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FROM QUANTUM TECHNOLOGY TO CHEMISTRY CLOSE TO THE ABSOLUTE ZERO POINT

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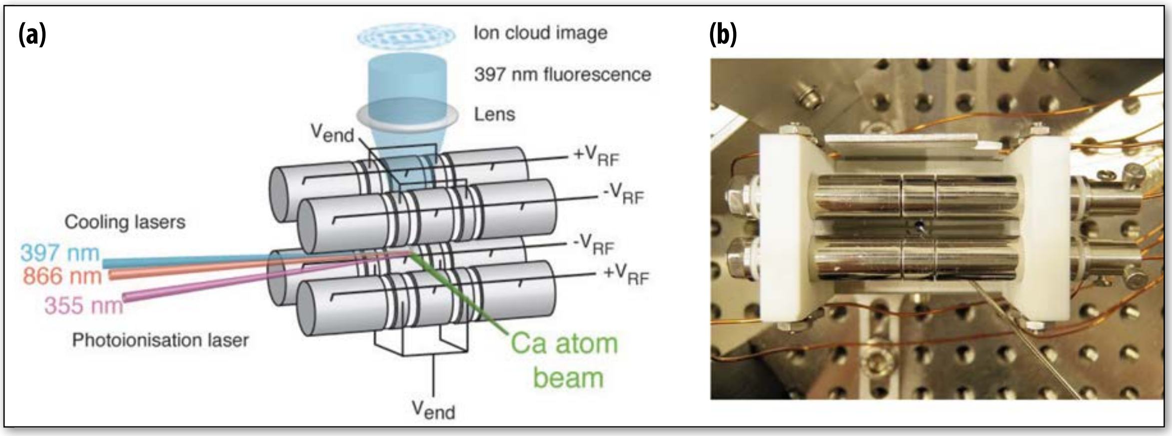
Ion Coulomb crystals are ordered structures of atomic or molecular ions stored in ion traps at temperatures close to the absolute zero point. These unusual "crystals" form the basis of extremely accurate clocks, provide an environment for precise studies of chemical reactions and enable advanced implementations of the technology for a quantum computer. In this article, we discuss the techniques for generating atomic and molecular Coulomb crystals and highlight some of their applications.

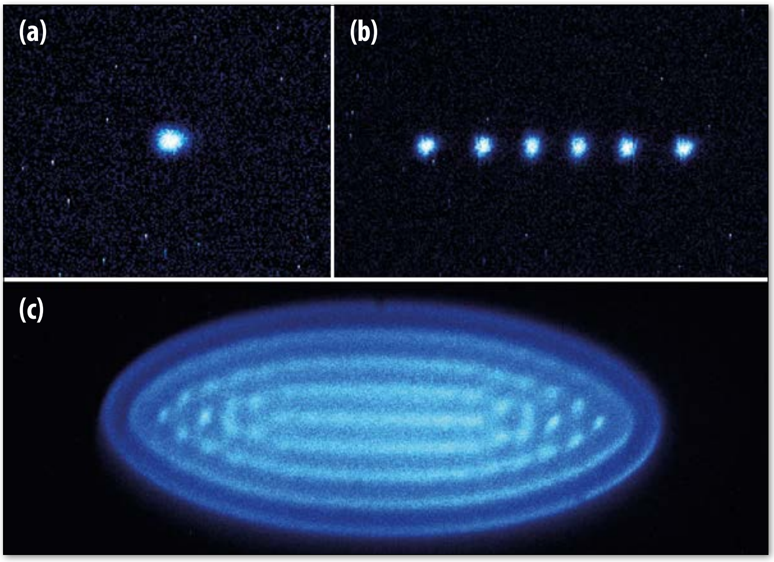
The recent progress in the generation of atoms and molecules at temperatures near the absolute zero point has paved the way for new exciting research directions in both physics and chemistry. A particularly intriguing form of cold matter is a "Coulomb crystal", an ordered structure of charged atoms or molecules (ions) stored in traps [1]. In such a crystal, it is possible to observe, address and manipulate single particles. This remarkable technology paves the way for a range of new applications. These include quantum logic and quantum simulation as new avenues for information processing, extremely precise atomic clocks as new time standards, precision spectroscopic measurements to address fundamental physical questions such as a possible time variation of fundamental constants, and controlled collision studies to unravel the fine details of chemical reaction mechanisms. The spectacular advances in this field have recently been recognized by the award of part of the Nobel Prize in Physics 2012 to David J. Wineland, one of its pioneers.

Generation of Coulomb crystals

There are two basic steps for producing a Coulomb crystal: the trapping of ions and their cooling. Trapping the ions is necessary because they strongly repel one another through their charge. A tightly packed cloud of ions would therefore immediately explode if it is not held together by external forces. The traps typically used in Coulomb-crystal experiments are linear radiofrequency traps, *i.e.*, electrodynamic traps consisting of an arrangement of electrodes to which time-varying



◂ FIG. 1: **(a)** Schematic of a Coulomb-crystal experiment. Laser-coolable ions such as Ca^+ are produced by ionisation from a Ca beam and are trapped in a linear radiofrequency ion trap. Laser beams are inserted into the trap for ionisation and cooling. The fluorescence generated during laser cooling is collected by a lens and imaged onto a camera. Adapted from Ref. [3]. **(b)** Photograph of a linear radiofrequency ion trap.



▲ **FIG. 2:** False-color fluorescence images of Coulomb crystals of laser-cooled Ca$^+$ ions in a linear radiofrequency ion trap. **(a)** A single Ca$^+$ ion, **(b)** a string of ions, **(c)** a large crystal. Adapted from Ref. [1].

and static voltages are applied (see Figure 1) [1]. A less frequently used alternative are so-called Penning traps which rely on magnetic and static electric fields to trap the charged particles [2].

