coulomb crystal and the polar molecules of NH\(_3\) and ND\(_3\) at room temperature. The reaction rates of Ca\(^+\) (\(^{3}d\(^2\)D\(_{3/2}\), \(^{4}p\(^2\)P\(_{1/2}\)) + NH\(_3\) (ND\(_3\)) \rightarrow \text{products}\) have been determined from time variation of the size of fluorescence images of Ca\(^+\) Coulomb crystals. The results show that the reaction rates are very slow, and therefore the reaction-rate measurements between sympathetically cooled molecular ions and slow NH\(_3\) (ND\(_3\)) molecules can be performed using a Ca\(^+\) Coulomb crystal as coolant.

1. Introduction
Cold ion-molecule reactions play important roles in the synthesis of interstellar molecules and the chemical evolution of interstellar clouds. Some of the database of reaction-rate constants related to astrochemistry have been built for a simulation study of interstellar clouds. [1, 2, 3]. Recently, it was pointed out that the rate constants of ion-polar neutral reactions are not sufficiently well known to understand the chemical evolution in interstellar clouds [4, 5]. In fact the reactions between ions and polar molecules have not been studied extensively in the laboratory due to experimental difficulties. A few studies have been performed by the drift tube and CRESU (the pulsed Laval nozzle variant) techniques [6, 7].

Recently a new method to determine the reaction rates between cold molecular ions and slow polar molecule has been proposed [8]. In this experiment, slow polar molecules produced by a Stark velocity filter collide with cold molecular ions which are prepared by a sympathetic cooling technique in a linear Paul trap [9, 10]. This method can be extended to study a multitude of cold ion-polar molecule reactions. We plan to perform such experiments namely measurements of cold ion-polar molecule reactions between sympathetically cooled molecular ions and cold polar molecules. In this connection we have already developed a Stark velocity filter and succeeded in producing cold polar molecules (PM) of ND\(_3\), NH\(_3\), CH\(_2\)O and CH\(_3\)CN [12]. Moreover, we have demonstrated sympathetic crystallization of cold CaH\(^+\) ions in the linear Paul trap [13]. The goal of our work is to take the benchmark data in order to test quantum chemical calculations and also to test the scaling formula of capture rates of cold ion-polar molecule collisions [11].
In this paper, we report on the results of the reaction-rate measurements of Ca$^{+*}$(3d$^2D_{3/2}$, 4p$^2P_{1/2}$) + NH$_3$ (ND$_3$) → products.

2. Experiment

2.1. Apparatus

A detailed description of our experimental apparatus is found in previous papers [14, 15, 16, 13]. Here we present a brief summary of the apparatus.

The linear Paul trap consists of stainless steel rod with a diameter of 8 mm. The closest distance between the trap axis and the surface of the rod is $r_0=3.5$ mm. The length of the center section is 10 mm. A compact miniature vacuum chamber enclosing the linear ion trap is evacuated by an ion pump and a turbo molecular pump backed by a rotary pump. The ion trap is mounted on a cryogenic baffle containing liquid-nitrogen to obtain an ultra-high vacuum. This cryogenic baffle is used as an auxiliary cryopump to sustain a Ca$^+$ Coulomb crystal for a long time.

For laser cooling of the stored Ca$^+$ ions two grating stabilized laser diodes (λ=397 and 866 nm) are used. Both lasers are locked to a frequency-stabilized Helium-Neon laser through a transfer cavity. The relative frequencies of the lasers are determined by monitoring the cavity signals [17]. With this stable laser arrangement an ion crystal can be sustained for more than half day. A laser-induced fluorescence (LIF) image at 397 nm is observed by a cooled charge-coupled device (CCD) camera at a right angle to the trap axis. The camera with a 10× lens system is mounted on a precision stage outside the vacuum chamber to find the imaging position. Since the magnification of the detection optical system is known, we can determine the size of the fluorescence image. Thus, the numbers of Ca$^+$ ions and sympathetically cooled molecular ions can be determined by applying the methods described in the previous papers [13, 16].

Table 1. Ca$^+$+PM reactions of interest. The reaction enthalpies (ΔH) were obtained by a quantum chemical calculation code [19].

| Reaction                | ΔH (eV) | Reaction                | ΔH (eV) |
|-------------------------|---------|-------------------------|---------|
| Ca$^+$+NH$_3$ → Ca(NH$_3$)$^+$ | -1.33   | Ca$^+$+ND$_3$ → Ca(ND$_3$)$^+$ | -1.34   |
| CaNH$^+$ + H            | +1.30   | CaND$_2^+$ + D          | +1.43   |
| CaNH$^+$ + H$_2$        | +1.61   | CaND$^+$ + D$_2$        | +1.71   |
| CaH$^+$ + NH$_2$        | +2.25   | CaD$^+$ + ND$_2$        | +2.34   |
| Ca$^+$+CH$_3$CN → Ca(CH$_3$CN)$^+$ | -1.29   | Ca$^+$+H$_2$CO → Ca(H$_2$CO)$^+$ | -1.26   |
| CaH$^+$ + CH$_2$CN      | +2.01   | CaH$^+$ + CHO           | +1.44   |

