

Molecular dynamics simulation of sympathetic crystallization of molecular ions

Stephan Schiller and Claus Lämmerzahl*

Institute for Experimental Physics, Heinrich-Heine-Universität Düsseldorf, 40225 Düsseldorf, Germany

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It is shown that the translational degrees of freedom of a large variety of molecules, from light diatomic to heavy organic ones, can be cooled sympathetically and brought to rest (crystallized) in a linear Paul trap. The method relies on endowing the molecules with an appropriate positive charge, storage in a linear radio frequency trap, and sympathetic cooling. Two well-known atomic coolant species ${}^9\text{Be}^+$ and ${}^{137}\text{Ba}^+$ are sufficient for cooling the molecular mass range from 2 to 20 000 amu. The large molecular charge required for simultaneous trapping of heavy molecules and of the coolant ions can easily be produced using electrospray ionization. Crystallized molecular ions offer vast opportunities for novel studies.

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After the enormous success achieved in the field of cold atom manipulation, significant efforts are under way to develop similar methods for molecules. Samples of trapped ultracold molecules could be used for performing studies of molecular structure, chemical reactions, quantum optics, and molecular Bose-Einstein condensates.

While methods for trapping of molecules, such as magnetic traps [1], electrostatic traps [2], radio frequency (Paul) or electromagnetic (Penning) traps [3] or dipole traps [4] have been demonstrated and are in part already well developed, translational cooling of molecules is a field still under intense development. Direct laser cooling is not applicable due to lack of closed transitions. A technique demonstrated early on for cooling of neutral and charged molecules is by means of cryogenic buffer gas such as ${}^4\text{He}$, see, e.g., Refs. [5–7]. Its extension to ${}^3\text{He}$ [1] allowed reaching temperatures below 1 K. Two recently developed methods are the production of ultracold diatomic neutral molecules by photoassociation of ultracold atoms [8] and the deceleration of polar molecules by time-dependent electric fields [9].

Another powerful method is sympathetic cooling of “sample” particles of one species by an ensemble of directly cooled (often by laser cooling) particles of another species via their mutual interaction. This technique, first demonstrated for ions in Penning traps [10,11], is being applied to an increasingly wide variety of neutral and charged particles (atoms, molecules, elementary particles) in various trap types for applications ranging from mass spectrometry to quantum computing.

In both Penning and radiofrequency traps, first studies showed that molecular ions could be sympathetically cooled (SC) by laser-cooled (LC) atomic ions to temperatures in the range of several K [12,13], and mass ratios down to $m_{\text{SC}}/m_{\text{LC}}=2/3$ were achieved [14]. An important aspect of ion traps is that for sufficiently strong cooling the formation of an ordered structure (Coulomb crystal) results [15,16]. Recently it has been shown that sympathetic crystallization

of molecular ions is possible in a linear rf trap where the molecules are stably incorporated into the atomic Coulomb crystal [17,18]. The molecular ions included MgH^+ , MgD^+ (cooled by Mg^+), and ${}^{16}\text{O}_2^+$ (cooled by ${}^{40}\text{Ca}^+$ or ${}^{24}\text{Mg}^+$), i.e., mass ratios down to 0.6. In sympathetic crystallization of atomic ions, a mass ratio range of 0.8–1.8 has been achieved [19,20].

The range of molecular mass that can be sympathetically cooled to temperatures of the order of 10 K, where the ion ensemble is still in a gas state, has very recently been debated in theoretical work [21–23]. A molecular mass range from 8 to 192 amu (mass ratios 1/3–8) was found using molecular dynamics simulations to be accessible using ${}^{24}\text{Mg}^+$ as coolant ion.

In the present simulations we study a much larger mass range and the regime of much lower temperatures ($\ll 1$ K) and study whether sympathetic crystallization can be reached. We find that essentially all molecular masses can be sympathetically crystallized by one of two commonly used species of laser-coolable ions, ${}^9\text{Be}^+$ and ${}^{137}\text{Ba}^+$. The only requirement for this general method is an appropriate charge state for the molecules. Single positive charges are sufficient for small molecules (mass 2 – 2000 amu). For heavier molecules higher positive charge states are required in order to allow for reliable simultaneous trapping. These are easily produced using electrospray ionization [24]. The ability to store molecules in an almost motionless state in a collision-free ultrahigh vacuum environment for essentially unlimited time is expected to open up vast opportunities for high precision spectroscopy and the study of slow molecular processes.

