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# Ion Coulomb crystals: a tool for studying ion processes

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#### Abstract

Ion processes can be studied by a wide variety of experimental setups ranging from small ion trap devises to large storage rings. In Penning as well as Paul (rf) traps, the effective oscillation frequencies of trapped particles have, e.g., extensively been used to gain information of the charge to mass ratio of produced atomic and molecular ions. For such investigations, space charges due to the simultaneous presence of multiple ions, is a limiting factor, and hence low density or single particle experiments are preferred. The purpose of the present article is to discuss the prospects of using traps in the opposite regime where space charges dominate and so-called ion Coulomb crystals form (at temperatures about  $\sim 10$  mK). The experimental results presented below show that in this regime, differences in single particle oscillation frequencies of simultaneously trapped ions lead to a spatial segregation of the ion species which can be used as means to study a large variety of ion processes. Since the detection relies generally on observations of changes in the spatial structure of the Coulomb crystals formed by the cold, trapped ions, it can often be non-destructive, i.e., the product ions of a certain process will stay trapped and be available for further experimentations. It is the intention of the present article to discuss, via some examples, the usefulness of ion Coulomb crystals as a tool in investigations of ion processes more than it is the aim to provide new data.

Keywords: Ion processes; Ion detection; Ion traps; Coulomb crystals

# 1. Introduction

Ion Coulomb crystals, i.e., the spatial ordered structures that appears when ions are cooled below a certain critical temperature, have only the past decade been studied experimentally in Penning and Paul traps (see, for example [1–6] and references therein). The reason for this being the temperatures needed to create ion Coulomb crystals are typical around 10 mK (see Section 3), which first by the development of laser cooling [7] became reachable. So far, most studies of ion Coulomb crystals have been done on single atomic species crystals using ions suitable for laser cooling. However, few investigations of two or more ion species crystals have been reported recently [8–10]. By simultaneously having a laser-cooled ion species trapped together with another ion species, it is possible, through the Coulomb interaction between the two species, to sympathetically cool [11] the whole ion ensemble into a crystalline state [8,9]. Due

to the effective trapping forces dependence on the mass and charge of the ions, the two ion species will normally spatial segregates (see Section 3). In the context of ion processes it is such multi-species crystals that are interesting, since the sympathetically cooled ions can be the species wanted as the target for investigations, and changes in the target ions charge state or mass through any interaction will lead to a spatial reordering of the multi-species crystal which can be observed, e.g., by monitoring fluorescence from the laser-cooled ions (see Section 4).

The rest of the article is organized as follows: first, in Section 2, an introduction is given to the essentials of the linear Paul trap setup applied in the experiments discussed in Section 4. Next, in Section 3, an introduction to ion Coulomb crystals are given including a short discussion of the characteristics important for understanding the experimental results presented in the following section. This latter section, Section 4, is divided into three sub-sections each devoted to a specific experiment. Finally, in Section 5, a conclusion including a short discussion of the future prospect of using Coulomb crystal is given.

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Fig. 1. (a) Sketch of the linear trap used in the experiments. The various parameters are defined in the text of Section 2. (b) Picture of the actual trap used. As a scale, the center-part of the electrode  $(2z_0)$  is 5.4 mm.

# 2. The linear Paul trap setup

The type of trap used in the experiments discussed below is a so-called linear Paul trap [12,13] and its realization is presented schematically in Fig. 1(a) and physically in Fig. 1(b). In short, it consists, like a standard quadrupole mass-filter, of four electrodes mounted such that by applying an rf voltage of the same phase to diagonal electrodes, but with a phase shift of 180° with respect to the nearest electrodes, a near-ideal two-dimensional quadrupole field exist in the plane perpendicular to the direction defined by the electrode (the z-direction). Each electrode is sub-divided into three parts such that a positive dc voltage can be applied to the eight end-pieces. While this dc voltage leads to static confinement along the trap axis (the z-axis), it leads to a defocusing force in the radial plane perpendicular to this axis. By appropriate choices of the dc and rf voltages and rf frequency, both axial and radial confinement can be obtained for given trap dimensions [14]. Defining the parameters:

$$a \equiv \eta \frac{8QU_{\rm dc}}{m\omega_{\rm rf}^2 z_0^2} \tag{1}$$

$$q \equiv \frac{2QU_{\rm rf}}{m\omega_{\rm rf}^2 r_0^2} \tag{2}$$

where *m* is the mass of the ion, *Q* is the ion charge,  $\omega_{\rm rf}$  and  $U_{\rm rf}$  are the frequency and amplitude of the rf field,