2.2. Laser-induced reactions between Ca$^+$ Coulomb crystals and polar molecules

In order to perform reaction-rate measurements using sympathetically cooled molecular ions we have to know the reaction rate between a specific polar molecule and a Ca$^+$ Coulomb crystal because the coolant Ca$^+$ ions must be kept for cooling molecular ions during the experiment. In the Ca$^+(4s^2S_{1/2}) +$ NH$_3$ reaction system only the slow radiative association process is an exothermic reaction, where the reaction enthalpy is calculated as ΔH = -1.33 eV [19]. However, for the laser-excited Ca$^{+*}$ the other reactions as listed in Table 1 possibly occur because the excited state energies of 4p$^2P_{1/2}$ and 3d$^2D_{3/2}$ of Ca$^{+*}$ are 3.1 and 1.7 eV, respectively. A similar situation applies in the other Ca$^+$ + PM reaction systems (Table 1).
We have experimentally studied the laser-induced reactions between a Ca$^+$ Coulomb crystal and the polar molecules of NH$_3$ and ND$_3$ at room temperature. The crystallized Ca$^+$ ions were excited to the $^2D_{3/2}$ and/or $^2P_{1/2}$ state by switching the cooling lasers ($\lambda = 397$ nm, 866 nm). When both the cooling lasers shine Ca$^+$ ions, almost all of the Ca$^+$ ions are in the ground state. In this case, there are only very small populations in the excited states. The populations in the excited states can be evaluated by solving optical Bloch equations of the 3-level system. On the other hand, we can transfer almost all of the Ca$^+$ ions into the metastable $^2D_{3/2}$ state simply by blocking the 866 nm laser. In order to keep the size of the Ca$^+$ Coulomb crystal the blocking time of the cooling lasers was set to 0.5 s, and the duration of the cooling lasers is set to 2.5 s.

Figure 1 (a) shows the LIF images of the Ca$^+$ Coulomb crystal before and after the laser-induced reaction. Since the size of the LIF image decreases and the dark area in the upper part extends as the reaction time increases, we confirmed that a large number of molecular ions were produced. As we already explained in the previous paper [13], the weak asymmetric static fields pushed heavier ions to the upper side of the image. In order to search the mass of the product molecular ions we performed the LIF mass spectrometry [20]. As shown in Fig. 1, the production of molecular ions was also confirmed by this measurement. Although the mass of the molecular ions was not identified by this destructive measurement, the ions are expected to be CaD$^+$, CaND$^+$ and CaND$_2^+$ from the energy diagram of the Ca$^+$+ND$_3$ reaction system [19].

The procedure of the state-selected reaction-rate measurement is as follows. First, we measured a decay rate ($\gamma_{bg}$) by the background-gas collisions (mainly H$_2$) before starting the reaction-rate measurement. Then an ammonia gas of a few times $10^{-6}$ Pa was leaked into the vacuum chamber. We measured a decay rate ($\gamma_2$) by irradiating both the cooling lasers. Finally, the reaction rate $\gamma_P$ of the Ca$^{++}(^2P_{1/2})$ + NH$_3$ (ND$_3$) reaction was derived by $\gamma_2 - \gamma_{bg}$. On the other hand, we measured a decay rate ($\gamma_3$) by chopping the 866 nm laser to determine the reaction rate $\gamma_D$ of the Ca$^{++}(^2D_{3/2})$ + NH$_3$ (ND$_3$) reaction, which can be obtained by $\gamma_3 - \gamma_2$.

Figure 2 shows decay curves of the relative numbers of Ca$^+$ ions which were determined by
the sizes of the Ca$^+$ fluorescence images [13]. By fitting the exponential function to the data, we obtained $\gamma_{bg}$ and the nominal decay rates of $\gamma_2$ and $\gamma_3$. Then the reaction rates of $\gamma_P$ and $\gamma_D$ are extracted by the above procedure. It is to be noted that the reaction rate of the Ca$^+$(2$^2S_{1/2}$) + NH$_3$ → Ca(NH$_3$)$_2^+$ is negligible. This was confirmed by comparing $\gamma_P$ and the decay rate determined by blocking both the cooling lasers.

We have determined $\gamma_P$ and $\gamma_D$ at several NH$_3$ pressures. Then the least-squares fits of $\gamma = \sum_i k_i n_i + kn$ to $\gamma_P$ and $\gamma_D$ were carried out in order to obtain the reaction-rate constant $k$, where $n$ is the number density of NH$_3$ molecules and $n_i$ and $k_i$ are the number densities and the reaction-rate constant of an impurity gas $i$. Since the variation of impurity gases was negligible, $\sum_i k_i n_i$ was regarded as a constant.

An example of the analysis is shown in Fig. 2(c). As assumed, the residual term $\sum_i k_i n_i$ was negligible. In the present experiment, only a lower limit value of the reaction-rate constant was determined from the slope of the decay curve because the actual NH$_3$ (ND$_3$) pressure should be slightly lower than the nominal pressure which was read on the place near the cryogenic ion trap region. A summary of the reaction-rate measurements is shown in Table 2.