In order to model sympathetic cooling in rf traps, it is crucial to take collisions into account precisely. Noninteracting ions perform an oscillation at the frequency of the applied rf field, but their cycle-averaged energy is constant if ion-ion interactions can be neglected. When interactions, i.e., collisions, between the ions are taken into account, energy gain from the rf field (rf heating) and transfer of energy from one species to another, i.e., sympathetic heating and cooling, occurs. Approximate models have been proposed to describe these mechanisms [21,22]. However, it is highly desirable to

*Present address: ZARM, University of Bremen, Am Fallturm, 28359 Bremen, Germany.

perform calculations that are essentially free of approximations. We therefore choose a molecular dynamics (MD) approach [25,26].

The simulations are based on solving Newton's equations of motion for the laser-cooled and sympathetically cooled ions

$$m_i \ddot{\mathbf{x}}_i = Q_i \mathbf{E}_{\text{trap}}(\mathbf{x}_i, t) + \mathbf{F}_{C,i}(\{\mathbf{x}_j\}) + \mathbf{F}_L(\dot{\mathbf{x}}_i, t), \quad (1)$$

where $i = 1, \dots, N_{\text{LC}} + N_{\text{SC}}$ (N_{LC} and N_{SC} are the numbers of laser-cooled and sympathetically cooled particles, respectively). Positions, charges and masses are \mathbf{x}_i , Q_i , and m_i , the Coulomb force $\mathbf{F}_{C,i} = (Q_i/4\pi\epsilon_0) \nabla_i \sum_j Q_j / r_{ij}$, where r_{ij} is the distance between particles i and j . Here $\mathbf{E}_{\text{trap}} = \nabla[(x^2 - y^2)\cos(\Omega t)V_{\text{rf}}/2r_0^2 + (z^2 - x^2/2 - y^2/2)U_{\text{dc}}/d^2]$ is the electric field in a linear ion trap [3], where z is along the trap axis. The radial and axial scales of the trap are r_0 and d . A necessary condition for stable trapping of noninteracting ions is a q parameter $q_i = 2(Q_i/m_i)V_{\text{rf}}/(\Omega^2 r_0^2)$ less than 0.9. However, it is well-known experimentally and theoretically that operation at significantly smaller q is favorable since rf heating is less pronounced [23,25]. On the other hand, a lower limit is given by experimental considerations $q_{\text{min}} \approx 0.05$. We therefore choose q parameters in the range 0.05–0.4 for both atomic and molecular ions. As a consequence, the simultaneous storage of heavy molecules ($m_{\text{SC}} \gg m_{\text{LC}}$) requires a molecular charge exceeding unity.

Laser cooling of the LC particles is described by the force \mathbf{F}_L . In actual experiments, its strength is such that cooling may require minutes. Such durations correspond to 10^8 or more rf periods, and cannot be simulated in high-precision MD when particle numbers are large. In order to compromise between a reasonable computing time and realistic laser cooling strength we have used stronger forces \mathbf{F}_L to speed up cooling. Most simulations were performed with a simple linear viscous damping $\mathbf{F}_L = -\beta \dot{\mathbf{x}}$ with friction coefficients in the range $\beta = (1.2 - 8) \times 10^{-22}$ kg/s. These are well below the maximum value (at optimum laser detuning from the cooling transition), $\beta_{\text{max}} \approx \pi^2 \hbar / \lambda^2 \approx 4 \times 10^{-21}$ kg/s for transitions at optical wavelengths λ . For some simulations, we have used more realistic forces, see below.

The diffusion of the LC ion momenta in momentum space due to recoils upon spontaneous emission gives rise to the Doppler cooling limit. This effect is included in the simulations.

The equations of motion are solved using a high-order Runge-Kutta method with adaptive step size. Initial conditions were in part chosen so as to give initial temperatures below room temperature, again in order to reduce the computational effort.

