Sympathetic crystallization of CaH^+ produced by laser-induced chemical reaction

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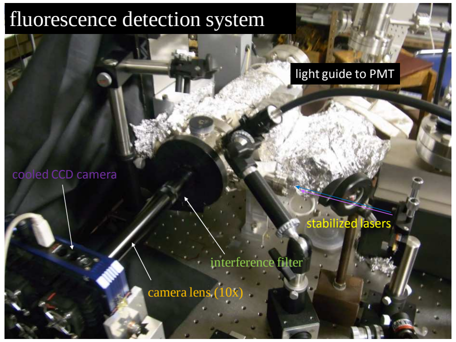
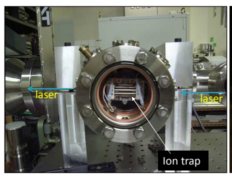
Abstract

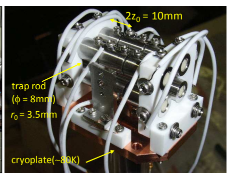
Sympathetically crystallized molecular ions in ion traps provide the ideal system for precision measurements of molecular vibrational and rotational transitions [1] as well as for studying ultracold molecular ion-polar molecule collisions [2]. The long-term measurement can be applied to the detection of time variation in fundamental physical constants, such as proton-to-electron mass ratio (m_p/m_e) [3]. Recently, Kajita *et al.*, proposed a new detection scheme of the time variation of m_p/m_e using a vibrational transition frequency of sympathetically crystallized CaH^+ ions [3, 4]. Here we investigated sympathetic Coulomb crystallization of CaH^+ ions produced by the laser-induced chemical reaction. By comparison of MD simulation images with experimental image, the number of crystallized molecular ions, the secular temperature and the structure were determined [5]. Moreover CaH^+ production rates and the dependence on the laser detuning were investigated.

Experimental Setup

A linear radio frequency ion trap (linear Paul trap) is used to simultaneously store the laser cooled atomic ions($^{40}Ca^+$) and the sympathetically cooled molecular ions(CaH^+). A compact miniature UHV chamber enclosing the 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 vessel containing liquid-nitrogen to obtain an ultrahigh vacuum. Neutral H_2 gas was introduced into the chamber via a variable leak valve. The laser-ablation method was used for producing and trapping Ca^+ ions. A Nd:YAG pulsed laser light was focused onto a metallic calcium sample, and the laser-ablated Ca^+ ions were directly trapped. Two grating stabilized diode lasers (λ = 397 and 866 nm) locked to a frequency-stabilized He-Ne laser are used for laser cooling of the trapped Ca^+ ions . An ion Coulomb crystal, which emits laser-induced fluorescence (LIF) at 397 nm, is observed by a cooled CCD camera at right angles to the trap axis and by a photomultiplier tube (PMT). The camera with the lens system and a UV filter is mounted on a precision stage outside the vacuum chamber to adjust to the imaging position of the Coulomb crystal. The magnification of the lens system was selected to 3× or 10× according to circumstances. The CCD exposure time is typically set to 10 s.

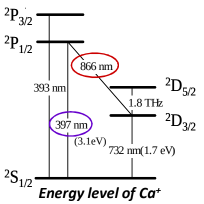






CaH^+ *Crystallization*

Laser cooling of Ca^+ and CaH^+ production



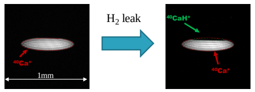
Reaction between Ca^+ and H_2 gas

$Ca^+ + H_2 \rightarrow CaH^+ + H$ - 2.27 eV

Calculated by Gaussian03

Since the reaction is endothermic about 2.3 eV for the ground state Ca^+, the reaction never proceeds without the laser excitations, and thus the cooling lasers (λ= 397 and 866 nm) must be irradiated for the production of CaH^+ ions.

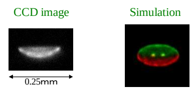
Doppler laser cooling of Ca^+ is performed on the 4s $^2S_{1/2}$ – 4p $^2P_{1/2}$ transition at a wavelength of 397 nm. An additional laser at 866 nm is required to re-pump population shelved in the metastable 3d $^2D_{3/2}$ level (τ~1s) in order to maintain the laser cooling cycle.



