

## Production of Ultracold Trapped Molecular Hydrogen Ions

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We have cooled ensembles of the molecular hydrogen ions  $\text{H}_2^+$ ,  $\text{H}_3^+$ , and all their deuterated variants to temperatures of a few mK in a radio frequency trap, by sympathetic cooling with laser-cooled beryllium ions. The molecular ions are embedded in the central regions of Coulomb crystals. Mass spectroscopy and molecular dynamics simulations were used to accurately characterize the properties of the ultracold multispecies crystals. We demonstrate species-selective purification of multispecies ensembles. These molecules are of fundamental importance as the simplest of all molecules, and have the potential to be used for precision tests of molecular structure theory, tests of Lorentz invariance, and measurements of electron to nuclear mass ratios and their time variation.

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Ultracold molecules represent a new frontier in the field of quantum optics and are excellent systems for high-precision measurements. One of the most promising applications for trapped ultracold molecules (ions or neutrals) is high-precision spectroscopic measurements, for example, of fundamental constants such as particle mass ratios [1], nuclear properties [2], QED effects [3], parity violation in enantiomers [4], searches for a permanent electric dipole moment of the electron [5], and Lorentz invariance [6].

Among molecules,  $\text{H}_2^+$  and its isotopomers  $\text{HD}^+$ ,  $\text{D}_2^+$ , etc., are of fundamental importance since they are the simplest molecules, containing only one electron and two simple nuclei. Their energy levels and transition rates can be calculated with a high degree of accuracy [1,3,7–9], providing reliable theoretical results for comparison with experiment. A number of such measurements have been performed to date [10–16]. These measurements have been limited by systematic shifts and broadening effects to spectroscopic accuracies around 1 part in  $10^6$ . New high-precision spectroscopic measurements on molecular hydrogen ions could yield much more precise energy values, improving on these measurements by 4 orders of magnitude or more. They could then yield an improved determination of the deuteron quadrupole moment, and also open an independent route toward determination of the electron-proton mass ratio  $m_e/m_p$  [17]. This involves measurements of one or more rovibrational transition frequencies in  $\text{HD}^+$  and  $\text{H}_2^+$  and comparison with precise first-principles calculations of the energies of these states as a function of  $m_e/m_p$ . Furthermore, measurements of ratios of the transition frequencies as a function of time allow a direct test of the time independence of nuclear-to-electron mass ratios ( $m_p/m_d$  and  $m_e/m_p$ ) [1].

For high measurement accuracy, cold, well-localized samples of these molecular ions are required in order to eliminate first-order Doppler shifts (in the Lamb-Dicke regime), to minimize second-order Doppler shifts, and to reduce other systematic effects.

$\text{H}_2^+$ ,  $\text{H}_3^+$ , and their deuterated isotopomers are also among the most abundant molecules in interstellar clouds, and precision studies of their chemistry and dissociative recombination are of importance in understanding the properties and evolution of such clouds [15,18]. The degree of control enabled by the ability to trap well-localized, cold molecules for long periods of time (up to several hours), in a tightly controlled chemical environment, combined with molecular quantum state preparation techniques, could open new approaches to these studies.

Several alternative methods to produce cold and ultracold molecules have emerged recently, such as deceleration of supersonic beams [5], selection of translationally cold molecules from a gaseous ensemble [19], buffer gas cooling with cold helium gas [20], implantation of molecules into cryogenic droplets of He [21], photoassociation of laser-cooled neutral atoms [22], and production of ultracold molecules via Feshbach resonances [23]. Neutral molecular Bose-Einstein condensation has also been achieved [24,25].

Another powerful method which can be applied to a wide variety of both charged and neutral species is sympathetic cooling [26–30]. For ions, the cooling of particles of one species by an ensemble of directly (laser) cooled particles of another species is very efficient due to their long-range electrostatic interaction. For sufficiently strong cooling, an ordered structure (Coulomb crystal) is produced [31]. In this work we report sympathetic cooling of molecular hydrogen ions, and their embedding and localization in Coulomb crystals of singly ionized beryllium.

