Formation of translationally cold MgH$^+$ and MgD$^+$ molecules in an ion trap

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We have produced and cooled the molecular ions MgH$^+$ and MgD$^+$ in a linear Paul trap. These ions were generated by the photochemical reactions Mg$^+(3p\,^2P_{3/2})$+H$_2$ (D$_2$)→MgH$^+$ (MgD$^+$)+H (D), and identified by the radial separation in the trap of ions with different charge-to-mass ratios. The molecular translational motion was cooled sympathetically by Coulomb interaction with laser-cooled Mg$^+$ ions to a temperature estimated to be below 100 mK. Ordered structures (ion crystals) containing more than 1000 ions, with more than 95% being molecular ions, were obtained. Such translationally cold and well-localized samples of molecular ions could become very useful for molecular physics and chemistry.

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During the past years, great achievements have been made in the field of laser cooling of neutral atoms and atomic ions [1,2]. Laser cooling has been an essential tool in the fast development of atom optics [3], and most Bose-Einstein condensate experiments are based on pre-laser-cooled atoms [4]. Laser cooling of trapped ions has made it possible to create large ordered structures, often referred to as ion crystals [5–7], which are interesting objects in plasma physics. In addition, single or strings of trapped, cold ions are extremely useful in the field of quantum optics, and a string of ions is also a promising candidate for implementing a quantum computer [8].

Sources of cold molecules could be very valuable for many molecular physics experiments, including high-resolution spectroscopy and coherent manipulation of internal and external degrees of freedom. Due to an initial population of several vibrational and rotational states of the molecules as well as the lack of closed optical transitions, the simple laser-cooling schemes demonstrated with atoms and atomic ions cannot be applied to molecules. There have, however, been a few suggestions for laser cooling of molecules [9–11], but only one experiment has been reported [9], showing a very weak cooling effect in CO$_2$ gas. Recently, Cs$_2$K$_2$ molecules with a translational temperature of a few hundreds of μK have been formed through photoassociation of cold Cs atoms in a magneto-optical trap [12,13]. Buffer-gas cooling by He atoms in a cryogenic environment is another cooling technique that recently has led to magnetic trapping of CaH molecules at temperatures of a few hundred millikelvins [14] and proven to be effective in cooling trapped ionic molecules down to 10 K [15]. The cooling of molecules in supersonic expanded beams has been known for quite some time to be a very effective and important tool for experiments requiring only short interaction times and temperatures in the few kelvin region [16].

In this Rapid Communication we present results on the formation of up to 1000 translationally very cold ($T<100$ mK) MgH$^+$ and MgD$^+$ molecular ions formed by a photochemical reaction, and sympathetically cooled in a linear Paul trap [17] through the Coulomb interaction with laser-cooled Mg$^+$ ions. The present experiments prove that a relative large quantity of trapped molecular ions can be translationally cooled to the low temperatures where spatial ordered structures appear. These structures are well suited to a variety of chemical physics studies, such as high-resolution molecular spectroscopy, photodissociation/ionization, and chemical reactions. The technique used to identify the product ions relies on radial separation of the various cold ions in the trap, and thus is very different from those used in previously reported trap experiments [15,18].

In Fig. 1, a sketch of the important parts of our experiment is shown. The Mg$^+$ ions are created by electron bombardment of a beam of neutral Mg atoms and trapped in a linear Paul trap similar to the one described in Ref. [7]. For Doppler cooling and fluorescence detection, two frequency-doubled dye lasers are used to produce light resonant with the $3s\,^2S_{1/2}-3p\,^2P_{3/2}$ transitions of the ^{24}Mg$^+$ and ^{26}Mg$^+$ ions, respectively. To minimize the radiation pressure force, each laser beam is split into two equally intense parts that are counterpropagating in the trap region. The fluorescence from the ions is imaged by a lens system with a magnification of about 10 onto an image intensified digital charge-coupled-device (CCD) camera. After finishing loading, impurity ions
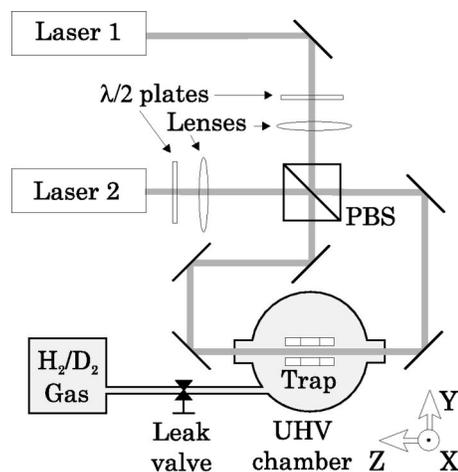

FIG. 1. Sketch of the experimental setup. The $\lambda/2$ plates and the polarization beam splitter (PBS) are used to balance the radiation pressure forces.