In order to characterize the state of the plasma, from the trajectories of the particles we calculate, for each species, the average kinetic energy per particle, $E_{\text{kin}}^{\text{tot}} = (2N_{\kappa})^{-1} \sum_{\kappa} m_i \langle \mathbf{v}_i^2(t) \rangle$, where $\langle \dots \rangle$ is the time average over one period of the rf field, the time averaged secular energy per particle $E_{\text{kin}}^{\text{sec}} = (2N_{\kappa})^{-1} \sum_{\kappa} m_i \langle |\mathbf{v}_i(t)|^2 \rangle$, and the average interaction energy per particle (at the end of a rf period). Here κ means LC or SC, respectively, and \sum_{κ} de-

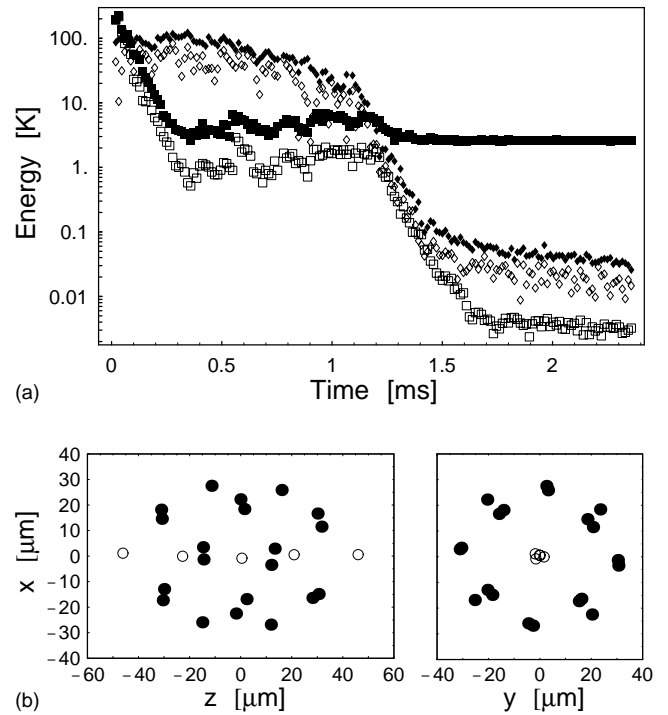


FIG. 1. Simulation with $N_{\text{LC}}=20$ laser-cooled ${}^9\text{Be}^+$ ions and $N_{\text{SC}}=5$ HD^+ molecules. (a) Energies per particle. (b) Spatial structure in the crystalline state (left: projection onto the x - z plane, right: x - y projection); solid circles: ${}^9\text{Be}^+$, circles: HD^+ . The trap parameters are $q_{\text{LC}}=0.13$, $q_{\text{SC}}=0.39$, rf frequency $\Omega/2\pi=8.5$ MHz, $V_{\text{rf}}/r_0^2=17.6$ V/mm 2 , $U_{\text{dc}}/d^2=30$ V/cm 2 . Viscous laser cooling with $\beta=2.4 \times 10^{-22}$ kg/s was used.

notes summation over the corresponding species. The secular energy, where the micromotion oscillation is averaged out, can be taken as an indication of the temperature of the sample, since it arises from the “disordered” motion of the interacting ions in the time-averaged trapping potential. In contrast, the micromotion contribution to the total energy arises from a regular motion. We note that in simulations where the rf potential is replaced by the pseudopotential, i.e., the time-averaged trap potential $V_{\text{pseudo}}(\rho) = \rho^2 Q^2 V_{\text{rf}}^2 / (4m\Omega^2 r_0^2)$ experienced by the particles in radial direction, the cooling is moderately faster. This implies that rf heating is nonnegligible even at the relatively low q values chosen here. In the following we describe three mass regimes of sympathetic crystallization.