LN_2 cooled. B.G .<1.0×10^{-6} Pa, H_2 4.7×10^{-6} Pa.
$\Delta\nu_{uv}$ = −40MHz Reaction time≒1000[s]

Simulation images of mixed-species Coulomb crystals

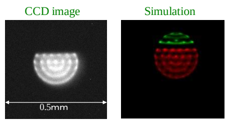
(a) $N(Ca^+)$ = 12, $N(CaH^+)$ = 15



Experimental condition
f=5.49[MHz] Vz=3.61[V] Vac=171.5[V]

Simulation parameters
Ca^+number : 12 CaH^+number : 15
Secular motion : 10[mK]

(b) $N(Ca^+)$ = 134, $N(CaH^+)$ = 40



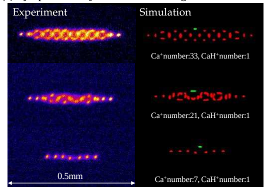
Experimental condition
f=5.49[MHz] Vz=7.1[V] Vac=171.5[V]

Simulation parameters
Ca^+number : 134 CaH^+number : 40
Secular motion : 7[mK]

As shown in the pictures, we successfully observed mixed-species Coulomb crystals of Ca^+ and CaH^+. Due to the existence of the asymmetric direct current voltages by the patch effect by electric charges on the electrodes, the CaH^+ Coulomb crystal was pushed to the upper side of the image. Both of the observed Ca^+ image and the simulated image by the molecular dynamics simulation show that the sympathetically cooled CaH^+ ions were also crystallized. From the simulation results, the number of crystallized molecular ions, the secular temperature and the structure was determined [5].

Gallery of mixed-species Coulomb crystals

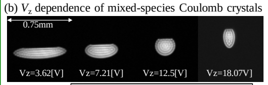
(a) Sympathetic crystallization of single CaH^+ ion



f=5.573[MHz], Vac=223,221.5[V], Vz=1.0[V],⊿UV=24[MHz]

We observed a single CaH^+ ion in a small Ca^+ Coulomb crystal. As shown in (a), fluorescence of Ca^+ crystals have a perforated structure. The CaH^+ ion exists in the dark spots.

(b) V_z dependence of mixed-species Coulomb crystals

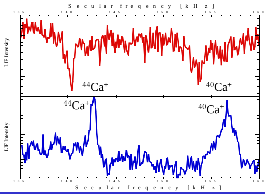


f=5.532[MHz], Vac=236[V],⊿UV=48[MHz]

From the observation at different V_z, the deformation of mixed-species Coulomb crystals was observed.

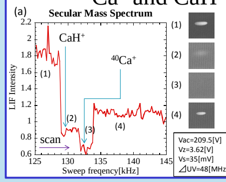
Mass Spectrum

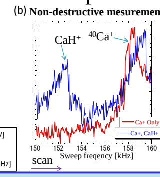
Laser induced fluorescence mass spectrometry by secular motional excitation



In this method, the fluorescence-intensity change of the laser-cooled ions is measured as a function of the perturbation rf frequency for secular motion excitation of trapped ions. If the perturbation frequency coincides with a secular motion frequency of sympathetically cooled ions, the ions are heated and Ca^+ ions are also heated by the Coulomb interaction. Consequently, the fluorescence intensity decreases (or increases) due to the change of the Doppler width of the laser cooling transition.

Ca^+ and CaH^+ Mass Spectrum

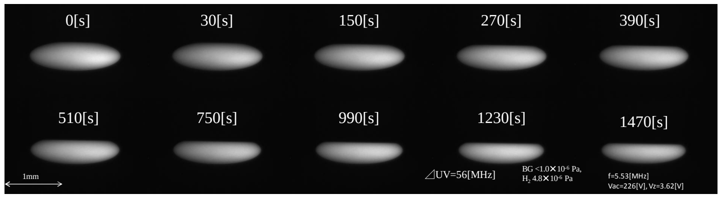


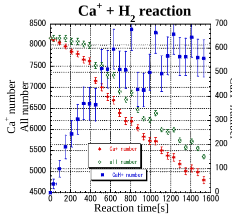


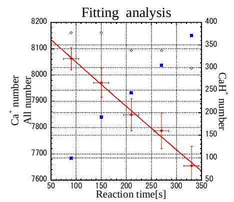
Presence of CaH^+ is demonstrated by these spectra using above method .
(a)UV detuning :near
(b)UV detuning :far