We use a linear quadrupole trap to simultaneously store both  $\text{Be}^+$  and molecular ions. The radio frequency trap is driven at 14 MHz, with a peak-to-peak amplitude of 380 V. This results in a radial Mathieu stability parameter  $q_r \approx 0.04$  for the  $\text{Be}^+$  [32], giving a radial secular oscillation frequency of 280 kHz. For the molecular hydrogen isotopomers  $q_r$  lies between  $\sim 0.05$  ( $\text{D}_3^+$ ) and  $\sim 0.2$  ( $\text{H}_2^+$ ).

The trap is enclosed in a UHV chamber kept below  $10^{-10}$  mbar. The chamber is equipped with a leak valve for the controlled introduction of gases, whose pressure may be measured by an ion gauge. The all-solid-state 313 nm laser system for cooling of  $\text{Be}^+$  has been described elsewhere [33].

To load  $\text{Be}^+$  ions into the trap, atoms are thermally evaporated from a beryllium wire, and ionized an electron beam. The molecular loading is achieved by leaking in neutral gas at a pressure of  $\sim 3 \times 10^{-10}$  mbar, ionized by an electron beam with an energy of 200 eV, and a current of  $\sim 30 \mu\text{A}$ , for a loading time of 5 s. This produces mixed-species crystals like those shown in Figs. 1(a) and 1(b). The ions with a higher charge-to-mass ratio (in this case the molecular ions) experience a stronger trap pseudopotential, and thus form a dark (nonfluorescing) core to the crystal. The asymmetric distribution of species along the  $z$  axis observed in Fig. 1(b) is caused by the light pressure of the cooling laser on the beryllium ions.

The observed crystals are faithfully reproduced by our molecular dynamics (MD) simulations, which include the full Coulomb interaction between all the ions, the effects of radiation pressure, and finite ion temperatures. Because of the close agreement between simulation and experiment, we can use the modeling to extract information such as the number, three-dimensional spatial distribution, and temperature of the different ion species from our CCD images.

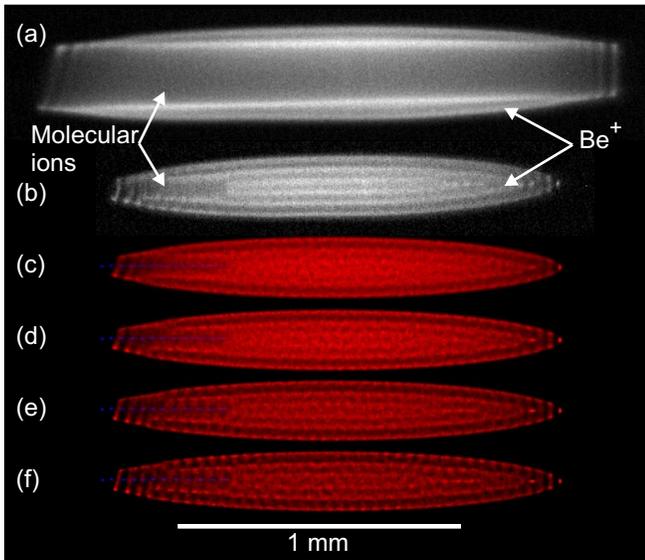


FIG. 1 (color online). Fluorescence images of (a) a large ion crystal with a high fraction of sympathetically cooled ions (approximately 1200 light ions and 800  $\text{Be}^+$  ions), (b) a smaller crystal containing around 690  $\text{Be}^+$  ions, and 12  $\text{HD}^+$  ions, and simulated images of this crystal at (c) 20, (d) 12, (e) 8, and (f) 6 mK. In the simulations, the beryllium ions are shown in red (gray) and the  $\text{HD}^+$  ions in blue (not shown in print). The simulations show this crystal to be around 10 mK in temperature. Laser cooling beam propagation is to the right, along the  $z$  axis.

The number of ions of different species given in Fig. 1(b) was found in this way.

We identify the trapped species by their mass-dependent motional frequencies. For individual ions in a radio frequency trap, the oscillation frequency is inversely proportional to their mass. In mixed-species crystals, the frequencies can be shifted by mutual Coulomb interactions of the species. In these experiments, this effect is not large enough to affect our use of the motional spectra for species identification. We excite the ions motion in the  $x$ - $y$  plane using an external electrode parallel with the  $z$  axis of the trap. An oscillating potential is applied and the  $\text{Be}^+$  fluorescence recorded as a function of excitation frequency. When the applied potential is resonant with a motional frequency of a crystal component, the ions are heated and the fluorescence of the beryllium ions in the crystal is affected. This heating causes an increase in fluorescence when the cooling laser is detuned far to the red of the cooling transition, as is the case here.