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are removed from the trap by a set of changes in the trap parameters that lead to unstable motion of ions with charge-to-mass ratios (Q/M) outside the range $[1/26,1/24]$ (in units of e/amu). After this purification procedure the trap primarily contains $^{24}Mg^+$, $^{25}Mg^+$, and $^{26}Mg^+$ ions in abundances close to the natural ones of $\sim 80\%$, $\sim 10\%$, and $\sim 10\%$, respectively. By leaking-in H_2 or D_2 gas, the pressure of the vacuum chamber is typically raised from the normal background gas pressure of 2×10^{-10} mbar to about 6×10^{-9} mbar.
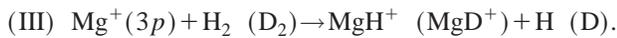
If the cooling lasers are switched off during the presence of the reacting gas, the Mg^+ ions will be in the $3s\,^2S_{1/2}$ state, and only the following reaction (I) is energetically allowed [19,20]:

$$\text{(I)} \quad Mg^+(3s) + H_2 \ (D_2) \rightarrow MgH_2^+ \ (MgD^+).$$
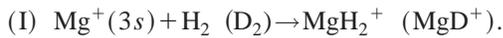
When the Mg^+ ions are laser excited to the $3p\,^2P_{3/2}$ state, the following reactions are energetically possible [19–21]:

$$\text{(II)} \quad Mg^+(3p) + H_2 \ (D_2) \rightarrow MgH_2^+ \ (MgD_2^+),$$

and

$$\text{(III)} \quad Mg^+(3p) + H_2 \ (D_2) \rightarrow MgH^+ \ (MgD^+) + H \ (D).$$

In reactions (II) and (III) the binding can in principle be achieved with the excess energy being carried away by an emitted photon. Since the trap potential depth is about 1 eV, practically all molecular ions formed by any of these reactions are expected to be trapped.

When several cold singly charged ion species are present in the trap at the same time, they will separate radially according to their masses, due to the fact that the effective radial trap potential is given by $U_{eff}(r)\propto r^2/M$. Since the product molecular ions of reactions (II) and (III) have different masses, the radial positions of the molecular ions with respect to the $^{24}Mg^+$ and the $^{26}Mg^+$ ions provide information about the dominant reactions.

Figure 2(a) presents a CCD image of an ion crystal (projected to the y-z plane) before leaking H_2 gas into the vacuum chamber. The fluorescence distribution obtained by integration of this picture along the z axis is shown in Fig. 2(b). The ion crystal consists mostly of $^{24}Mg^+$ ions, with only the outermost shell containing partly $^{25}Mg^+$ and partly $^{26}Mg^+$ ions [22]. In Fig. 2(c) a sketch of the cross section (x-y plane) of the ion crystal shell structure is presented to illustrate this point. The typical spacing of the ions is about 30 μm. The two gray scales used in Figs. 2(b) and 2(c) indicate the contribution from the two fluorescing isotopes to the projected signal. The light gray $^{26}Mg^+$ signal is weak since this isotope is not abundant enough to fill a shell; therefore, it is mixed with the nonfluorescing $^{25}Mg^+$ ions. Similarly, the central string of the ion crystal is only partly filled with $^{24}Mg^+$ ions due to the presence of doubly charged magnesium ions as well as light singly charged background gas ions created during the loading process. Next, H_2 gas was let in at a pressure of 6×10^{-9} mbar with only the $^{24}Mg^+$ cooling laser present to avoid possible photochemical reactions with the $^{26}Mg^+$ ions. This procedure made it possible for the
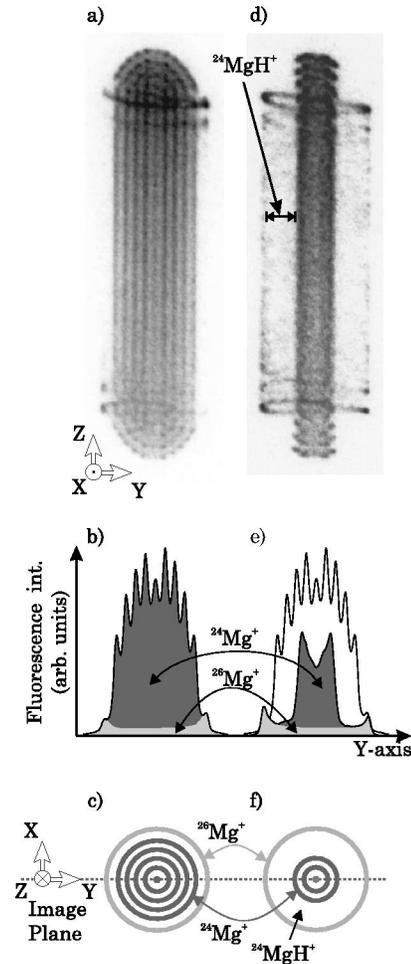