respectively,  $U_{dc}$  is the voltage applied to the end-pieces,  $z_0$ and  $r_0$  are the trap dimensions defined in Fig. 1(a), and  $\eta$ is a positive geometric parameter dependent on  $z_0$  and  $r_0$ , it can be shown that when *a* and *q* lie within certain stability regions [14] stable single ion motion exist. The motion is generally complex, but when q < 0.4 a single ion not too far from the trap center will feel an effective harmonic potential:  $\phi(z, r) = \frac{1}{2}m(\omega_z^2 z^2 + \omega_r^2 r^2)$  (3)

where  $\omega_z$  and  $\omega_r$  are the oscillation frequencies along the *z*-axis and in the radial plane, respectively, given by

$$\omega_z = \frac{1}{2}\omega_{\rm rf}\sqrt{a} \tag{4}$$

$$\omega_r = \frac{1}{2}\omega_{\rm rf}\sqrt{\frac{1}{2}(q^2 - a)}\tag{5}$$

In the radial plane, the ions will in addition to the force from the effective potential above, be subjected to a fast oscillating force at the rf frequency, but it can be shown that the amplitude of the corresponding motion (often named micro-motion) always will be much smaller than the distance of the ion from the *z*-axis when q < 0.4 [15]. In what follows, we will hence completely neglect this fast quiver motion.

The trap used in the experiments and shown in Fig. 1(b) has the following dimensions:  $r_0 = 3.50$ ,  $z_0 = 2.70$ ,  $z_{\text{endcap}} = 20.00 \text{ mm}$  and R = 4.00 mm, which have been chosen for having a nearly perfect radial quadrupole rf field



Fig. 2. Picture of the trap inside the cylindrical vacuum chamber used in the experiments. The chamber has a inner diameter of 30 cm. The numbers in the picture indicate: (1) the linear Paul trap; (2) the magnesium and calcium ovens, which are the sources for the atomic beams passing through the center of the trap; (3) oven shutter; (4) skimmer plates, used to collimate the effusive beams from the ovens in order to avoid platting of the trap electrodes; (5) electron gun including deflection plates installed to make an electron beam cross the atomic beams in the center of the trap for ion production; (6) one of two opposite positioned openings for sending in light beams for laser cooling of the ions along the trap axis (the *z*-axis); (7) an optical fiber piece with known diameter, which can be translated into the trap center for calibration of the magnification of the lens system used to image the fluorescence of the laser-cooled ions; (8) one of two opposite positioned openings to cross the atomic beams at nearly right angles in the trap center for producing ions by photo-ionization. Not seen in this picture is a CCD-camera monitoring the fluorescence from the laser-cooled ions through a window in a not-shown top-flange of the vacuum chamber. Also not seen is a leak-valve controlled inlet of various gasses into the trap region.

[16] and a near-harmonic dc axial potential over a few mm. These choices of trap dimensions results in  $\eta = 0.248$ . The applied rf field is resonantly coupled to the trap electrodes at a frequency  $\omega_{\rm rf} = 2\pi \times 3.88$  MHz with an amplitude  $U_{\rm rf}$  typically about a few hundred volts. With a typical dc voltage of  $\sim 1$  V, Eq. (3) gives rise to a potential depth of about  $\sim 1$  eV. Since this energy is many orders of magnitude higher than the thermal energy of the ions in Coulomb crystals (see Section 3), the storage time of the ions can easily be hours or more. In Fig. 2, a photo of the trap (see



Fig. 3. Pictures showing two-dimensional projections of pure  ${}^{24}Mg^+$  ion Coulomb crystals containing  $\sim 500$  ions for a series of different axial potentials. The real crystals can be imagined by noting that they have rotational symmetry around the horizontal symmetry axis. In all the pictures, the rf voltage was constant, while the dc voltages  $U_{dc}$  on the eight end-pieces was changed from (a)  $U_{dc} = 0.01$  V to (e) 10 V.

Fig. 1(b)) and other important equipment in the experimental vacuum chamber is presented.

