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Single-Ion Recycling Reactions**

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In the past decade, there has been a tremendous progress in gas-phase chemistry involving sympathetically cooled molecular ions.[1–14] This includes experiments with single molecules,[3–6,11] which besides having the potential to provide more detailed information than obtainable in experiments with ensembles, can be a requirement for certain types of experiments. For instance, to enter the new branch of ultracold chemistry,[2,7] ultracold ion chemistry, where novel quantum effects are expected at temperatures in the microkelvin range,[14,15] direct or sympathetic sideband laser cooling[16] of a single or, at most, a few ions are required. In addition, for reaction experiments in this regime, an experimental method by which a single target ion can be regenerated would be extremely valuable to avoid detrimental excess micromotion[5,6] inflicted by reloading in radio frequency traps.

Regeneration of a target ion would furthermore be vital for chemical studies of rare species, such as the important case of transactinide ions, that is, ions of elements with atomic numbers $Z \geq 104$. Because of strong relativistic effects in the electron structure of the transactinides, the chemical properties of these ions are especially intriguing.[17] Though some chemical properties of transactinide elements up to copernicium ($Z = 112$) have been characterized,[18] the detailed chemistry of these elements is still vastly unexplored because of their extremely low production rates (typically a few detected per day or less) at only a few accelerator facilities worldwide. With half-lives of up to 32 h for currently produced transactinide isotopes (^{268}Db),[19] and with the "island of stability"[20] in sight, a whole new realm of chemistry would, however, be within reach, provided a technique allowing repeated use of a single target ion.

Herein, we report for the first time on recycling reactions in which the same two laser-cooled and trapped rare isotope $^{48}Ca^+$ ions (^{48}Ca natural abundance: 0.189 %) reacted repeatedly with a gas mixture of HD (83 %) and H_2 (17 %) molecules by regenerating the $^{48}Ca^+$ ion through photodissociation by a short laser pulse each time a molecular ion was formed. From the total of 87 recorded single-ion reaction events, the fractional $^{48}CaD^+$ molecular ion formation was found to be 0.56 ± 0.05. Furthermore, a total reaction rate constant on the order of 3×10^{-11} cm^3 s^{-1} for $^{48}Ca^+$ ($4p\ ^2P_{1/2}$) was inferred.

The applied technique should be easily extendable to obtain detailed information on chemical reactions with a large variety of single ions, including transactinide ions, sympathetically cooled by another simultaneously trapped and laser cooled ion. In this case the nonfluorescing target ion is sympathetically cooled by a fluorescing coolant ion, and detection of a reaction is achieved by the same nondestructive mass measurement technique applied to discriminate between the formed CaH^+ and CaD^+ ions discussed here. In Ref. [3], this method was used to observe substitution reactions of the type $MgH^+ + D_2 \rightarrow MgD^+ + HD$.

In the experiment, two $^{48}Ca^+$ ions are loaded into a linear Paul trap by isotope-selective photoionization[21] and cooled to a temperature of about 10 mK through Doppler laser cooling[16] by primarily exciting the $4s\ ^2S_{1/2}$–$4p\ ^2P_{1/2}$ transition and repumping on the $3d\ ^2D_{3/2}$–$4p\ ^2P_{1/2}$ transition (see Figure 1 A). At these low temperatures, the two $^{48}Ca^+$ ions localize at equilibrium positions set by the trapping potential and the repulsive Coulomb interaction between the ions. A fluorescence image of the two $^{48}Ca^+$ ions recorded by a charged-coupled device (CCD) camera is shown in Figure 1 B. Subsequently, HD or H_2 is leaked into the vacuum chamber (background pressure: 4×10^{-10} mbar) to obtain a partial pressure of 1×10^{-7} mbar at room temperature, and a $^{48}CaH^+$ or a $^{48}CaD^+$ ion is formed in a gas-phase reaction.