The estimated reaction-rate constant of Ca$^{++}$(2$^2P_{1/2}$)+NH$_3$ (ND$_3$)→ products is $k_P > 1.3 \times 10^{-9}$ (4.1$\times 10^{-10}$) cm$^3$/s, where the population of the 4$^2P_{1/2}$ state of Ca$^+$ is calculated to be 4.2$\times 10^{-4}$ in the present experimental conditions by solving optical Bloch equations for the 3-level system [13].

The estimated values are consistent with the reaction-rate constant calculated by the well-known scaling formula of $k_t = (0.4767x + 0.62)k_L$, $x = \mu_D/\sqrt{2\alpha kT}$, where $k_L$ is the Langevin rate, $\mu_D$ is the dipole moment, and $\alpha$ is the polarizability [11]. In the present reaction system, the formula gives $k_t = 2.3 \times 10^{-9}$ cm$^3$/s.

On the other hand, a lower limit value of the reaction-rate constant of Ca$^+$(2$^2D_{5/2}$)+NH$_3$ (ND$_3$) was 1.1(0.8)$\times 10^{-11}$ (8.5(3.7)$\times 10^{-11}$) cm$^3$/s, where we adopted $\rho_D = 1$. The values are much smaller than $k_P$. This suggest that there is a small energy barrier in the reaction path of the D-state reaction.
Table 2. Lower limit values of the reaction-rate constants of the Ca\textsuperscript{+}+NH\textsubscript{3} (ND\textsubscript{3}) reactions. \(k\) and \(k\) are the populations of the 4\(p\)\(2\)\(P\textsubscript{1/2}\) and 3\(d\)\(2\)\(D\textsubscript{3/2}\) states of Ca\textsuperscript{+}, respectively.

| Reaction                                      | \(k\) (cm\textsuperscript{3}/s) |
|-----------------------------------------------|----------------------------------|
| \(\text{Ca}^+\left(2\text{P}_{1/2}\right) + \text{NH}_3 \rightarrow \text{products}\) | \(5.4(3.0) \times 10^{-13}/\rho_P\) |
| \(\text{Ca}^+\left(2\text{D}_{3/2}\right) + \text{NH}_3 \rightarrow \text{products}\) | \(1.1(0.8) \times 10^{-11}/\rho_D\) |
| \(\text{Ca}^+\left(2\text{P}_{1/2}\right) + \text{ND}_3 \rightarrow \text{products}\) | \(1.7(1.9) \times 10^{-13}/\rho_P\) |
| \(\text{Ca}^+\left(2\text{D}_{3/2}\right) + \text{ND}_3 \rightarrow \text{products}\) | \(8.5(3.7) \times 10^{-12}/\rho_D\) |

2.3. Summary and Future Prospects
In summary we measured the reaction rates of the laser-induced reactions between a Ca\textsuperscript{+} Coulomb crystal and the polar molecules of NH\textsubscript{3} and ND\textsubscript{3}. The results show that the reaction rates are very slow compared to typical reaction rates of ion-polar neutral reactions, and therefore the reaction-rate measurements between sympathetically cooled molecular ions and slow NH\textsubscript{3} (ND\textsubscript{3}) molecules can be performed using a Ca\textsuperscript{+} Coulomb crystal as coolant.

As another technical issue, various cold molecular ion samples must be prepared in the linear ion trap by the sympathetic cooling method. We have already demonstrated the sympathetic cooling of CaH\textsuperscript{+} [13], N\textsubscript{x}\textsuperscript{+} and ND\textsubscript{x}\textsuperscript{+}(\(x = 2, 3\)) ions. Figure 3 shows the LIF images of the Ca\textsuperscript{+} Coulomb crystal before and after the production of ND\textsubscript{x}\textsuperscript{+}(\(x = 2, 3\)) molecular ions by electron impact ionization. We clearly see a dark area along the major axis of the crystal in the right picture shows the existence of cold molecular ions. The number of the molecular ions is estimated to be more than 300. The rf frequency and the amplitude are \(f_{rf} = 4.842\) MHz and \(V_{ac} = 192\) V, respectively. The laser detuning of 397 nm is set to \(-30\) MHz. A sample ND\textsubscript{3} gas of about \(5 \times 10^{-8}\) Pa was leaked in the detection vacuum chamber through the variable leak valve. The electron beam energy was set to 250 eV.

Figure 3. The LIF image of the Ca\textsuperscript{+} Coulomb crystal before and after the production of ND\textsubscript{x}\textsuperscript{+}(\(x = 2, 3\)) ions by electron impact ionization. The dark area along the major axis of the crystal in the right picture shows the existence of cold molecular ions. The number of the molecular ions is estimated to be more than 300. The rf frequency and the amplitude are \(f_{rf} = 4.842\) MHz and \(V_{ac} = 192\) V, respectively. The laser detuning of 397 nm is set to \(-30\) MHz. A sample ND\textsubscript{3} gas of about \(5 \times 10^{-8}\) Pa was leaked in the detection vacuum chamber through the variable leak valve. The electron beam energy was set to 250 eV.

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