Figure 2 shows the motional excitation spectrum of a cold crystal with a small, stringlike molecular core following the loading of neutral HD gas. The spectrum shows three motional resonances. These are the signatures of individual sympathetically cooled species. The species other than  $\text{HD}^+$  are generated by chemical reactions during the loading process, whereby the directly ionized  $\text{HD}^+$  gas reacts with neutral HD background gas, forming various di- and triatomic molecular ions, including  $\text{H}_2\text{D}^+$  and  $\text{HD}_2^+$ , and (undetected) neutral atoms. The reactions of the diatomic hydrogen molecules with their positively charged ions to form triatomic molecular ions (e.g.,  $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$ ) are exothermic by around 1.7 eV. The signature of the  $\text{D}^+$  ions is also present, and this may be produced by direct electron-impact dissociation of neutral  $\text{D}_2$  molecules. Similarly, during loading of neutral  $\text{H}_2$  gas, significant amounts of  $\text{H}_3^+$  can be generated, as seen in Fig. 3. Excitation of ion clouds after the loading of  $\text{H}_2$  gas shows a strong response at a mass of 3 atomic mass units, and a weaker response at mass 2, indicating that the majority component in the trap is  $\text{H}_3^+$ . Finally, after  $\text{D}_2$

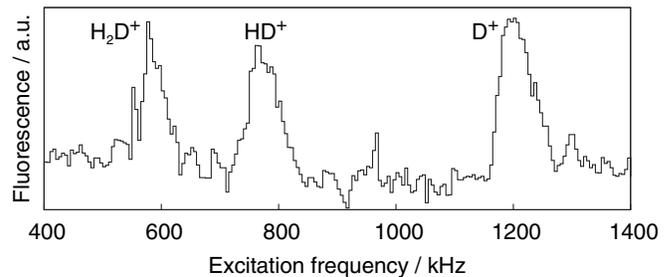


FIG. 2. Typical motional excitation spectrum of a crystal following the loading of HD gas. The resonance frequencies are perturbed from their single-ion values due to the Coulomb interactions between the different trapped species [39].

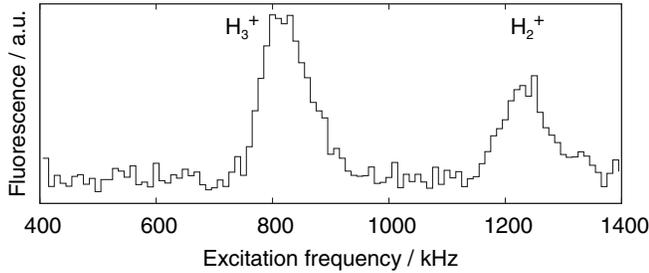


FIG. 3. Motional excitation spectrum of a crystal following the inlet and ionization of  $H_2$  gas, showing the presence of both  $H_3^+$  and  $H_2^+$  ions.

loading, measurements show the presence of ions with masses 2 ( $D^+$ ), 4 ( $D_2^+$ ), and 6 ( $D_3^+$ ).

It is possible to gain information about the core temperature from the observed crystal structures. The thermal motion of the fluorescing ions leads to blurring of our CCD images, and these can be compared with simulated images (Fig. 1). For the experimental crystal of Fig. 1, agreement is found for a  $Be^+$  temperature of 8 mK. This sets an upper limit, as our experimental images are also limited in sharpness by our detection optics, CCD resolution, and sensor noise. The upper limit varies depending on crystal size and cooling parameters, and is typically in the range 5–15 mK. These temperatures are consistent with measurements of the fluorescence line shape of the beryllium ions.

For all species of molecular ions studied here, our MD simulations show that the core of the crystal, sympathetically cooled by the laser-cooled beryllium ions, is also crystalline and is strongly thermally coupled to the beryllium ions. The strength of this coupling allows us to estimate an upper temperature limit for the core ions, which is typically within a factor of 2 of the beryllium temperature. We may therefore conclude that the sympathetically cooled molecular ions have temperatures in the region of 10–30 mK. We have found that smaller crystals are generally colder. This may be compared with a demonstration of sympathetic cooling to the Doppler-limit for laser cooling ( $\sim 1$  mK) in a two-ion crystal [34].