# 3. Ion Coulomb crystals

Due to the combination of the trapping forces and the Coulomb repulsion of ions with the same sign of the charge state, when cooled to sufficient low temperatures spatial ordered states are formed. For a trapped single ion species, crystallization appears when [17,18]

$$\Gamma = \frac{E_{\text{pot}}}{E_{\text{kin}}} = \frac{Q^2}{4\pi\varepsilon_0 a k_{\text{B}} T} > 150$$
(6)

where  $E_{pot}$  is the ions potential energy with respect to their nearest neighbor at a distance given by the Wigner–Seitz ra-

dius *a*, and  $E_{\rm kin}$  is the average kinetic energy of the ions at temperature *T*. For normal trapping conditions, where  $a \ge 10 \,\mu$ m, inequality (6) leads to a crystallization temperature  $T < 10 \,\mathrm{mK}$ . From simulations similar low temperatures are found needed to obtain spatially ordered structures of two ion species simultaneously trapped. Due to the low crystallization temperatures, only by applying laser cooling [7] it has hence been possible to create ion Coulomb crystals so far.

The detailed crystal structures depend on the actual trapping potential as well as the quantity of various ion species. For a single ion species in an effective harmonic potential, according to theory [18], the ideal crystalline structure is body-centered-cubic (bcc) in the limiting case of an infinite crystal. Such structures are only observed in the centers of cold ion ensembles consisting of about  $10^5-10^6$  ions [3,4], while for smaller amounts of ions, the ions organize



Fig. 4. Images of the fluorescence from a bi-crystal consisting of  ${}^{40}Ca^+$  ions and  ${}^{44}Ca^+$  ions. (a) Fluorescence from the  ${}^{40}Ca^+$  ions part of the crystal. (b) Fluorescence from the  ${}^{44}Ca^+$  ions part of the crystal. (c) Combined image.

themselves in a near-hexagonal structure inside concentric shells which are spheroidal [10,19]. In Fig. 3, images of the fluorescence from pure  $^{24}Mg^+$  ion crystals obtained by an image-intensified CCD-camera are shown. In these two-dimensional projections of the Coulomb crystals, light from separate shells is observed (without any clear indication of the near-hexagonal in-shell ordering). A unique property of Coulomb crystals in harmonic traps is the constant density (when averaged over distances larger than the single particle separation) of single species crystals. It can be shown [10] that the density for the linear Paul trap, with the definition of the previous section, can be written as

$$\rho = \frac{\varepsilon_0 U_{\rm rf}^2}{m r_0^2 \omega_{\rm rf}^2} = \frac{3}{4\pi a^3} \tag{7}$$

which is independent of the charge state of the ion and for typical achievable trap parameters gives a density of  $\sim 10^8 \text{ ions/cm}^3$ .

For two-species crystals, the structures are more complicated. Since the potential given by Eq. (3) is dependent on the mass and charge of the trapped ions, two different ion species will normally separate radially as has been studied earlier in details in the case of  ${}^{24}Mg^+/{}^{40}Ca^+$  bi-crystals [10]. In Fig. 4, an image of a bi-crystal, consisting of two singly charged isotopes of calcium, is shown. Here, one clearly observes how the lighter  ${}^{40}Ca^+$  ions segregate around the trap axis in a close to cylindrical structure, while the heavier  ${}^{44}Ca^+$  ions form a surrounding shell structure with a spheroidal outer boundary. The density of the individual ion species is constant and for each species given by Eq. (7).

As we shall discuss in the next section, it is the knowledge of the spatial segregation of different ion species and the knowledge of their densities that makes ion Coulomb crystals interesting in connection with various ion processes.

#### 4. Studies of ion processes

In this section, the prospect of using Coulomb crystals in investigations of ion processes in general will be discussed based on some recent studies carried out in our group using the trap setup presented in Section 2.

# 4.1. Multi-photon ionization of Mg/Mg<sup>+</sup>

In a series of experiments, we have started testing the use of Coulomb crystals in femtosecond laser experiments. The first simple goals have been to look for multi-photon ionization of Mg and Mg<sup>+</sup>. By crossing an atomic beam of Mg in the center of the trap region by a fs-laser beam with pulses (rep. rate 1 kHz) of ~100 fs with a center wavelength of ~800 nm and with an average power of up to 500 mW, we have been able to produce both Mg<sup>+</sup> and Mg<sup>2+</sup> ions. As indicated in Fig. 5, singly charged magnesium can be produced by at least a five-photon process, while di-

Fig. 5. Selected levels of Mg and Mg<sup>+</sup> with indication of the number of photons involved in specific multi-photon ionization processes (the numbers in parentheses) when using light around  $\lambda = 800$  nm. Also shown is the transition driven by the laser, which cools the Mg<sup>+</sup> ions.

