

Sympathetic cooling of fullerene ions by laser-cooled Mg⁺ ions in a linear rf trap

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A large sample ($N \approx 10^4$) of fullerene ions ($m=720$ a.u.) is cooled by means of a much smaller number (≈ 100) of laser-cooled magnesium ions ($m=24$ a.u.). The results demonstrate that sympathetic cooling of large molecules to low temperatures is feasible. The temperature of the $^{24}\text{Mg}^+$ ions in the mixed $\text{Mg}^+-\text{C}_{60}^+$ ion cloud stored in an rf trap is found to be $T_{\text{Mg}}=5$ K from their fluorescence signal. Molecular dynamics simulations are used to obtain the corresponding equilibrium temperature of the fullerene ions, and show that $T_{\text{C}_{60}}=14$ K.

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I. INTRODUCTION

Laser cooling of trapped atoms and atomic ions allows one to study them at ultralow temperatures (millikelvin for ions, and microkelvin for neutral atoms). Experiments conducted in this unique setting have advanced many areas of physics. However, laser cooling can only be applied to an object with a spectrum that has a recyclable transition. This is not the case for molecules and many elements. Therefore recently there has been a lot of interest in applying the so-called *sympathetic cooling* method to extend ultralow-temperature conditions to those species that cannot be laser cooled directly. The idea of sympathetic cooling is quite simple—when two different species are trapped simultaneously and one of them is laser cooled, the other specie will eventually also cool down through interaction. This effect has been observed in early laser cooling experiments in Penning [1] and rf ion traps [2]. Currently sympathetic cooling is studied with various atomic [3–5] and small molecular ions [6–8]. The same concept is also being applied outside of ion trap research. For example, Bose-Einstein condensation of potassium atoms via sympathetic cooling in an ultracold cloud of rubidium atoms was demonstrated [9]. Our interest in sympathetic cooling is due to the possibility of applying it to cool a large number of molecular ions to millikelvin temperatures, thus making it a unique tool for molecular spectroscopy.

Some theoretical works [10,11] have suggested that sympathetic cooling is the most efficient when it involves ion species of similar mass, and experimental efforts in sympathetic cooling have mostly concentrated on such close-mass ion mixtures. Yet others [12] are predicting that this only holds true at high temperatures, while at low temperatures having significant mass disparity may even be beneficial. However so far all of the theories are based on binary Coulomb collisions as the mechanism of rf heating; therefore, they should not be counted on to provide quantitatively correct results at the very low temperatures where ion correlation effects are strong. Further theoretical and computer simulation efforts are needed to expand the understanding of sympathetic cooling in rf traps.

There are only a limited number of atomic ion species that have an energy level structure practicable to use for laser cooling. It is important to understand how this limitation affects the applicability of the sympathetic cooling method. Here we report experimental and computer simulation results for the case when the laser-cooled ions are much lighter than the sympathetically cooled ions (the mass ratio is 30). This regime is particularly relevant for the sympathetic cooling of large molecular ions.

II. EXPERIMENTAL METHODS

A block diagram of the apparatus used in this experiment is shown in Fig. 1. The linear rf ion trap consists of four parallel cylindrical rods, which are split into three equal segments. This arrangement creates an electrode structure suitable for confining the ions in both radial and axial directions. The radius of the electrodes is 3 mm, the distance from the trap axis to the electrode surfaces is 2.61 mm, and the length of each electrode segment is 50 mm. This trap is of similar design to the one used in Ref. [13] and is built as part of an effort to study properties of fullerenes in an rf ion trap. The ion trap is located inside an UHV chamber with a background pressure of about 2×10^{-10} mbar. Magnesium and fullerene ions are generated by electron bombardment of their respective neutral thermal beams. Helium buffer gas (buffer gas pressure 10^{-6} mbar) is leaked into the chamber for the duration of the ion generation to lower the temperature of the ion cloud and to reduce molecular fragmentation.