FIG. 2. (a) CCD pictures of fluorescence from $^{24}Mg^+$ and the $^{26}Mg^+$ ions in an ion crystal before introduction of H_2 gas. (b) Fluorescence distributions obtained by integration of the fluorescence signal from (a) along the z axis. (c) A sketch showing the ion crystal shell structure in the x-y plane, with a core of $^{24}Mg^+$ ions and an outermost shell of $^{26}Mg^+$ ions. In (b), the contributions from the two isotopes to the fluorescence signal are indicated by the two gray scales. (d), (e), and (f) correspond to (a), (b), and (c), respectively, but after H_2 gas loading (see the text for more details). The molecular $^{24}MgH^+$ ions fill the region between the fluorescing core ($^{24}Mg^+$) and the outermost shell ($^{26}Mg^+$). In (e) the integrated fluorescence distribution from (b) is shown for comparison.

ions to stay crystallized during the gas load. A sequence of pictures taken at various times during a constant gas load clearly showed how the $^{24}Mg^+$ content in the crystal was lowered. Figure 2(d) shows a picture after the gas had been introduced. During the short exposure time of this picture, the laser resonant with the $^{26}Mg^+$ ions was also present. Comparing the pictures in Figs. 2(a) and 2(d) as well as the fluorescence distributions of Figs. 2(b) and 2(e), one sees that the core containing $^{24}Mg^+$ ions has been reduced dramatically, whereas the number and radial position of the $^{26}Mg^+$ ions are unchanged. In both Figs. 2(a) and 2(d), the $^{26}Mg^+$ ions are primarily located in rings in the x-y plane towards the ends of the crystals. This effect can be due to small laser beam imbalances as well as patch potentials from

nonperfect trap electrodes. Between the ^{24}Mg$^+$ and ^{26}Mg$^+$ ions, a region solely containing singly charged ions with the mass of 25-amu ions has appeared in Fig. 2(d), indicating that it is reaction (III) that dominates. A sketch of an ion crystal cross section (x-y plane) after the reaction is provided in Fig. 2(f) to further illustrate this.

We also performed experiments in which the H$_2$ gas was let in without any of the cooling lasers present. When the pressure had resumed its background level, we unblocked the cooling lasers and recrystallized the ion cloud. Even though the total size of the crystals decreased, their shapes and the relative amount of ions with different masses did not change. This indicates that the presence of the H$_2$ gas, when the Mg$^+$ ions are in the $3s\,^2S_{1/2}$ ground state, predominantly leads to collisional losses and not to the formation of molecular ions by reaction (I). We can hence conclude that only in the presence of a resonant light field, giving rise to a population of the excited $3p\,^2P_{3/2}$ state of the ^{24}Mg$^+$ ions, are measurable reactions taking place and the product molecular ions primarily ^{24}MgH$^+$ ions formed by reaction (III).

A second proof of the dominance of the photochemical reaction (III) was achieved by repeating the sequence of the experiments above with D$_2$ gas instead of H$_2$ gas. Since the ^{24}MgD$^+$ ions have the same mass as the ^{26}Mg$^+$ ions, the ^{26}Mg$^+$ ions are expected to mix spatially with the ^{24}MgD$^+$ molecular ions in the ion crystal. The experiments showed that the ^{26}Mg$^+$ ions became diluted and scattered in the region between the core of ^{24}Mg$^+$ and their radial position before the reaction, proving the production of singly charged ions with a mass of 26 amu, consistent with the formation of ^{24}MgD$^+$ ions by reaction (III).

