

Efficient rotational cooling of Coulomb-crystallized molecular ions by a helium buffer gas

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The preparation of cold molecules is of great importance in many contexts, such as fundamental physics investigations^{1,2}, high-resolution spectroscopy of complex molecules^{3–5}, cold chemistry^{6,7} and astrochemistry⁸. One versatile and widely applied method to cool molecules is helium buffer-gas cooling in either a supersonic beam expansion^{9,10} or a cryogenic trap environment^{11,12}. Another more recent method applicable to trapped molecular ions relies on sympathetic translational cooling, through collisional interactions with co-trapped, laser-cooled atomic ions, into spatially ordered structures called Coulomb crystals, combined with laser-controlled internal-state preparation^{6,7,13–23}. Here we present experimental results on helium buffer-gas cooling of the rotational degrees of freedom of MgH^+ molecular ions, which have been trapped and sympathetically cooled¹³ in a cryogenic linear radio-frequency quadrupole trap. With helium collision rates of only about ten per second—that is, four to five orders of magnitude lower than in typical buffer-gas cooling settings—we have cooled a single molecular ion to a rotational temperature of $7.5^{+0.9}_{-0.7}$ kelvin, the lowest such temperature so far measured. In addition, by varying the shape of, or the number of atomic and molecular ions in, larger Coulomb crystals, or both, we have tuned the effective rotational temperature from about 7 kelvin to about 60 kelvin by changing the translational micromotion energy of the ions²⁴. The extremely low helium collision rate may allow for sympathetic sideband cooling of single molecular ions, and eventually make quantum-logic spectroscopy²⁵ of buffer-gas-cooled molecular ions feasible. Furthermore, application of the present cooling scheme to complex molecular ions should enable single- or few-state manipulations of individual molecules of biological interest^{4,5}.

Cooling of molecules through collisional interactions with a cryogenically cooled He buffer gas has in the past decades been applied to produce both translationally and internally cold neutral^{7,12} as well as ionic^{3,11,26} molecular species. For trapped ions, such experiments have been conducted in various types of radio-frequency traps, with the lowest temperatures, of ~ 10 – 20 K, reached in multipole traps^{11,26}. In such experiments, translational, vibrational and rotational degrees of freedom have to be cooled simultaneously, with the result that He densities of the order of 10^{14} – 10^{15} cm^{-3} are required to achieve efficient cooling.

In recent years, researchers have investigated alternative strategies to produce cold molecular ions. These have been based on combining translational sympathetic cooling through interactions with directly laser-cooled atomic ions^{6,7,14–23} with laser-based methods for internal-state preparation^{18–20}. In these scenarios, the translational-cooling scheme is indeed very versatile and can fairly easily bring the translational temperature into the millikelvin¹³ and even the microkelvin range, although internal-state preparation has to be tailored to the specific molecule^{18–20}. The ideal state preparation scheme would, however, be one that provides extremely low translational temperatures and cold internal-state distributions simultaneously, and, in addition, allows for coherent manipulation of the molecules.