Ion confinement along the axis of the trap is achieved by applying a dc bias to each of the three segments of the trap electrodes and the two end electrodes at each end of the trap. During the detection phase the dc offset of the center segment is the lowest in order to collect the ions in the central segment, in front of the secondary electron multiplier (SEM) detector, used for ion counting, and the photomultiplier (PMT), used for fluorescence detection.

The confinement of ions in the radial direction is achieved by applying rf voltage to opposite electrode pairs, so that the radial dependence of the electric potential around the trap axis is quadrupolar:

$$\phi(x, y; t) = \left(\frac{U}{2} - V_0 \cos(\Omega t) \right) \frac{x^2 - y^2}{r_0^2}, \quad (1)$$

where $-V_0 \cos(\Omega t)$ is the applied rf voltage, U is the quadrupole dc offset (zero in our case), and r_0 is the distance from

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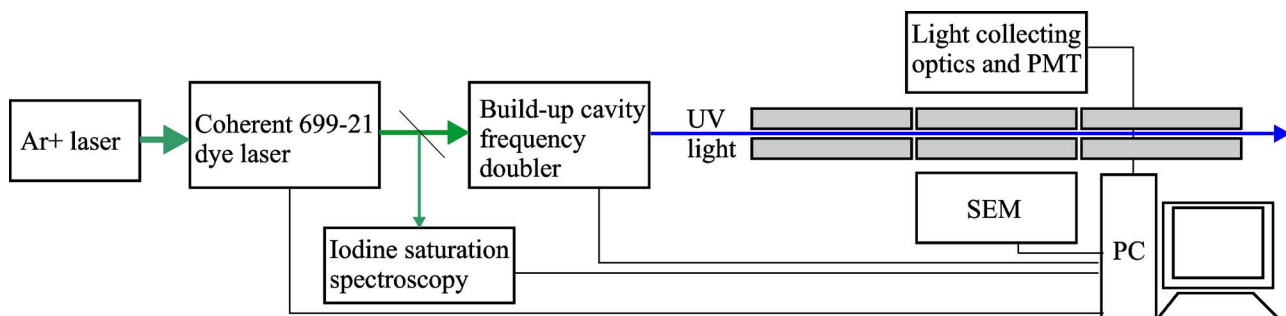


FIG. 1. (Color online) Block diagram of the ion trap, laser system, and detection arrangement.

the trap axis to the electrode surface. The radial motion of an ion in this potential is described by the Mathieu equations [14] with parameters $a = \frac{4eU}{mr_0^2\Omega^2} = 0$ and $q = \frac{4eV_0}{mr_0^2\Omega^2}$. The main property of the Mathieu equation is that for $a=0$ the motion of an ion is confined and the average kinetic energy is conserved for $0 < q < 0.91$. The time-averaged effect of the oscillating potential is that of a harmonic potential that reaches a depth $\bar{D} = \frac{e^2V_0^2}{m\Omega^2r_0^2}$ at the distance r_0 from the center of the trap.

The well-known description of the ion motion as given in the previous paragraph is only accurate for a single ion. However, there are usually more than just one ion stored in the trap, and their Coulomb interaction results in a gradual increase of the kinetic energy with time (this effect is called *rf heating*). The rf heating rate depends on many parameters, such as the temperature of the ions, T ; the amplitude of the rf voltage, V_0 (or the trapping parameter q); and the number of ions, N . The dependence of the rf heating on temperature [15] is as follows: it is practically absent at low temperatures $T < 0.5$ K, sharply increases to a maximum at about $T \approx 1$ K, and then slowly decreases as the temperature gets higher. The rf heating increases very rapidly with the trapping voltage amplitude (faster than the fourth power of V_0), and it increases linearly with the number of ions.