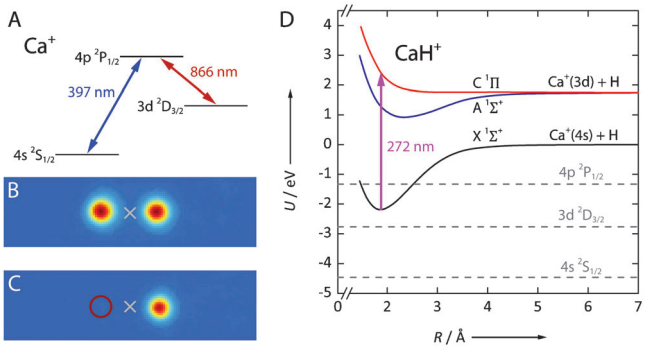

Figure 1. Laser cooling of Ca^+ ions and potential curves for CaH^+. A) The relevant electronic energy levels of the atomic Ca^+ ion with indications of laser-driven transitions during Doppler laser cooling. B) Fluorescence image of two laser-cooled $^{48}Ca^+$ ions (red/blue: high/low intensity). C) Fluorescence image of one laser-cooled $^{48}Ca^+$ ion and one nonfluorescing $^{48}CaH^+/^{48}CaD^+$ ion, indicated by the red circle. In both images the distance between the two ions is 22 μm, and the center of the trap is indicated with a gray cross. D) The relevant lowest lying singlet potential curves[23] for CaH^+ with indication of the photodissociation transition induced by laser light at a wavelength of 272 nm. The dashed lines signify the three electronic energy levels of the Ca^+ ion shown in (A) relative to the binding energy of the HD molecule.

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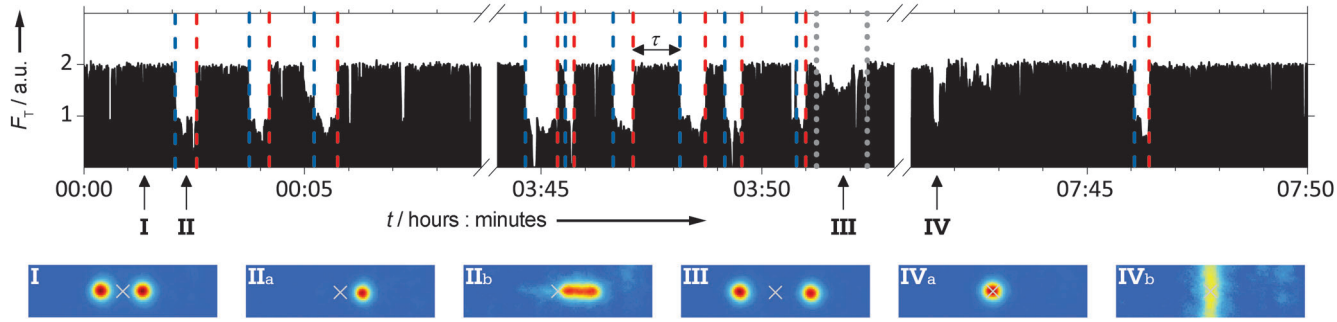

Figure 2. Monitoring of recycling reactions. Upper graph: The total $^{48}Ca^+$ ion fluorescence signal F_T (arbitrary units) obtained from the recorded CCD images such as those presented below. The fluorescence level is corrected for slow linear drifts in the laser powers during the experiment. Images I–IV: examples of images recorded during the experiment with the same two $^{48}Ca^+$ ions. The horizontal extension of the images corresponds to a distance of 100 μm, and the gray crosses indicate the center of the trap. The vertical dashed blue lines on the graph indicate reaction events, accompanied by a drop in the total $^{48}Ca^+$ ion fluorescence signal. The red dashed lines indicate the times at which a $^{48}CaH^+$/$^{48}CaD^+$ ion is photodissociated to regenerate a fluorescing $^{48}Ca^+$ ion. The time until reaction τ is defined as the time interval from a dissociation event to the following reaction. The two vertical dotted gray lines indicate the time from detection to removal of an impurity ion.