Production rate

(a) Large ion Coulomb crystals

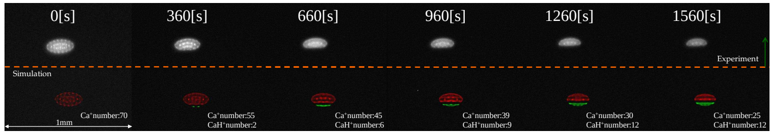




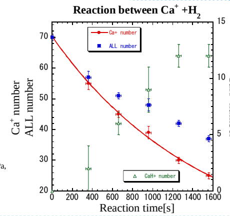


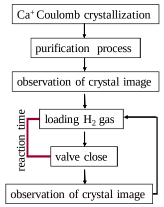
⊿UV=56[MHz], BG <1.0×10^{-6} Pa, H_2 4.8×10^{-6} Pa

(b) Small ion Coulomb crystals



Trap Paramater
f=5.532[MHz]
Vac=204.5[V]
Vz=5.3[V]
⊿UV=32[MHz]
BG <1.0×10^{-6} Pa,
H_2 4.8×10^{-6} Pa





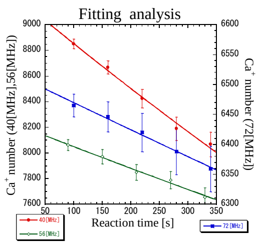
From the comparison of MD simulation images with experimental image, the number of small Coulomb crystals(10~100) was determined. On the other hands, The number of large Coulomb crystals(1000~10000) was estimated by the product of calculated ion density and Coulomb crystal's volume.

The number of Ca^+ ions decayed exponentially with the reaction time due to the laser-induced reaction. The reaction rates were determined using a least-squares fit technique, and the lower limit of the reaction rate constant at room temperature was deduced.

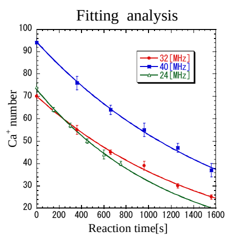
In the case of the large ion crystal (a), the decay rate of Ca^+ ions was accelerated after 350 s, because the number of coolant Ca^+ ions decreased while the number of CaH^+ ions increased. Accordingly, for the least-squares fitting analysis we selected the data which were mesured at a reaction time less than 350 s.

The laser-detuning dependence of the reaction rates was also measured for large and small ion crystals. At the same laser detuning the reaction rates of small Coulomb crystals was higher than those of large crystals. This result shows the fact that the smaller ion crystals are cooled to the lower temperatures.

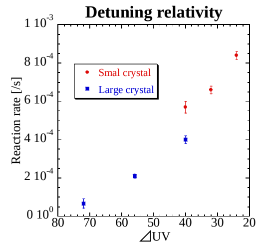
(a)



(b)



BG <1.0×10^{-6} Pa, H_2 4.8×10^{-6} Pa

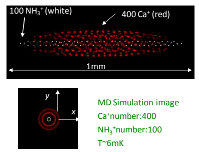


BG <1.0×10^{-6} Pa, H_2 4.8×10^{-6} Pa

Outlook

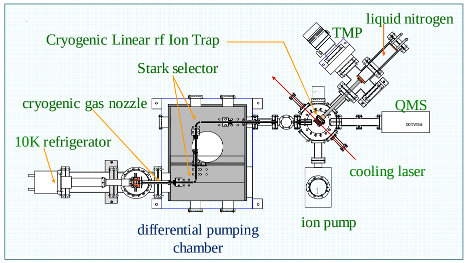
Next step

- Production of various ultracold ions
  – CaO^+, $CaOH^+$, F^+, NH_3^+etc...
- Applying correction DC voltages



Future

- Ultrahigh-resolution molecular spectroscopy
- Study of ultracold molecular ion-polar molecule collision reactions



References

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