Crystals with a single species of sympathetically cooled particles may be required for future experiments. By detuning the cooling laser far from resonance, an ion crystal can undergo a phase transition to a disordered fluid state. In this situation, the coupling between different ion species is much weaker than in the crystalline state, and the secular motion of the unwanted species can be strongly excited, ejecting the ions from the trap, with minimal effect on other species. The ions can then be recrystallized by retuning the cooling laser close to resonance (Fig. 4). This procedure can be used to remove as many different species as required, producing highly pure two-component crystals.

In summary, we have produced ultracold multicomponent ion crystals containing one or more species of mo-

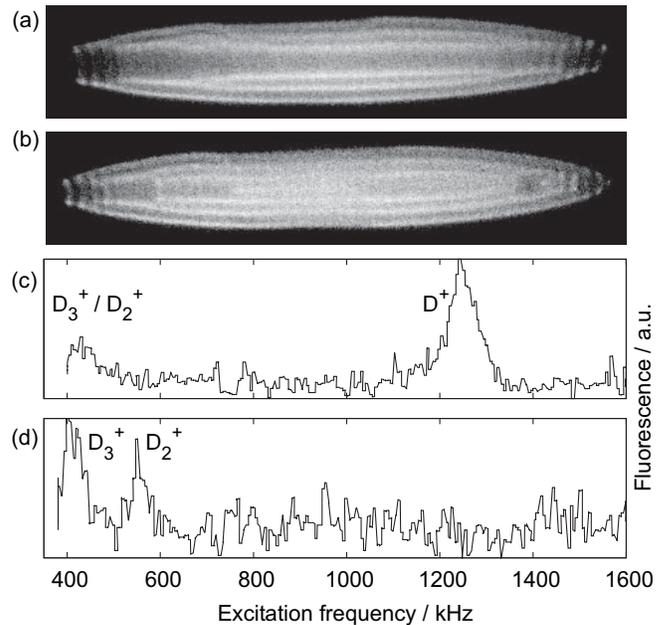


FIG. 4. Partial purification of a mixed-species crystal, following loading of  $D_2$  gas. CCD images (a) before and (b) after the ejection of mass 2 ions (deuterons), with corresponding motional spectra (c) and (d), respectively.

lecular hydrogen ion isotopomer, embedded in a  $Be^+$  ion ensemble. Species cooled were  $H_2^+$ ,  $H_3^+$ ,  $HD^+$ ,  $H_2D^+$ ,  $HD_2^+$ ,  $D^+$ ,  $D_2^+$ , and  $D_3^+$  ions. The number of molecules can be varied between a few and several thousand. The mass ratio of 0.22 between sympathetically cooled and laser-cooled ions is the lowest achieved so far for large ion crystals in a Paul trap.

The crystals are suitable for further experiments, such as the study of mixed-species collective plasma phenomena, cold chemistry, and collisions. The cold molecular ions could be combined with a source of cold neutral species (such as a magneto-optical trap or a cold molecular beam) for ultracold ion-neutral reaction studies. The purified single molecular species crystals obtained are the basis for first laser spectroscopy studies of cold molecular ions. Rovibrational transitions can be detected by selective photodissociation from the excited vibrational level and detection of the product ions or of changes in the crystal structure.

The molecular ions produced in this work are translationally cold, and, due to the energies and decay times of higher vibrational states, we expect them to be vibrationally cold. They are, however, expected to be rotationally warm (around 300 K) due to the blackbody radiation environment of the ion trap and the lack of strong coupling between the internal and external degrees of freedom [35]. For maximizing signal strength, and enabling precise control of molecular states for future precision tests of fundamental physics, cooling of the molecules' rotational energy will be required. Several schemes suitable for application

to hydrogen molecular ions have been proposed [36,37]. For achieving ultimate precision, it appears possible to use a single molecular ion coupled to a single atomic ion, which acts as both coolant and indicator of the molecular state [38]. In order to exploit this technique, it will be necessary to implement the above, or a similar, rotational cooling scheme.

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