Cooling of molecular hydrogen isotopomers. One challenging goal in ultracold molecule studies will be the precision spectroscopy of the simplest (i.e., one-electron) molecules, the hydrogen ions H_2^+ , HD^+ , D_2^+ . The experimental accuracy can potentially be improved by several orders, surpassing by far the current theoretical precision [27]. It will then become possible to test and challenge calculation methods, especially of the relativistic and QED contributions. Moreover, since the vibrational energies depend explicitly on the electron-to-proton mass ratio m_e/m_p [28], their measurement might allow us to determine the value of this fundamental constant by spectroscopic means, providing an alternative and potentially more accurate approach than mass

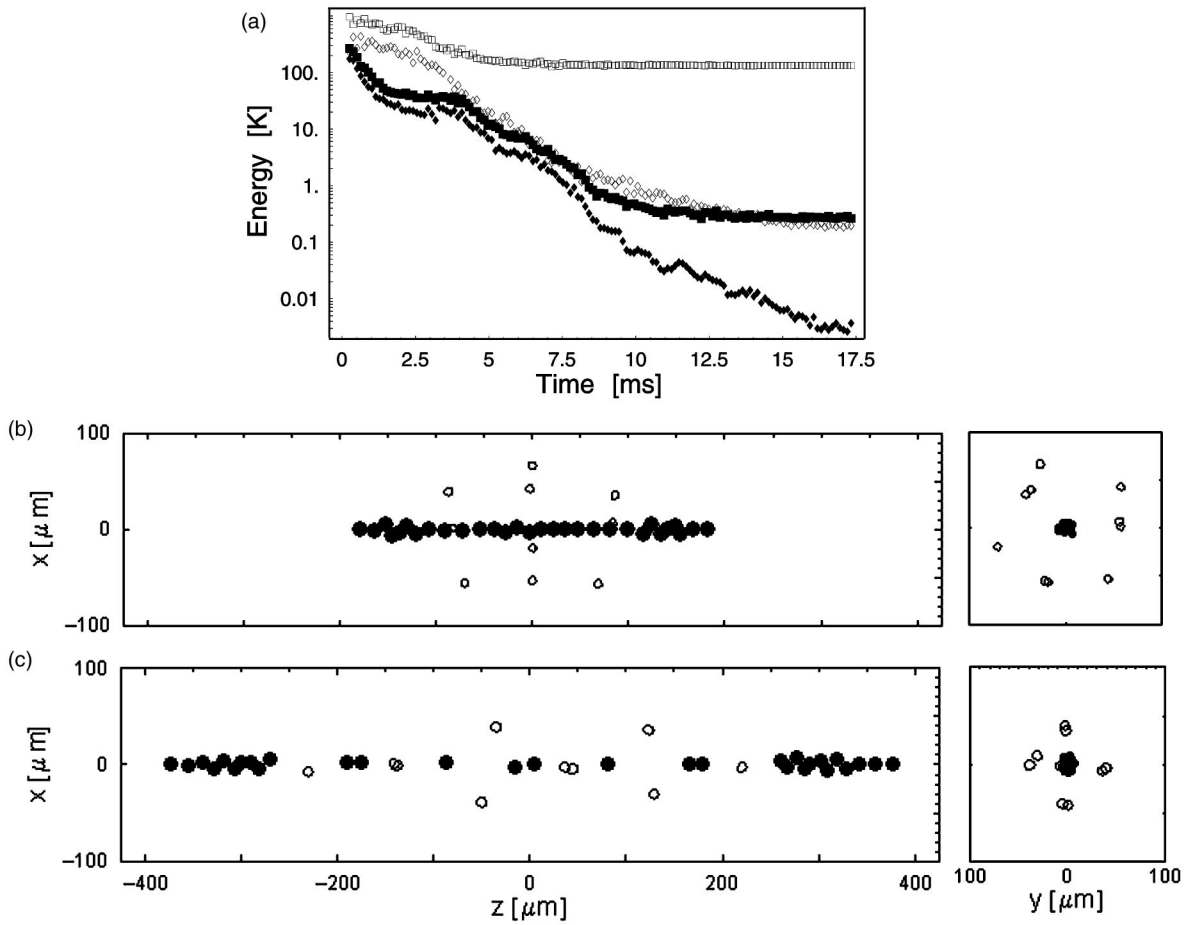


FIG. 2. Sympathetic cooling of 10 molecular ions of mass 20 000 and charge $20e$ by 30 $^{137}\text{Ba}^+$ ions. (a) Energies. (b) Spatial structure (solid circles, $^{137}\text{Ba}^+$ ions; circles, molecular ions). (c) Spatial structure for a simulation where the axial potential is weaker. Parameters $q_{\text{LC}}=0.33$, $q_{\text{SC}}=0.045$, $\Omega/2\pi=1.6$ MHz, $V_{\text{rf}}/2r_0^2=23.8$ V/mm 2 , $U_{\text{dc}}/d^2=12$ V/cm 2 for (b), 3 V/cm 2 for (c). Viscous laser cooling with $\beta=4.8\times 10^{-22}$ kg/s was used.

measurements in Penning traps [29].

