Production and application of cold molecular ions by sympathetic laser cooling

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1. Introduction

Over the past decades atomic and molecular physics was in a scientific revolution caused by the development of cooling methods of atoms and molecules [1-4]. Scientific communities studying quantum optics [5], precision spectroscopy [6,7] and cold chemical reactions [8] are strongly interested in producing cold atoms, molecules and the ions because of their various potential applications.

For example, in the field of fundamental physics the measurement of the time dependence of electron-proton mass ratio, $\beta = m_p / m_e$, by precise molecular spectroscopy of cold molecular ions was proposed [9]. In 2009 *Kajita et al*. proposed a new scheme to perform precision spectroscopy of pure vibrational transitions of a single cold molecular ion, such as $^{40}CaH^+$, using quantum logic spectroscopy [10]. Since the ultimate uncertainty of the vibrational spectroscopy of $^1\Sigma(n_v, J, F, M) = (0, 0, 1/2, \pm 1/2) \rightarrow (1, 0, 1/2, \pm 1/2)$ transition is expected to be lower than 10^{-16}, we will be able to obtain the variation in β by observation of such the transition for a long term.

As a first step of spectroscopic study of CaH^+, we investigated the production process of CaH^+ by laser-induced reaction of $Ca^+(4p^2P_{1/2}) + H_2 \rightarrow CaH^+ + H$. The reaction rates were measured under typical experimental conditions and the reaction rate coefficient at room temperature was deduced. Moreover we studied sympathetic Coulomb crystallization of CaH^+ ions by laser-cooled Ca^+ ions in a linear Paul trap. The characterization of two species Coulomb crystals was performed by comparing experimental fluorescence images to simulated images which are obtained by molecular dynamics (MD) simulations.

In the field of astrochemistry, the reaction rate coefficients of cold chemical reactions as well as a reaction network model in interstellar clouds are of interest to understand their chemical evolution. Low temperature molecular ion-polar molecule reactions especially play an important role in the chemical evolution of dark interstellar clouds [11]. Recently a new method for studying cold ion-polar molecule reactions was developed by combining a laser cooling technique with a Stark velocity filter [7]. This experimental method can be extended to study cold chemical reactions between sympathetically cooled molecular ions and slow polar molecules. Then, for this purpose we have been developing a new apparatus consisting of a cryogenic linear ion trap and a Stark velocity filter.

In order to measure cold ion-polar molecule reaction rates using sympathetically cooled molecular ions, the reactivity between polar molecules and the laser cooled Ca^+ ions must be known. Therefore we also investigated laser-induced reactions between a Ca^+ Coulomb crystal and ammonia molecules (NH_3 and ND_3) to evaluate the reactivity. In the experiment we perform the state selected reaction rate measurement of $Ca^{+*}(3d^2D_{3/2}, 4p^2P_{1/2}) + NH_3(ND_3) \rightarrow$ *products* at several ammonia pressures. Then we deduced the reaction rate constant at room temperature.

2. Experimental Setup

The experimental apparatus consists of a cryogenic linear Paul ion trap, frequency stabilized lasers and fluorescence detection system. The ion trap is cooled by liquid nitrogen vessel and is enclosed in a compact ultra high vacuum chamber. Ca^+ ions are produced by laser ablation method. For laser cooling of the stored Ca^+ ions two grating stabilized laser diodes (λ = 397 and 866 nm) are used. Both the laser frequencies are locked to a frequency-stabilized Helium-Neon laser through a transfer cavity and the laser beams are incident along the trap axis. Laser induced fluorescence (LIF) at 397 nm is observed by a cooled charge-coupled device camera and a photomultiplier tube at a right angle to the trap axis. Molecular ions for sympathetic cooling experiment are produced by laser-induced chemical reactions, electron impact ionization and simultaneous laser ablation method.

3. Results and Discussion

A calcium hydride ion (CaH^+) is produced by the laser-induced chemical reaction of $Ca^+(4p^2P_{1/2}) + H_2 \rightarrow CaH^+ + H$. Since the reaction is endothermic by about 2.3 eV for the ground state Ca^+, the reaction

never proceeds without laser excitations, and therefore the cooling lasers must be irradiated for the production of CaH^+ ions. Generated CaH^+ ions were confirmed by the observation of secular motion spectra via Ca^+ fluorescence and the modified fluorescence images of crystallized Ca^+ ions.

An example LIF image of a mixed-species Coulomb crystal is shown in Fig. 1(a). Due to the existence of the asymmetric direct current voltages by the patch effect of electric charges on the electrodes, the CaH^+ Coulomb crystal was pushed to the upper side of the image. The corresponding MD simulation image shows that the sympathetically cooled CaH^+ ions were also crystallized (Fig. 1(b)) [12]. The number of crystallized CaH^+ was determined to be 40 ions. In addition, the secular temperature of 7 mK is also determined.