In our sympathetic cooling experiments, magnesium and fullerene ions are stored in the trap simultaneously. The two different outer segments of the trap are used to separately load the magnesium and fullerene ions. A positive dc bias voltage (typically +10 V) is applied to the center segment of the trap during loading, so that the center segment serves as the separating barrier between the magnesium and fullerene segments. After the ions are stored in the separate segments, the dc barrier is gradually lowered and then given a small negative bias voltage (typically -0.5 V), causing both ion species to trickle into the center segment where they mix together. This loading method was implemented because a more straightforward approach of generating fullerene and magnesium ions in the same trapping area when the three trap segments are combined together was ineffective, with the magnesium ion loading efficiency extremely low. We believe that this is due to the relatively high kinetic energy with which the magnesium ions are introduced into the trap (they enter the trap along the trap axis with initial energy of a few eV).

The number of ions in the trap during the experiment is estimated by obtaining a rough mass spectrum using the so-

called *q*-scan method. In this method the trapping amplitude is gradually lowered to reduce the depth of the trapping potential well. When the depth becomes too low to contain certain ions, they are ejected from the trap and are counted by the SEM. Because the potential depth depends on the mass of an ion, being shallower for heavier ions, the ions of larger mass are ejected earlier—i.e., at higher trapping voltages. The detection efficiency of the magnesium ions is estimated to be around 20%, and the detection efficiency of the fullerene ions is a few times lower due to their higher mass, and therefore lower impact velocity on the SEM. Since this method is destructive (the trap is emptied during the detection), it is always the last step of the experiment. To verify the degree of our control over the number of ions to be loaded into the trap, the loading procedure was repeated several times with the same settings, and a *q* scan was obtained each time.

The laser cooling is realized using the $3s^2S_{1/2} \rightarrow 3p^2P_{3/2}$ optical transition of $^{24}\text{Mg}^+$ ions, which has a wavelength of 279.6 nm. This UV wavelength is generated by frequency doubling the 560 nm visible light from a Coherent 699-21 dye laser operating on Rhodamine 110 dye. The typical output power of the dye laser was 400 mW, from which the external frequency doubler generated up to 1.2 mW of UV laser power. With magnesium and fullerene ions loaded into the trap, the UV laser beam is directed along the trap axis to cool the magnesium ions, and the fluorescence signal from the PMT is recorded as the UV frequency is slowly scanned across the cooling transition. At the beginning of the laser scan the UV frequency is red detuned a few GHz below the cooling transition. Then the laser frequency is slowly increased at a typical rate of 60 MHz/s. A portion of the dye laser beam is split off and is used to obtain a Doppler-free saturation spectrum of molecular iodine, which is recorded simultaneously with the Mg^+ fluorescence signal. Since the positions of the iodine hyperfine absorption peaks are known very accurately [16], they provide the reference points for the precise determination of the laser frequency. The laser frequency at intermediate points of the scan is determined by linear interpolation.

Fluorescence line profiles obtained in this way are shown in Fig. 2. The line shape of the fluorescence signal would have been that of a Voigt line shape if the temperature were constant while the laser frequency is scanned across the transition. However, the cooling efficiency of the laser radiation