Measuring the integrated fluorescence from the ^{24}Mg$^+$ ions in an ion crystal as a function of time, one can find the absolute reaction rates of reaction (III) if the H$_2$ (D$_2$) gas pressure and the averaged population of the excited state $3p\,^2P_{3/2}$ are known. In the present setup, the gas pressure can only be measured with an accuracy of a factor of 2 by an ionization gauge, while it is more complicated to estimate the absolute degree of excitation, since it depends on several parameters, such as the laser power or frequency and residual micromotion [23,24] along the laser beam axis. A rough estimate gives a reaction rate constant of about 5×10^{-10} s^{-1} cm^3 for H$_2$. Since the trap characteristics and the pressure gauge accuracy are only weakly dependent on time, we can find the dependence of the reaction rates on the laser detuning for a specific laser power. Figure 3 shows the total fluorescence from the ^{24}Mg$^+$ ions as a function of time, together with exponential fits, in the case of a D$_2$ gas load at 6×10^{-9} mbar for three different laser detunings. As expected from reaction (III), the reaction rate is decreasing with increasing detuning and the corresponding decrease of the population of the $3p\,^2P_{3/2}$ state. We have observed the clear trend that the reactions are faster for H$_2$ than for D$_2$, and we are working on precise values for the relative reaction rates. The ion crystals on which the fluorescence data in Fig. 3 are based contained initially more than 1000 ^{24}Mg$^+$ ions, of which more than 95% were transformed into MgD$^+$ ions by reaction (III) before the ion crystals melted. In terms of the
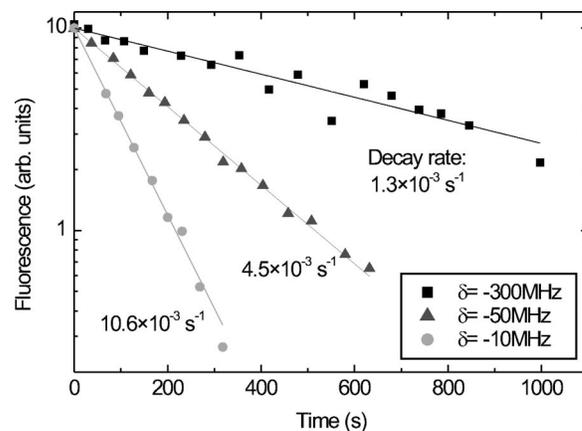

FIG. 3. Data series representing the total fluorescence from the ^{24}Mg$^+$ ions as a function of time during a D$_2$ gas load for various laser detunings δ from the $3s\,^2S_{1/2}-3p\,^2P_{3/2}$ transition. The lines represent fits to exponential decays with a constant background.

total number of ions as well as the relative content of sympathetically cooled ions, the ion crystals described are, to our knowledge, by far the largest obtained so far.

Since both the ^{24}Mg$^+$ and the ^{26}Mg$^+$ ions in Fig. 2(d) are well crystallized, which, according to molecular dynamics simulation, they only would be at temperatures of a few tens of millikelvins [25], we may conclude that the translational temperature of the MgH$^+$ (MgD$^+$) ions is of the same magnitude, and certainly below 100 mK. Since the molecular ions produced have a storage time of tens of minutes in the trap, the temperatures related to the vibrational and rotational degrees of freedom are expected to be close to the trap chamber temperature (about 300 K) due to the interaction with blackbody radiation. This fact is supported by a storage ring experiment in which initially hot CH$^+$ ions were observed to cool rotationally to the temperature (again about 300 K) of the beam tubes in about 20 s [23]. Having an ion trap in a cryogenic environment, passive cooling of the internal degrees of freedom to below 1 K should be possible.

Since the ionic molecules at the trap axis can be localized spatially within a few μm^3, a string, partly consisting of molecular ions, would be a perfect target for molecular physics at the single molecule level, and could be applied, in e.g., coherent-controlled photoionization or photodissociation experiments. The molecular-ion identification technique presented above is nondestructive, and hence the product ions could serve as the starting point for further chemical reactions, and more elaborate reaction chains could be studied step by step. It should be possible to produce, trap, and cool many other molecular ions. E.g., by electron bombardment, we have recently produced and trapped N$_2^+$ ions, which were sympathetically cooled to the same temperatures as those reached in the experiments above. In our view, ion traps with laser-cooled ions can hence turn out to be general and versatile tools to produce very cold molecular ions of interest for a large variety of physics and chemistry experiments.

In conclusion, we have produced MgH$^+$ (MgD$^+$) ions by photochemical reactions between the Mg$^+$ ions in the

excited $3p\,^2P_{3/2}$ state and H_2 (D_2) molecules. The molecular ions were cooled translationally to temperatures below 100 mK through the Coulomb interaction with laser-cooled Mg^+ ions and were spatially well localized in ion crystals. These crystals could contain more than 1000 ions, with up to 95% being molecular ions.

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