In the present Letter, we present results of He buffer-gas cooling in a novel setting where MgH^+ ions are trapped in a cryogenically cooled, linear, radio-frequency quadrupole trap and translationally cooled through Coulomb interaction with simultaneously trapped, laser-cooled atomic Mg^+ ions¹⁸. Under these conditions, the interaction with the He buffer gas is needed only to cool the rovibrational degrees of freedom, and, consequently, He densities of only $\sim 10^{10}$ cm^{-3} , that is, four to five orders of magnitude lower than in typical buffer-gas cooling settings, are sufficient for efficient cooling. The internal-state cooling rate has simply to exceed any heating rates present in the trapping environment. Because the vibrational degree of freedom of the MgH^+ ions is already frozen out at room temperature ($>99.9\%$ probability of being in the vibrational ground state), at the cryogenic temperatures considered here this degree of freedom can be entirely disregarded. In contrast to previous experiments on He buffer-gas cooling, we directly measure the full rotational-state distribution of the cold molecules. For a single MgH^+ ion, we obtain a rotational-state distribution corresponding to a temperature of $7.5^{+0.9}_{-0.7}$ K, the lowest yet reported for a buffer-gas-cooled molecular ion. Furthermore, by exploiting the fact that ions positioned away from the radio-frequency field-free axis of the linear trap exhibit a driven motion at the trapping radio frequency, called ‘micromotion’²⁴, we are able to tune the effective collisional temperature between the MgH^+ ions and He atoms from ~ 7 K to ~ 60 K, just by changing the shape, size or ion composition of the Coulomb crystal. Importantly, we prove that the rotational temperature is in equilibrium with the effective collisional temperature. These results have immediate ramifications for studies of state-dependent processes involving smaller molecular ions of astrophysical interest. Furthermore, they should make it possible to perform single-ion experiments with larger molecular ions of biological relevance under significantly improved control.

The apparatus used in the experiments is described in detail elsewhere^{23,27}, and the essential parameters for calculating the effect of micromotion on the collisional dynamics are presented in Supplementary Information. A typical experimental sequence starts with isotope-selective loading of $^{24}\text{Mg}^+$ ions into the trap through resonance-enhanced photoionization of atoms from an effusive beam crossing the centre of the trap²³. By exciting the $3s\ ^2S_{1/2} \rightarrow 3p\ ^2P_{3/2}$ transition of these ions using light of wavelength 280 nm, they are laser-cooled into a Coulomb crystal. Next, H_2 gas is leaked into the inner trap enclosure (kept at ~ 5 K) through a thin stainless steel tube in thermal contact with a surrounding thermal shielding box at ~ 40 K, and MgH^+ ions are produced in exothermic reactions with Mg^+ ions in the $3p\ ^2P_{3/2}$ state¹³. When the desired fraction of atomic ions has reacted, a valve controlling the H_2 gas inlet is closed and He gas is leaked in through the same tube. Within a fraction of a second (see below), the rotational-state distribution of the MgH^+ ions in the vibrational ground state equilibrates under the specified collisional conditions. Finally, through the application of resonance-enhanced multiphoton dissociation (REMPD) with rotational-state resolution, we determine the population in the individual rotational states (this technique is described in detail in ref. 18).

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In Fig. 1, projection images of a series of Coulomb crystals, in which MgH^+ ions experience various buffer-gas collision conditions due to the spatially dependent, radio-frequency-field-induced micromotion, are presented (upper panels) together with the respective measured rotational-state distributions (middle panels). It is clear in all five cases that the rotational distributions closely resemble thermal ones at different temperatures. Because the full three-dimensional velocity distribution of the MgH^+ ions due to micromotion is well known for any given crystal (Supplementary Information), knowledge of the velocity distribution of the He buffer gas in the trapping region will completely characterize the collision conditions. Fortunately, because a single MgH^+ ion sympathetically cooled by a single atomic ion as in Fig. 1a does not exhibit appreciable micromotion (the micromotion energy has been measured to be well below an equivalent temperature of 1 K), only the buffer-gas velocity distribution contributes to the collisional dynamics here. Consequently, if we assume thermal equilibrium between the translational and rotational degrees of freedom in the collision, we can infer the He gas temperature from the measured rotational-state distribution. Using this distribution, we arrive at a He gas temperature of $8.7^{+1.0}_{-0.7}$ K (Supplementary Information). The corresponding single-ion collisional-speed distribution in the centre-of-mass (COM) frame is presented in the lower panel of Fig. 1a. Using a He temperature of 8.7 K for each of the other four cases in Fig. 1, we present the calculated speed distributions in the COM frame as solid curves in the lower panels together with thermal distributions with the same average kinetic energy (dashed lines). Although the micromotion velocity distribution is not thermal, the speed distribution is still very close to being thermal. This is because micromotion is induced only along a single spatial direction at any given point in space, whereas the He velocity distribution can be assumed isotropic.