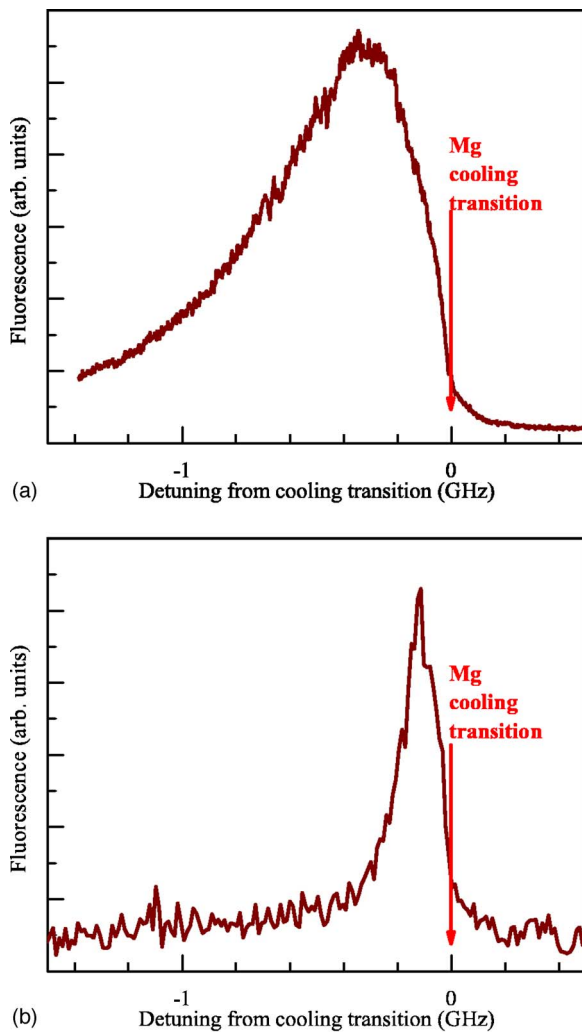


FIG. 2. (Color online) The fluorescence signal of the $^{24}\text{Mg}^+$ ions in the magnesium-fullerene mixture under different conditions. (a) UV laser power at the input window of the vacuum chamber is $400\ \mu\text{W}$, trapping voltage amplitude $V_0=430\ \text{V}$. The number of magnesium and fullerene ions is estimated to be 10^4 each. The linewidth is determined to be $740\ \text{MHz}$. (b) UV laser power is $400\ \mu\text{W}$, trapping voltage amplitude $V_0=384\ \text{V}$; number of fullerene ions is again 10^4 , but the number of magnesium ions is 10^2 . The linewidth is determined to be $200\ \text{MHz}$.

changes with the laser frequency and reaches a maximum below the transition frequency [17], where the lowest temperature is achieved during the scan. After the laser passes this optimal frequency and gets closer to the transition, the cooling weakens, resulting in an increase in temperature and therefore a drop in the fluorescence as seen in Fig. 2. While a better understanding of the rf heating process is needed for the accurate interpretation of the fluorescence curves, we can make a conservative upper bound estimate of the lowest temperature attained during the frequency scan [18]. For this we take the distance from the position of the magnesium resonance to the point where the fluorescence reached half of the maximum value as the half width at half maximum (HWHM) value of a Voigt line shape. We take the temperature corresponding to this value of HWHM as the lowest temperature attained during the laser scan.

The number of magnesium ions detected after the laser scan is much lower than without the laser scan due to the ejection of many of the magnesium ions heated up in the last stage of the laser scan. The rf heating is very high at the trapping voltages that are needed to trap both magnesium and fullerene ions ($q_{\text{Mg}} > 0.3$). When the laser frequency exceeds the transition frequency the laser cooling turns into laser heating. Laser heating and rf heating together heat the magnesium ions to the energies sufficient to escape from the trap.

III. RESULTS

Throughout the measurements the fullerene loading conditions were kept the same, with approximately 10^4 fullerene ions stored in the trap. A set of measurements was performed with the same number of Mg^+ ions as fullerene ions (10^4). The trapping voltage amplitude was varied between $384\ \text{V}$ and $480\ \text{V}$, and UV laser powers of $400\ \mu\text{W}$ and $700\ \mu\text{W}$ were used. One of the fluorescence line profiles observed under these conditions is shown in Fig. 2(a). The ultimate temperature of Mg ions as determined from their fluorescence profile varied from $550\ \text{MHz}$ to $750\ \text{MHz}$, which corresponds to temperatures of $40\text{--}70\ \text{K}$. The experiments were limited to a narrow interval of trapping voltage amplitudes V_0 due to the following factors. First, the trapping voltage should be high enough to produce a potential barrier \bar{D} deep enough to contain the fullerene ions. Experimentally it was determined that this corresponds to the condition $V_0 > 300\ \text{V}$ (or $q_{\text{C}_{60}} > 0.01$). Conversely, the trapping voltage cannot be arbitrarily increased, since the Mathieu equation dictates that magnesium ions can be stored in the trap only if $q_{\text{Mg}} < 0.91$, or $V_0 < 820\ \text{V}$. We have found that the practical region of trapping voltage amplitudes is narrower, $350\ \text{V} < V_0 < 500\ \text{V}$, because outside that interval it becomes increasingly difficult to trap magnesium and fullerene ions simultaneously. At lower trapping voltages the trapping potential is shallow for fullerene ions, and the process of mixing of the fullerene and magnesium ions expels an increasingly large portion of fullerene ions out of the trap. At higher trapping voltages, the magnesium ions are subject to increasing rf heating, and similarly are expelled in the mixing process.