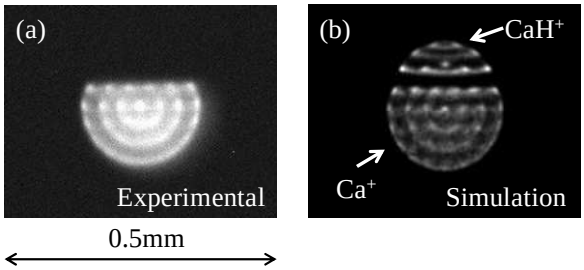

Figure 1. (a)Two-species Coulomb crystal composed of 134 Ca^+ and 40 CaH^+ ions. (b) Simulation image reproducing the observed image (a).

We measured the reaction rate of $^{40}Ca^+(4p^2P_{1/2}) + H_2 \rightarrow {}^{40}CaH^+ + H$ under the present experimental conditions. In the experiment, first we sequentially observed LIF images of the Ca^+ crystal during the reaction time, which was indicated in each image (Fig. 2). Then the numbers of Ca^+ and CaH^+ were obtained by the help of the MD simulations. The reaction rate was obtained with the decay curve of the number of Ca^+ ions (as shown in Fig. 3). Finally the similar measurements were performed for small (< 100 ions) and large (> 6000 ions) Coulomb crystals as a function of the 397 nm laser detuning. The result is shown in Fig. 4. Since the volume of a large Coulomb crystal is considered to be proportional to the number of Ca^+ ions [13], the reaction rate was determined by a decay curve of crystal volume for the large Ca^+ crystals.

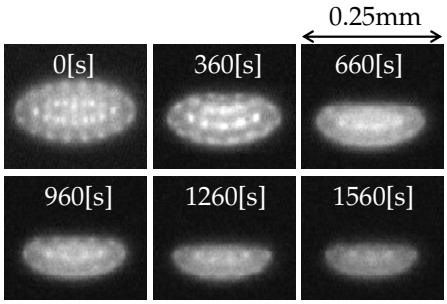

Figure 2. Systematic observation of LIF images of two-species Coulomb crystals during laser-induced chemical reaction. Initial Ca^+ ion number is 74. Introduced H_2 gas pressure : 4.8×10^{-6} [Pa].

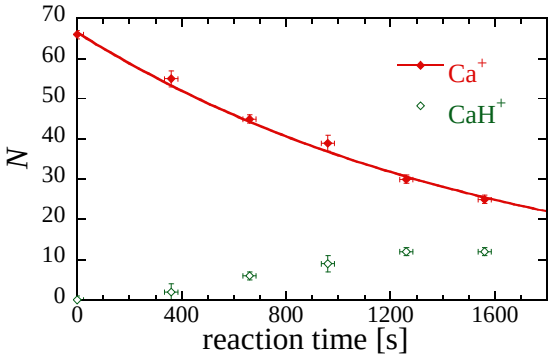

Figure 3. A plot of the ion numbers of Ca^+ and CaH^+ as a function of the reaction time. The solid line shows the best fitting exponential curve $N(Ca^+) = N_0(Ca^+)e^{-\gamma t}$ to sets of the data.

We deduce the reaction rate coefficient k of $^{40}Ca^+(4p\ ^2P_{1/2}) + H_2 \rightarrow {}^{40}CaH^+ + H$. Using the nominal H_2 pressure of 4.8×10^{-6} Pa in the vacuum chamber and the data of the maximum reaction rate in Fig.4, the deduced reaction rate coefficient is $(7.0 \pm 0.3) / \rho_e \times 10^{-13}$ cm^3/s. The P-state population ρ_e under the present experimental conditions was evaluated to be about 0.09% with the 3-level optical Bloch equation. The value gives the reaction rate coefficient of 8×10^{-10} cm^3/s, which is on the same order of the Langevin rate, $k_L = 1.5 \times 10^{-9}$ cm^3/s.

The detailed discussion and other results will be presented at the oral presentation and the master thesis.

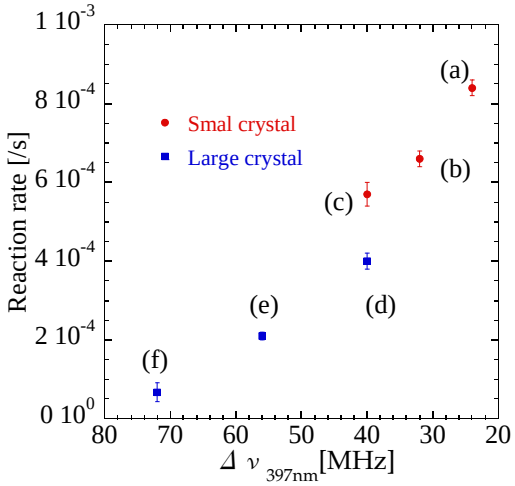

Figure 4. The 397nm laser detuning dependence of the reaction rate. Initial Ca^+ ion number (a) 74 (b) 70 (c) 94 (d) 8917 (e) 8161 (f) 6480.

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