In addition to the full rotational distributions presented in Fig. 1, we have measured the rotational ground-state population for a larger set

of Coulomb crystals. In Fig. 2a, this population is plotted as a function of the average micromotion energy, E_{avg} , and is seen to be a monotonically decreasing function of E_{avg} . Larger error bars for the black points result from an uncertainty in the dissociation efficiency when not measuring the whole rotational distribution. In the inset of Fig. 2a, we plot the dissociation efficiency for the measurements with full determination of the rotational distribution, together with a conservative estimate of its range for the remaining cases at higher values of E_{avg} . Assuming rotational ground-state populations corresponding to those of thermal distributions, we show the inferred rotational temperature versus E_{avg} in Fig. 2b. Moreover, in the inset in Fig. 2b we plot the calculated COM collisional-speed distribution for the experiment with the highest value of E_{avg} . This distribution is quite distorted relative to a thermal one with the same average energy. In Fig. 3, we finally plot the rotational collisional temperature, T_{coll} , defined as

$$T_{\text{coll}} = \frac{2}{3k_B} E_{\text{coll}}$$

with

$$E_{\text{coll}} = \frac{75}{58} k_B T_{\text{He}} + \frac{4}{29} E_{\text{avg}}$$

where k_B is Boltzmann's constant and T_{He} is the He temperature. Details about the latter formula can be found in Supplementary Information. Within the uncertainties, we find excellent agreement between the measured rotational and the calculated collisional temperatures, for all data points. The only a-priori unknown parameter for the collisional dynamics, T_{He} , we fixed from the MgH^+ single-ion experiment to be 8.7 K. Importantly, independent control of the shape, size and composition of the ion crystal makes us able to exploit micromotion to tune the rotational