rect double ionization will need absorption of more than 14 photons. When Mg<sup>+</sup> ions are first formed, Mg<sup>2+</sup> can be produced either by a direct 10-photon process from the 3s  ${}^{2}S_{1/2}$  ground state or by a seven-photon process from the  $3p^{2}P_{1/2}$  state excited resonantly by the laser used to laser cool the Mg<sup>+</sup> ions. Due to the fact that ionization of Mg<sup>+</sup> ions is not much more difficult when excited by the cooling laser (seven-photon process) than ionization of Mg atoms (five-photon process), when producing Mg<sup>+</sup> ions by using a sequence of  $\sim 100$  pulses, we also create Mg<sup>2+</sup> ions. Since these doubly charged ions feels a stronger radial trapping potential than the  $Mg^+$  ions (see Eq. (3)), they end up as a non-fluorescing cylindrical structure (see Fig. 6) in the middle of a surrounding fluorescing Mg<sup>+</sup> ion bi-crystal component when the latter ion species is laser-cooled. If the flux of the atomic beam and the spatial as well as temporal laser intensity profile are well-known, by determining the number of ions in the bi-crystal, or equivalent the total size of the crystal since the densities of the ion species are known from Eq. (7), after a fixed fs-laser exposure time, the ionization cross-section for Mg atoms can be determined. The ionization cross-section for Mg<sup>+</sup> ions could in principle be found in the same experiments, since at the end of the fs-laser pulse sequence both the number of single and doubly charged ions can be determined. Alternatively, one could start with a (nearly) pure Mg<sup>+</sup> ion crystal as shown in the first picture of Fig. 6 and expose this crystal of well-known density to fs-laser pulses and observe how the central core of non-fluorescing Mg<sup>2+</sup> ions grows in time as shown by the rest of the picture sequence of Fig. 6. The volume of





Fig. 6. Sequence of images showing how an inner non-fluorescing core of  ${}^{24}Mg^{2+}$  develops in time when an initial nearly pure  ${}^{24}Mg^+$  crystal is exposed to laser pulses of a duration of about 100 fs and with a central wavelength of 800 nm.

the bi-crystal of Fig. 6 does not change significantly during the sequence, in accordance with Eq. (7), which states the density should be independent on the charge state of a given ion. Though the density of a given ion species does not depend on the charge state, in many situation where one initially have a bi-crystal consisting of a radially strong confined laser-cooled ion species and another weaker bounded singly charged ion species, one can anyway easily study photo-ionization processes on the sympathetically cooled ion species. If the doubly charged ion will be stronger confined than the laser-cooled ions, they will produce a dark core inside the laser-cooled ion species component. Since this experimental situation can be realized for many sympathetically cooled ion species, when laser-cooled species is available, the technique can be used for photo-ionization studies of a large variety of ions.

# 4.2. Reactions between $Mg^{2+}$ and $O_2$

Low-energy gas-phase chemical reactions involving ions is another field where Coulomb crystals are interesting objects. By using the Coulomb crystals as a cold ion target, reactions at low (thermal or lower) temperatures can be studied by exposing the crystal to a beam of the wanted reactant or by just leaking a gaseous species of interest at very low pressure into the trap vacuum chamber. In the latter case the partial pressure should not exceed  $\sim 10^{-8}$  mbar in order not to heat up the cold crystal. When reactions are taking place with laser-cooled ions in the crystal, non-fluorescing ions are produced and eventually trapped. In a previous experiment, we have used a Coulomb crystal of Mg<sup>+</sup> ions to study reactions between such ions and H<sub>2</sub>/D<sub>2</sub> [9]. Since the kinetic energy of the reaction products in this experiment where significantly smaller ( $\sim 0.1 \text{ eV}$ ) than the trap depth ( $\sim 1 \text{ eV}$ ) the produced MgH<sup>+</sup>/MgD<sup>+</sup> ions where trapped and could be monitored as a dark region formed outside the lighter reactant ions [9]. Simply by monitoring the rate at which the volume of the fluorescing reactance ions was diminished due to reactions, reaction rates could be established by knowing the density of the leaked-in  $H_2/D_2$  gas. To illustrate that the reacting target ions do not necessarily have to be monitored by fluorescence in order to use Coulomb crystal for reaction studies, in Fig. 7, images from an experiment to study reaction between  $Mg^{2+}$  and  $O_2$  is shown. Image (a) in Fig. 7,