A precise measurement will require cold trapped molecules in order to minimize Doppler broadening. The heteronuclear HD^+ is of particular interest since it has dipole-allowed vibrational transitions [30] that could be excited by infrared lasers such as optical parametric oscillators [31] or diode lasers.

A simulation of sympathetic cooling of 5 HD^+ ions by 20 laser-cooled $^9\text{Be}^+$ ions is shown in Fig. 1. The laser quickly cools the Be^+ ions to a liquid state, characterized by comparable Coulomb interaction energy and secular energy (plasma parameter $\Gamma\sim 2$). The atomic ion temperature remains constant while the molecular ions are sympathetically cooled. Only once the molecular secular energy becomes comparable to the atomic secular energy does the latter decrease further. The secular energy of the Be^+ ions finally reaches the Doppler limit. The secular energy of the molecules reaches that level significantly more slowly, since the cooling power of the atomic ions becomes smaller as they settle into the crystalline state.

The spatial structure resulting from the cooling [Fig. 1(b)] can be understood by considering the different pseudopotentials felt by the two particle species [32]. It is three times

larger for the lighter HD^+ ions as compared to the $^9\text{Be}^+$ ions. The total energy of the ensemble is minimized if the HD^+ molecules lie on-axis. The Be^+ ions form a shell structure around them. It is moderately prolate, since the radial pseudopotential and axial potential are similar in strength (Be^+ -oscillation frequencies $\omega_\rho/2\pi=340$ kHz, $\omega_z/2\pi=285$ kHz). The axial arrangement of the HD^+ ions is favorable for spectroscopic investigations, since on axis the micromotion is zero, with a corresponding simplification of their transition spectrum. Since the Be^+ ions form a three-dimensional structure, their micromotion energy remains relatively high compared to their secular energy [Fig. 1(a)]. This is because the off-axis locations of the ions imply corresponding micromotion velocities, proportional to the radial distances.

Simulations with a more realistic (i.e., weaker) cooling force [33,36] were also performed. Qualitatively, the same behavior resulted, however, as expected, sympathetic crystallization was reached after a substantially longer time, about 10 times slower than in Fig. 1(a).

A sample of molecular ions is not always sympathetically cooled in its entirety. For example, in a simulation of 40 Be^+

ions and 10 HD^+ ions, the final state of the system contained 6 on-axis crystallized HD^+ ions embedded in a prolate Be^+ crystal, while 4 HD^+ ions remained hot. It is clear that for small particle numbers the number of cooled particles depends on details of the initial conditions.

The above simulations for HD^+ are of course also applicable to the astrophysically important H_3^+ . We have also performed simulations for other hydrogen ions. We have found (partial) sympathetic crystallization for all masses, from 2 amu (H_2^+) to 5 amu (DT^+).

Cooling of dye molecules. Dye molecules are interesting model systems for studies of complex (i.e., polyatomic) ultracold molecule manipulation because they are well characterized and can easily be excited optically. Various dye molecules have masses exceeding a few times the mass of heavy atoms. Here we consider the case of cooling rhodamine 6 G, a molecule of mass 493 that can be transferred to the gas phase singly charged by means of electrospray ionization. The coolant ion is chosen to be $^{137}\text{Ba}^+$. In this case, the larger mass-to-charge ratio of the molecules leads to a shell structure with the atomic ions in the center and on axis. The small fraction of the molecules which is well embedded in the atomic ensemble cools and crystallizes on the same timescale as the atomic ions. The remainder experiences a much weaker cooling due to the absence of a ‘‘caging’’ effect. The time scale for cooling and crystallization of all molecules was found to be 10 times larger than for the atomic ions.