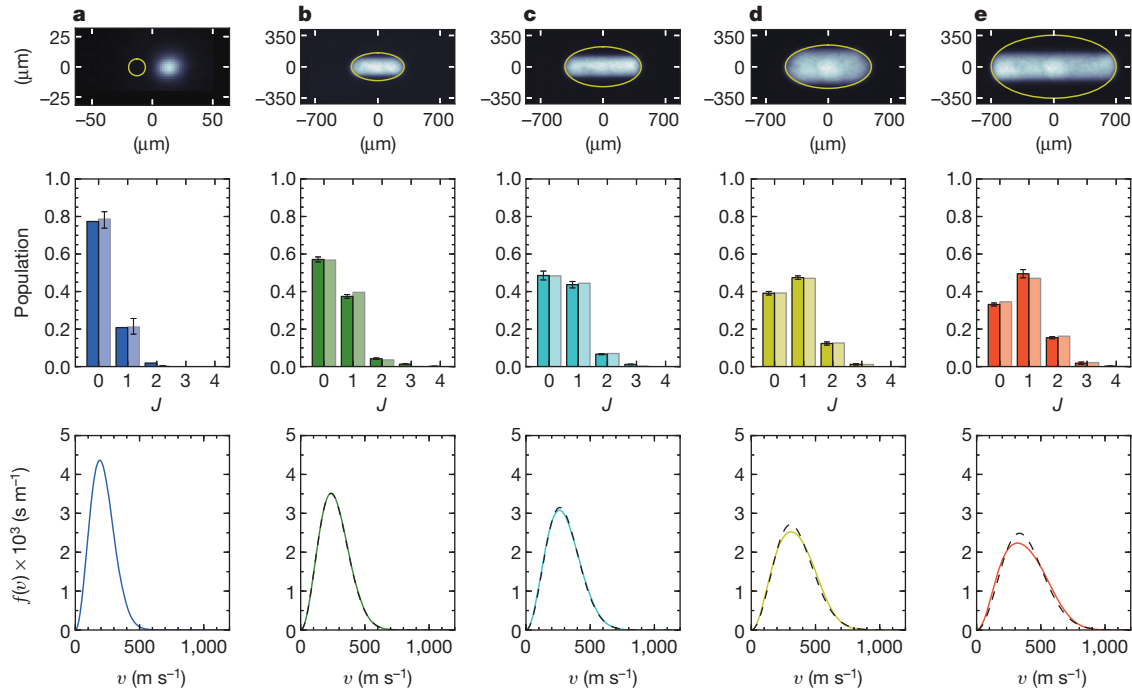


Figure 1 | Spatial, rotational and collisional speed distributions. Upper panels: projection images of a series of Coulomb crystals with a varying numbers of Mg^+ and MgH^+ ions: ($N_{\text{Mg}}, N_{\text{MgH}}$) = (1, 1) (a), (950, 600) (b), (1,750, 2,750) (c), (4,900, 1,250) (d), (5,500, 13,200) (e). In b–e the yellow ellipse indicates the outer boundary of the Coulomb crystals, and in a the circle indicates the position of the single MgH^+ ion. The crystals are cylindrically symmetric around the horizontal axis. Only the fluorescing Mg^+ ions are visible (white regions). Centre panels: measured rotational-state distributions including 1-s.e.m. error bars (dark-coloured bars), as well as best fits to thermal distributions (light-coloured bars) for the crystals b–e. J , rotational quantum

number. For the single MgH^+ ion (a), the heights of the dark-coloured bars are obtained from the number of REMPD-induced dissociation events and the number of applied REMPD pulses. The total number of dissociation attempts was 665. The corresponding best fit of the rotational temperature is obtained from a maximum-likelihood estimate (light-coloured bars). The error bars indicate the 1-s.d. uncertainty of this estimate. The estimated rotational temperatures are 7.6 K (a), 12 K (b), 15 K (c), 20 K (d) and 23 K (e). Lower panels: calculated collisional-speed distributions in the COM reference frame of the MgH^+ –He system, for a He gas at $T_{\text{He}} = 8.7$ K (solid lines), together with thermal distributions with the same kinetic energies (dashed lines).

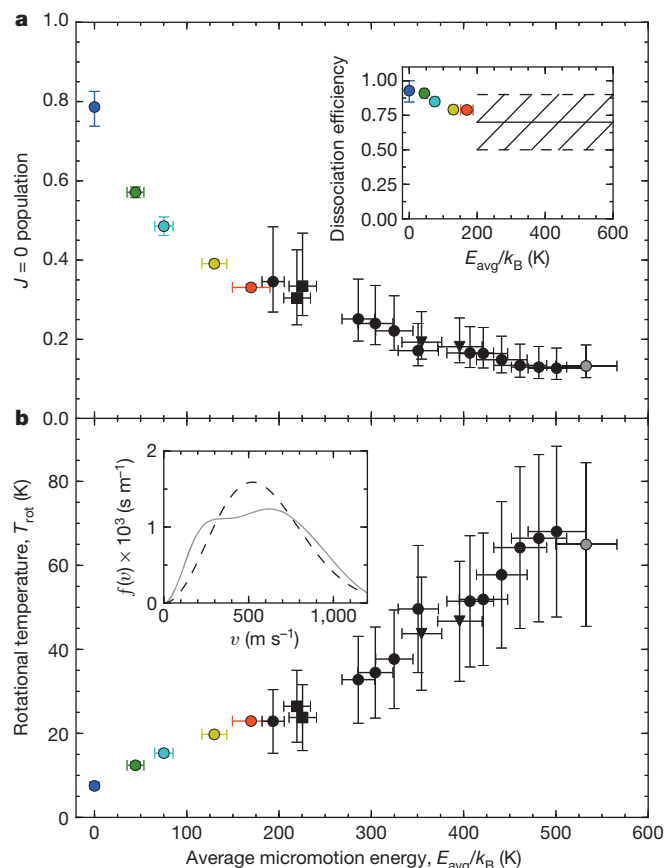


Figure 2 | Rotational ground-state populations and temperatures.