Fig. 7. Sequence of pictures "showing" the reactions between  ${}^{24}Mg^{2+}$  ions in a Coulomb crystal and thermal O<sub>2</sub> molecules. (a) Nearly pure  ${}^{24}Mg^+$  crystal; (b) same crystal as in (a), but after converting some  ${}^{24}Mg^+$  ions into non-fluorescing  ${}^{24}Mg^{2+}$  ions (central cylindrical structure) by multi-photo-ionization using a fs-laser (see scheme in Fig. 4); (c–h) images of the crystals in intervals of 10s when a O<sub>2</sub> gas at a pressure of  $\sim 2 \times 10^{-9}$  mbar is present.

shows an initially nearly pure <sup>24</sup>Mg<sup>+</sup> crystal. The next picture shows how by multi-photon ionization a large part of the ions are transformed into <sup>24</sup>Mg<sup>2+</sup> ions, seen as the large non-fluorescing cylindrical core. After this ionization process, a thermal O<sub>2</sub> gas was leaked into the trap chamber at a pressure around ( $\sim 2 \times 10^{-9}$  mbar). The images (c–h) shows in time intervals of 10 s how the non-fluorescing inner core reduces in size due to reactions. While Mg<sup>+</sup> do not significantly react with O<sub>2</sub>, it is known [20] that Mg<sup>2+</sup> reacts very fast through the most prominent charge transfer reaction:

$$Mg^{2+} + O_2 \rightarrow Mg^+ + O_2^+$$
 (8)

The excess energy of this reaction is about 2.8 eV, leading to kinetic energies of the Mg<sup>+</sup> and O<sub>2</sub><sup>+</sup> ion of 1.6 and 1.2 eV, respectively, if O<sub>2</sub><sup>+</sup> is not produced in an excited state. With an effective trap depth of  $\sim$ 1.0 eV in the experiments, most of the product ions will escape the trapping potential. This is the reason for the shrinking size of the whole crystal. In such an experiments, by carefully measuring the volume of the non-fluorescing part of the crystal as a function of time under constant O<sub>2</sub> pressure conditions, the thermal rate for the reaction (8) can be established. It should be noted that this methods could also be used in the case where the sympathetically cooled reacting ion species is situated outside an inner cylinder of laser-cooled ions. By the knowledge of the shapes of bi-crystals many other reactions can hence be studied in a similar way.

### 4.3. Charge exchange collisions between Ca isotopes

As discussed in Section 4.1, ions can easily be produced by non-resonant photo-ionization using fs-lasers and subsequently be trapped. In experiments, where, e.g., a specific ionic isotope of an element is of interest, such multi-photon Ca:



Fig. 8. Reduced calcium level diagram showing the levels of interest for the resonant two-photon ionization experiments with Ca atoms discussed in the text. The thin arrow connecting the  ${}^{1}P_{1}$  and the long-lived  ${}^{1}D_{2}$  state indicates a likely spontaneous emission process, taking place before the final ionization step. IL is an abbreviation for ionization limit.

ionization process can provide no selectivity. If on the other hand resonant processes, driven by, e.g., narrow bandwidth CW laser systems, are used, very high isotope selectivity can be achieved [21–23]. By using the resonant two-photon ionization process shown in Fig. 8, we are able to selectively load any natural abundant isotope of calcium into our trap by having the ionizing laser beam crossing a thermal atomic beam of calcium at right angles at the trap center. In Fig. 9, is shown the relative amount of ions loaded into the trap when scanning the frequency of the ionizing CW laser across the  $4s^2$   $^1S_0$ –4s5p  $^1P_1$  resonance of the respective Ca isotopes. The dotted line in Fig. 9 presents the amount of  $^{40}Ca^+$  ions produced directly at each laser frequency. Since 97% of natural calcium has mass 40, its contribution dominates the "background" signal at the resonance of the other



Fig. 9. Spectrum showing isotope selective production of calcium ions by resonant two-photon ionization. The horizontal axis is the frequency of a CW laser scanned across the  $4s^2 \ ^1S_0-4s5p \ ^1P_1$  transitions ( $\lambda = 272 \text{ nm}$ ) of the various Ca isotopes. Note that the vertical axis is logarithmic.