Such an event can easily be detected by the sudden disappearance of the fluorescence from one of the sites originally occupied by a $^{48}Ca^+$ ion[3,11] (see Figure 1C). Through Coulomb interaction with the remaining $^{48}Ca^+$ ion, the formed $^{48}CaH^+$/$^{48}CaD^+$ ion is sympathetically cooled within about 10 ms to a temperature close to that of the $^{48}Ca^+$ ion.[3,22] As indicated in Figure 1D, the reaction is state specific, since it is only energetically allowed when the $^{48}Ca^+$ ion is in the excited 4p $^2P_{1/2}$ level.[23] To identify the molecular ion formed, the nondestructive sympathetically cooled single-ion mass spectrometry (SCSI-MS) technique is applied at this stage.[11] After a clear identification, the formed $^{48}CaH^+$/$^{48}CaD^+$ ion is exposed to a pulse (about 100 ms) of continuous-wave (CW) laser light at 272 nm (the same light used for isotope-selective production of the $^{48}Ca^+$ ions), which leads to dissociation into $^{48}Ca^+ + H/D$, and thus regeneration of the original $^{48}Ca^+$ ion.

In the upper panel of Figure 2, excerpts of the results from a nearly eight hour experimental run using the same two $^{48}Ca^+$ ions are presented as the total fluorescence integrated over the whole CCD image. As expected, after each reaction (indicated by vertical blue lines) the integrated fluorescence level decreases to a level of about half that of two $^{48}Ca^+$ ions (image IIa: shortly after reaction, and image IIb: during a mass measurement; for details see Ref. [11]), and every time the photodissociation pulse is applied (indicated by vertical red lines), the high prereaction fluorescence level is recovered (image I). A drop in the integrated fluorescence signal is not necessarily a signature of a reaction. In the event that a $^{48}Ca^+$ ion collides elastically with one of the energetic background gas molecules, the ion can heat up temporarily, and either for up to several seconds leave one ion cold (image IVa) or lead to a significant heating of both ions (image IVb). By examining the CCD-images, these potentially false events can easily be identified and disregarded. Additionally, a number of times a third ion is spuriously formed, as can be detected by the change in the equilibrium positions of the two fluorescent $^{48}Ca^+$ ions (image III). How these ions are formed is still not completely clear, but they can be removed by a rather brief (about 30 s) change in the trapping parameters, such that their motion becomes unstable in the linear Paul trap used.[24] In total, 87 reactions forming either $^{48}CaH^+$ (38 events) or $^{48}CaD^+$ ions (49 events) were recorded.

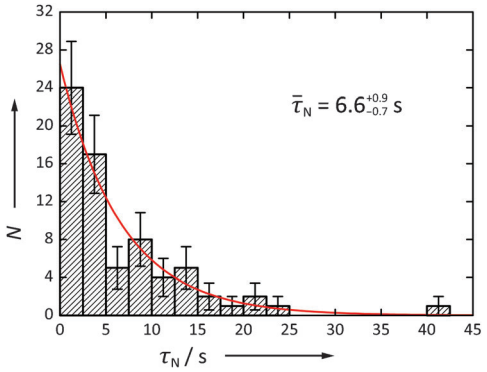

Figure 3. Histogram of normalized times until reaction τ_N. The histogram presents the number of reaction events N occurring within different time bins after a $^{48}Ca^+$ ion has been regenerated. The times until reaction time τ_N are extracted from the data partially presented in Figure 2, but normalized to one corresponding to an ion in the 4p $^2P_{1/2}$ level. The vertical bars represent the uncertainties based on standard counting statistics (1 s.d.). The maximum-likelihood estimate of the mean value of τ_N is $\bar{\tau}_N$ =6.6 s (1 s.d.). The red exponential curve corresponds to $\bar{\tau}_N$ =6.6 s.