a, Measured rotational ground-state population versus average micromotion energy (see text and Supplementary Information). Error bars, 1 s.d. Inset: measured dissociation efficiencies for the experiments presented in Fig. 1 and estimations of those for the experiments where only dissociation out of the $J=0$ state was carried out. The dashed lines indicate conservative boundaries of the latter. **b**, Rotational temperatures corresponding to the measured $J=0$ populations. The coloured points correspond to the fitted distributions in Fig. 1. Error bars, 1 s.d. Inset: calculated collisional-speed distribution for the rightmost, grey-coloured, data point. For this extreme micromotion energy, a strong deviation from a thermal distribution is noticeable. The different black symbols correspond to different applied radio-frequency voltages: $U_{\text{rf}} = 125$ V (triangles), 145 V (circles) and 185 V (squares). We note that the vertical error bars on some points are smaller than the size of the data points.

temperature from ~ 7 K to ~ 60 K, and hence cover temperatures both considerably below and considerably above the steady-state temperature without the buffer gas (33 K). For the case of single molecular ions, the rotational temperature may be tuned as well, by momentarily moving the ion into regions with large, but controlled, micromotion.

An alternative method to reach low rotational temperatures is passive radiative cooling in a cryogenic environment. However, for the lowest temperature we report, such a scheme will require cooling periods several orders of magnitude longer, and it will furthermore be inapplicable for internal-state cooling of non-polar molecules, for which buffer-gas cooling is known to work²⁸.

We have also studied the cooling dynamics by measuring the times taken for the rotational ground state to refill after first being emptied by a set of REMP pulses. Because our REMP laser system is currently limited to a 10-Hz repetition rate, observation of the refilling dynamics required a decrease in the He buffer-gas pressure by a factor of ten relative to the values used for the experimental results presented in Figs 1–3. In Fig. 4, we plot the rotational ground-state population as a function of the delay of a second set of REMP pulses after full depletion of the ground state. From the fit to the data points, we find a

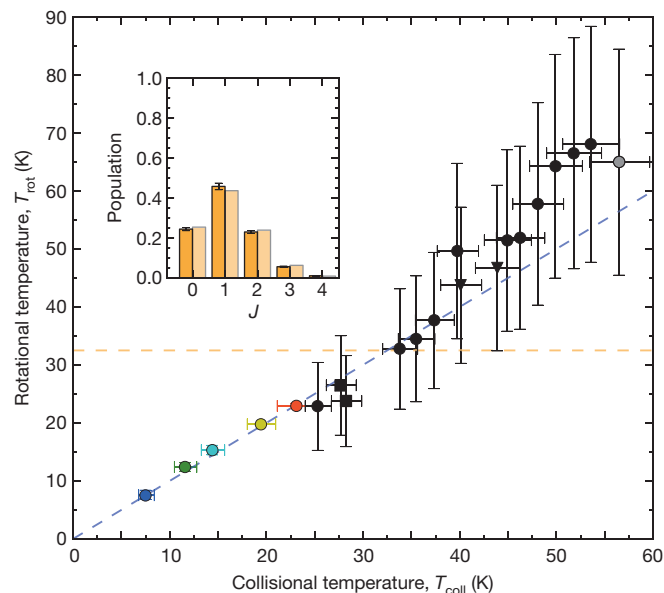


Figure 3 | Rotational temperature versus collisional temperature.