Cooling of large molecules. Large molecules such as amino acids or proteins can be transferred into vacuum in high charge states by electrospray ionization [24]. In this method, protons are attached to molecules that emerge from a solution spray. Large molecules are produced with a distribution of charge states, with typical specific charges in the range $m/Q = 700 - 1500$. For example, the charge states for a protein of mass 17 000 can range from 11 to 25 [34]. Such specific charges are sufficiently near those of laser-coolable heavy atomic ions ($^{137}\text{Ba}^+$, $^{172}\text{Yb}^+$, $^{199}\text{Hg}^+$). Since the q parameters $\sim Q_i/m_i$ are within an order of magnitude, simultaneous trapping is possible. Moreover, the large charge ensures a good coupling between molecular ensemble and atomic ensemble. Finally, the pseudopotential of the molecular ions ($\sim Q_{\text{SC}}^2/m_{\text{SC}}$) can be comparable or even larger than that of the atoms, thanks to the large molecular charge. A good spatial overlap of the subensembles is therefore ensured. Figure 2 shows two simulations for molecular ions of mass 20 000 amu and charge $20e$. As can be seen, the molecular ions are strongly cooled as far as their secular energy is concerned. However, a large micromotion energy remains in the crystallized state because of the nonaxial arrangement of the molecular ions and their large mass. This nonaxial arrangement occurs in spite of the fact that the pseudopotential of the molecules is larger than that of the atoms. Indeed, the Coulomb interaction energy is an important contribution that determines the overall arrangement of the particles. This

can be seen by noting that the Coulomb energy of a given spatial structure is not invariant under particle exchange $\text{LC} \leftrightarrow \text{SC}$, due to the differing molecular and atomic charges. For a sufficiently large axial potential [Figs. 2(a), 2(b)] the total energy is minimized by forcing the molecular ions off axis resulting in a shell structure. For a smaller axial potential [Fig. 2(c)] the structure is stringlike, but molecular ions that are adjacent bulge out from the axis because of their strong repulsion. Where several molecular ions are crystallized in adjacent positions, they form sections of a helix [35]. Here again we find that molecules that are well embedded in the atomic ion ensemble, i.e., those that are individually located between atomic ions [e.g., the two SC ions in Fig. 2(c) furthest from the center in the z direction], cool as fast as the LC ions while the off-axis molecular ions cool much more slowly.

We have also performed simulations for molecular masses 2000, 5000, and 10 000 amu, with the same mass to charge ratio of 1000 amu/ e . We find a similar behavior of crystallization as in the examples above. As the charge becomes smaller only molecular Coulomb structures of the shell type occur, and due to the weaker LC-SC interaction, a fraction of the molecules remain uncooled.

The above examples show that sympathetic crystallization is possible for ion masses significantly larger or smaller than the coolant ion mass. Based on the present and previous [23] results, it can be stated that simply charged molecular ions of mass between that of $^9\text{Be}^+$ and $^{137}\text{Ba}^+$ can also be sympathetically crystallized.

In conclusion, we have shown that a wide variety of charged molecules can be trapped and cooled to mK temperatures with masses from 2 to 20 000 amu, i.e., from diatomic molecules to polymers and proteins. The molecules are incorporated into an ordered structure. The spatial arrangement within the Coulomb crystal depends on the masses and charges of the coolant and the molecular ions. We have pointed out that sympathetic crystallization should be very advantageous for precision spectroscopy of the various ions of molecular hydrogen.

Since emphasis was placed on using a laser cooling force of realistic magnitude and on employing a high-precision numerical code, the simulations were performed for small particle numbers (up to 50). Experimentally, this regime is both accessible and suited for detailed studies of molecular properties. In the future, the simulations can be extended to larger numbers, by developing faster but approximate algorithms or using more powerful computers, and to other types of traps (multipole-rf traps [6] and Penning traps). This should allow detailed comparisons of dynamics and structure of sympathetic crystallization between theory and experiments currently under way.

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- [36] The semiclassical cooling force with full dependence on particle velocity and detuning of the laser frequency from resonance [33] was used, but enhanced by a factor ~ 8 . The detuning was repetitively scanned in a sawtooth manner from far red—detuned to $-\gamma/2$ where γ is the cooling transition linewidth. The laser beam direction was at 54.7° with respect to the trap symmetry axes.