We have also performed sympathetic cooling using a much smaller amount of magnesium ions in the mixture ($\approx 10^2$, 100 times less than the number of fullerene ions). The resulting fluorescence line profile is shown in Fig. 2(b), with the half width of the fluorescence corresponding to a temperature of $5\ \text{K}$ for magnesium ions in the mixture. This significantly lower temperature for a smaller sample of magnesium ions illustrates that rf heating due to their collisions with fullerene ions is not as significant as due to collisions with magnesium ions. This conclusion is verified by a set of measurements in which we did not observe any difference between the fluorescence line profiles of magnesium with and without fullerenes present in the trap.

A direct experimental determination of the fullerene ion temperature using the linewidth of an optical transition is not

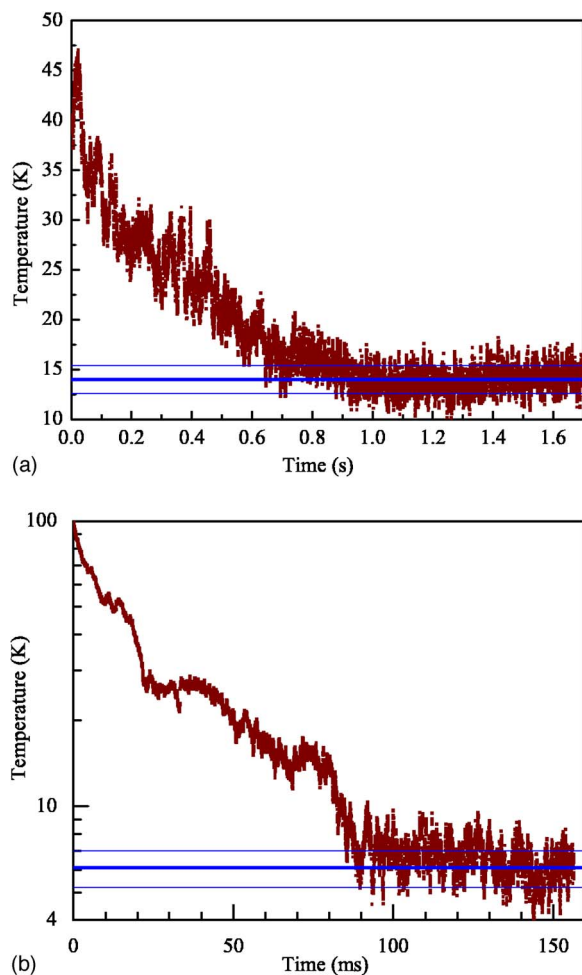


FIG. 3. (Color online) Time evolution of the axial kinetic energy of the fullerene ions. Horizontal lines indicate the equilibrium temperature and its standard deviation. (a) Simulation conditions matching those of our experiment with smaller number of magnesium ions, corresponding to the fluorescence line shape shown in Fig. 2(b). The length of the simulated segment is 1 mm. The number of ions $N_{C60}=200$, $N_{Mg}=2$. This corresponds to a total of 10^4 and 10^2 ions, respectively, over a 50 mm length. (b) The number of magnesium ions is increased to have the same linear density of magnesium and fullerene ions. The length of the simulated segment is 400 μm . The number of ions $N_{C60}=N_{Mg}=80$. This corresponds to a total of 10^4 of each ion specie over a 50 mm length.