Since the fluorescence level is directly proportional to the probability of finding the ion in the 4p $^2P_{1/2}$ level, the calibrated imaging system enables extraction of the mean population of this level over the course of the experiment from the recorded images. Each recorded time until reaction time τ, defined as the time passing from a dissociation event to the following reaction event, can be normalized to one, corresponding to an ion being in the 4p $^2P_{1/2}$ level. As is evident from Figure 3, after this normalization the investigated reaction can be described well by a single exponential time constant. A maximum-likelihood estimate of the mean normalized time until the reaction is found to be $\bar{\tau}_N = 6.6$ s. Based on the pressure reading of our ion gauge, this result corresponds to a rate constant on the order of 3×10^{-11} cm^{3}s^{-1}

for the reaction of $^{48}Ca^+$ ($4p\ ^2P_{1/2}$) with the gas mixture of HD and H_2 at room temperature.

To further highlight the potential application of single-ion recycling experiments for quantitative measurements, we

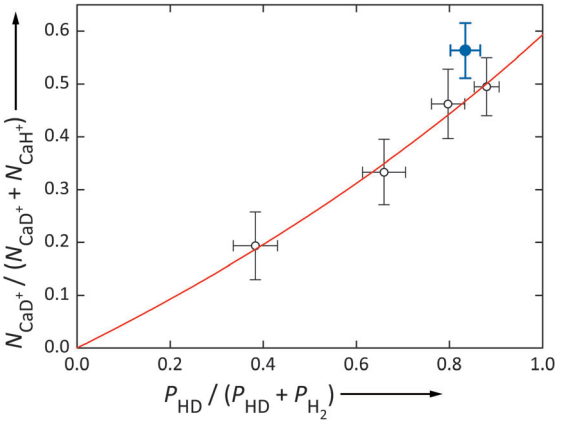

Figure 4. Fractional CaD^+ molecular ion formation versus relative HD pressure. Results of single-ion reactions between $Ca^+(4p\ ^2P_{1/2})$ and a mixed gas of H_2/HD. The black data points originate from a series of experiments with single $^{40}Ca^+$ ions, while the blue data point is obtained from the single recycling experiment with the two $^{48}Ca^+$ ions. The vertical bars represent statistical uncertainties (1 s.d.), and the horizontal bars represent experimental uncertainty in determining the pressures. The red curve represents the best fit to the $^{40}Ca^+$ data by the model applied in Ref. [3].

present in Figure 4 the deduced fractional CaD^+ molecular ion formation for both the single experiment with the two rare $^{48}Ca^+$ ions and a much longer series of experiments with the much more naturally abundant $^{40}Ca^+$ ion. Clearly within the error bars, the results for the two isotopes coincide as could be expected for room-temperature reactions, where the isotope shifts of the Ca^+ ion levels should play a negligible role. The extrapolated fractional CaD^+ molecular ion formation at the limit for reactions with a pure HD gas of 0.59 ± 0.03 (1 standard deviation, s.d.) is in stark contrast to analogous experiments with Mg^+ ions where the MgD^+ production was predominant.[3] A detailed understanding of this intriguing difference will require simulations of the reaction dynamics for the two cases. It may, however, likely be linked to the existence of a crossing of the entrance reaction potential surface with energetically lower lying surfaces asymptotically converging to the electronic d state in the case of the Ca^+ reactions.

In two other reaction experiments, we exposed two trapped $^{40}Ca^+$ ions first to H_2O and then O_2 molecules. Here, the masses 57 u and 56 u were recorded after reaction, indicating the formation of $^{40}CaOH^+$ and $^{40}CaO^+$, respectively. In both cases, as with CaH^+/CaD^+, we successfully regenerated the $^{40}Ca^+$ ion by applying a dissociation laser pulse at 272 nm. This result implies that these types of reactions could be investigated in the present experimental setup, and that the technique used is quite generally applicable. For more complex molecules the situation can become more challenging, since several lasers may be needed, for regeneration through, for example, resonance enhanced multi-photon dissociation (REMPD).[25] While the present experiments were all carried out with a thermal source of molecules, reaction studies involving velocity and/or state-selected molecules should be feasible through the application of, for example, a state-specific velocity filter,[26] a Stark[27] or a Zeeman[28] decelerator.

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