Rotational temperatures, T_{rot} , corresponding to the measured $J=0$ populations as in Fig. 2b, with the average micromotion energy replaced with the effective collisional temperature (see text and Supplementary Information). Error bars, 1 s.d. The light purple dashed line indicates $T_{\text{rot}} = T_{\text{coll}}$, and the horizontal dashed orange line indicates the rotational temperature in the case of no buffer gas ($T = 33$ K). Inset: the corresponding rotational-state distribution. Error bars, 1 s.e.m. We note that the vertical error bars on some points are smaller than the size of the data points.

refilling rate of about 1 s^{-1} , which for the above experimental condition translates into a rate of 10 s^{-1} . With a He temperature of 8.7 K, and assuming the cooling rate to be roughly equal to the Langevin collision rate, we estimate the He density and pressure to be 10^{10} cm^{-3} and 10^{-8} mbar, respectively, or four to five orders of magnitude lower than usually used in buffer-gas cooling experiments^{7,11}. Owing to this extremely low pressure, the He gas does not preclude sympathetic crystallization of the MgH^+ ions initially formed with kinetic energies in the range of ~ 0.1 eV. Moreover, the method should also allow for the introduction of molecular ions from an external source. We have indirectly tested

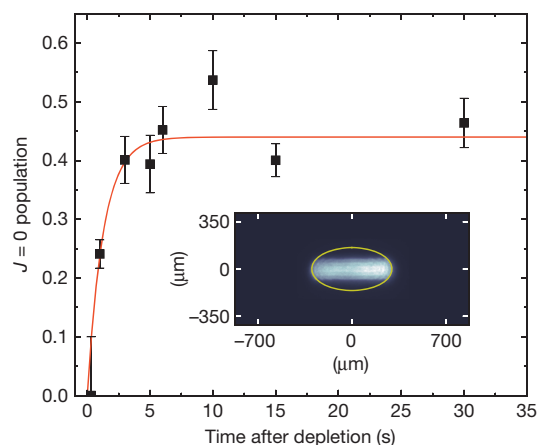


Figure 4 | Cooling dynamics. Measured rotational ground-state population at different delays after its depletion. Error bars, 1 s.d. The He density was roughly ten times lower than that used in producing the results presented in Figs 1–3, to be able to resolve the dynamics with the low repetition rate (10 Hz) of the REMP laser. The red curve is an exponential fit to the data, yielding a refilling rate of $0.8 \pm 0.2 \text{ s}^{-1}$. From this rate, we extrapolate the rate under the experimental conditions of Figs 1–3 to be $\sim 10 \text{ s}^{-1}$. Inset: projection image of the crystal with $(N_{\text{Mg}}, N_{\text{MgH}}) = (650, 950)$ used for this refilling data.

this possibility by producing a single, non-laser-cooled $^{25}\text{Mg}^+$ ion with a kinetic energy of several electronvolts by means of isotope-selective photoionization, and sympathetically crystallizing it with a single, laser-cooled $^{24}\text{Mg}^+$ ion in the presence of the He buffer gas. Finally, we have demonstrated that it is possible to increase the buffer-gas pressure, and thus the cooling rate, by a factor of at least five relative to the conditions leading to the results presented in Figs 1–3. Such higher cooling rates may be important for efficient rovibrational cooling of larger molecules with significantly more internal motional degrees of freedom.

The low buffer-gas collision rate achieved in the present experiment should enable investigations of laser-induced coherent processes as a function of the rotational temperature at the single-molecular level by momentarily moving the molecular ion away from the radio-frequency nodal line of the trapping potential. Applied to single molecules of biological interest, this could potentially be important for unravelling complex energy transport mechanisms such as those governing the coherent phenomena observed in light-harvesting molecules²⁹. Even lower temperatures may potentially be reached using a buffer gas consisting of laser-cooled atoms. Although challenges remain in relation to potential reactive collisions, recent results have demonstrated vibrational cooling of BaCl^+ ions from 300 K to 200 K by means of a gas of calcium atoms laser-cooled to a few millikelvin³⁰.

In the future, the technique presented here could even open up the possibility of combining internal-state buffer-gas cooling with translational sympathetic sideband cooling. Combined with a probabilistic state-preparation scheme for single-molecular ions³¹, this could bring within reach complete quantum-state preparation of a broad range of molecules for spectroscopic and ultracold ion-chemistry studies.

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Supplementary Information is available in the online version of the paper.

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