Fig. 10. A time sequence of images showing how a crystal initially consisting of a mixture of fluorescing  ${}^{40}Ca^+$  ions and non-fluorescing  ${}^{44}Ca^+$  ions, through change exchange processes of the form  ${}^{44}Ca^+ + {}^{40}Ca \rightarrow {}^{44}Ca^+$  due to continuous exposure of the bi-crystal to a thermal beam of calcium (97%  ${}^{40}Ca$ ), transforms into a nearly pure  ${}^{40}Ca^+$  crystal. At all times, the crystal takes up the region in space indicated by the ellipses drawn.

isotopes present in Fig. 9. For the special case of <sup>46</sup>Ca, with a natural abundance of only 0.004%, the background signal of <sup>40</sup>Ca only represents about a fifth of the ion yield at the <sup>46</sup>Ca resonance frequency. The ion yield was determined at each frequency setting by making resonant charge exchange with atoms from the thermal calcium beam (97% <sup>40</sup>Ca) and eventually transforming most of the trapped ions into <sup>40</sup>Ca<sup>+</sup> ions. By a subsequent determination of the volume of the nearly pure <sup>40</sup>Ca<sup>+</sup> Coulomb crystal created by applying laser cooling, the yield can be found by using Eq. (7). Since the kinetic energy involved in the charge exchange collisions is much smaller that the trapping potential, no significant loss of ions is made by the process. More details about the experiments behind the data presented in Fig. 9, including isotope shifts as well as hyperfine splitting in the case of <sup>43</sup>Ca of the  $4s^2 {}^1S_0$ -4s5p  ${}^1P_1$  transition, can be found elsewhere [23].

In Fig. 10, a sequence of images shows the fluorescence of  ${}^{40}Ca^+$  ions at various times during the charge exchange process:

$${}^{44}\text{Ca}^+ + {}^{40}\text{Ca} \to {}^{44}\text{Ca} + {}^{40}\text{Ca}^+ \tag{9}$$

for the case of an initially pure  ${}^{44}Ca^+$  crystal. From time series like these presented in Fig. 10, the cross-section for the charge exchange process at thermal energies can be es-

tablished by monitoring the growth rate of the  ${}^{40}Ca^+$  ion component of the crystal when exposed to a beam of known flux. Unfortunately, in our experiments so far we have only been able to indirectly infer the atomic beam flux from the particular geometry of the oven and skimmers and from an oven temperature deduced through a spectroscopically determination of the velocity distribution of the calcium atoms in the beam. At present the uncertainty in the determination of the real flux is hence so high that more direct flux measurement by, e.g., quartz oscillators [24] are needed before a value of the cross-section can be given.

Other near-resonant charge exchange/transfer processes, where neither of the involved ions are fluorescing, could as well be studied utilizing Coulomb bi-crystals. If just a reorganizing of laser-cooled ions present in the crystal can be observed (which would normally be the case), one can easily detect the charge changing processes.

# 5. Conclusion

As stated earlier in the present article, the aim of the results presented has not been to provide new data, but rather by experimental examples to show how in the future ion Coulomb crystals might be very useful with respect to many types of ion processes. The combination of long storage times (~hours) and a nearly 100% detection efficiency of individual ion events without background signal, makes it possible to do experiments where often the noise level will be set only by the statistical fluctuation in the number of ions undergoing the process under study. Due to this, only a few hundred to a few thousands ions (the amount of ions used in experiments of Section 4) are needed to do experiments with "detection noise" at the percent level. This feature might in particular be interesting when experimenting with rare ion species, or when studying very infrequent processes. The use of sympathetic cooling, makes furthermore the technique very versatile since many ion species would be able to be sympathetically cooled by a specific laser-cooled ion species. Though there exist not many atomic ions suitable for laser cooling, the few existing ones are spread out in the periodic table with the lightest being Be<sup>+</sup> and the heaviest being Hg<sup>+</sup>. This makes it possible to use the presented technique with ions in the mass/charge range of  $[1, \sim 400]$  in units of amu/e, where e is the elementary charge. By using a Penning trap which can trap ions with a broader span in mass/charge, one should be able to use a similar technique with ions mass/charge values above 1000.

Finally, since the technique presented often leads to trapping of the product ions of a certain process, one can, e.g., study a sequence of reactions [19] or even think about doing cooling of the internal degrees of freedom of produced molecular ions [25].

In conclusion, we have shown that ion Coulomb crystals might become a general tool for investigations of a large variety of ion processes.

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