possible at this stage. Therefore, to deduce the temperature of the fullerene ions achieved in our experiments, we performed molecular dynamics (MD) simulations. The MD simulation method is similar to the one we used to study rf heating rates [15]. Specifically, the ion cloud is modeled as being infinitely long and periodic boundary conditions are applied along the trap axis. The number of ions for each specie was chosen based on the total number of ions in the trap. The axial temperature of the magnesium ions was maintained constant at 5 K to simulate the effect of the observed laser cooling along the trap axis. The evolution of the fullerene kinetic energy is shown in Fig. 3. The evolution of the kinetic energy was monitored over many rf oscillation periods, sufficient to establish that the temperature of the fullerene ions has reached equilibrium.

Figure 3(a) corresponds to the cooling of the fullerene ions under conditions under which the fluorescence line profile shown in Fig. 2(b) was observed. As one can see from the graph, the average temperature of the fullerene ions reaches 14 K after approximately 1 s. This shows that despite the fact that interaction of magnesium and fullerene ions has no noticeable effect on the laser cooling of the magnesium, it clearly is sufficient to cool down fullerenes to almost the same temperature as the coolant ions. The reason for that is the large difference in rf heating rates of magnesium and fullerenes. The rf heating rate increases very rapidly with the trapping parameter q [5,15], from the square to the fourth power of q , depending on the temperature. Since the trapping parameter q is inversely proportional to the mass and there is a large mass disparity (a factor of 30) between fullerene and magnesium ions, the rf heating rate of fullerenes is 10^3 – 10^6 times smaller than that of magnesium ions. So, while the interaction between the species is very weak, it is sufficient to overcome an even weaker heating rate experienced by fullerene ions.

We have also increased the number of cooled magnesium ions in the simulation to have the same number of both ion species, with the result shown in Fig. 3(b). Again, the axial temperature of the magnesium ions was kept at 5 K (it should be noted that we have not realized this temperature in our experiments with equal ion mixing ratio). In this case the temperature of the fullerene ions decreases at a significantly higher rate, as only 100 ms is needed to reach an equilibrium temperature, which is also lower (6 K). Naively one would expect the cooling rate of the fullerene ions to increase by the same factor that the number of magnesium ions is increased (factor of a 100). However, one should keep in mind that the rf heating rate of the fullerene ions increases as their temperature is decreased. The result can therefore be interpreted as a factor of 10 increase in the fullerene rf heating rate when their temperature is decreased from 14 K to 6 K.

IV. CONCLUSIONS

In summary, we have demonstrated sympathetic cooling of a large number ($N \approx 10^4$) of heavy molecular ions by means of laser-cooled light atomic ions. Two cooling conditions were experimentally investigated. In the first case, a very small number ($\approx 10^2$) of laser-cooled magnesium ions was used as a cooling component in the mixture. The magnesium temperature was determined to be 5 K, and the MD simulations indicate that the fullerenes have achieved a temperature of 14 K. In the second case, the number of coolant ions was much higher ($\approx 10^4$), which resulted in higher rf heating rate, and the magnesium temperatures were significantly higher (40–70 K). This shows that when using the sympathetic cooling method in an rf trap to cool the ions of mass that is significantly higher than the mass of the laser-cooled species, it is beneficial to use a smaller number of laser-cooled ions. In the future we expect to obtain lower temperatures for molecular ions when using the coolant ions

of closer mass (such as barium ions to cool fullerenes) and when we study multiply charged fullerene ions (since the trapping parameters depend on the mass to charge ratio and one can view the increased charge as lowering the effective mass of the ion).

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