Cooling the ions is necessary because Coulomb crystallisation can only occur if the potential energy of the ions exceeds their kinetic energy by a factor of ≈ 170 [3]. For light particles such as atoms, this can only be achieved if the temperature of the ion cloud is reduced to a few thousands of a degree above the absolute zero point (for large particles such as dust, this can already be achieved at much higher temperatures). Such low temperatures can be attained by laser cooling the ions, *i.e.*, by reducing their velocity through the repeated absorption of photons from a laser beam. Laser cooling, however, is only applicable to ions with a particularly simple quantum structure which enables the repeated absorption and emission of photons on the same spectroscopic transition. Certain atomic ions, for instance the ions of alkaline earth atoms magnesium, calcium and barium, fall into this category.

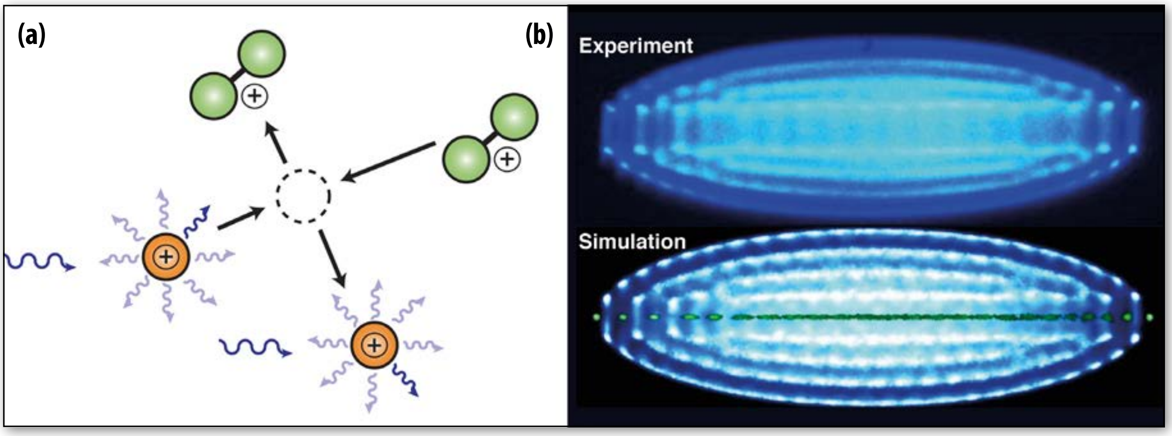
Figure 2 shows false-color fluorescence images of different Coulomb crystals of calcium ions in a linear Paul trap. Coulomb crystals can appear as single localized ions (a), as strings of ions (b) or as large crystals containing hundreds to thousands of particles (c). The images were recorded by collecting the fluorescence emitted by the ions during laser cooling and collecting them with a camera coupled to a microscope. Because of the finite depth of focus of the microscope, the images show a cut through the crystals along their central plane. The distance between the ions in the crystals typically amounts to a few tens of micrometres. Thus, big crystals such as the one shown in Figure 2(c) are macroscopic objects with sizes close to millimetres.

Large crystals have a spheroidal shape because of the harmonic trapping potential. In fact, the term "crystal" is a misnomer in this case because Coulomb crystals in harmonic traps do not have translational symmetry as required of a true crystal. Historically, the term originated in analogy to "Wigner crystals", ordered structures of electrons in solids originally predicted by the Hungarian-American physicist Eugene Wigner.

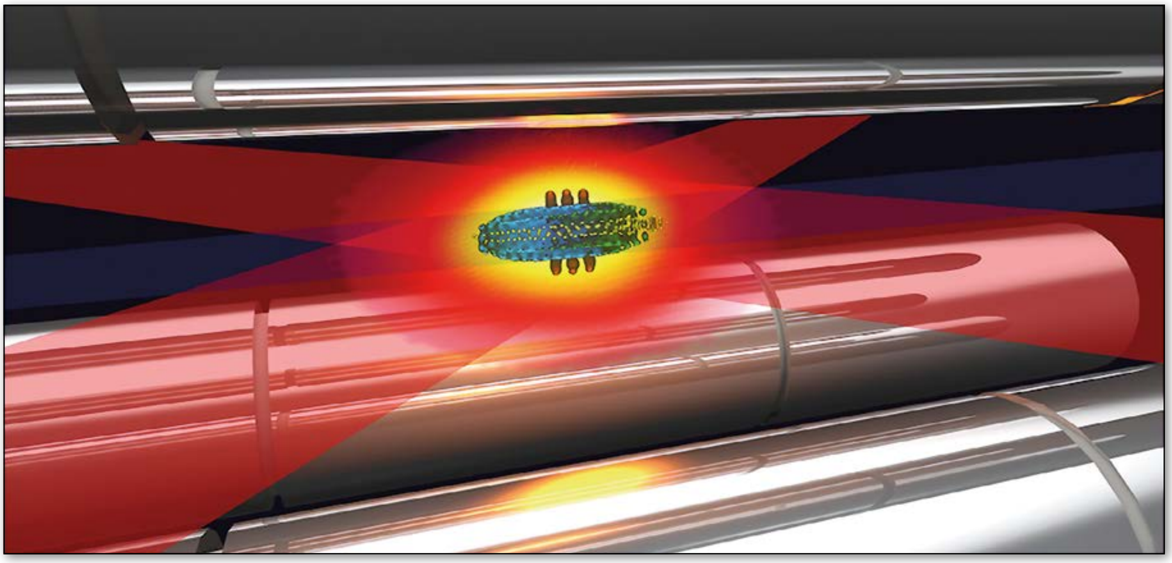
Coulomb-crystallizing molecules

In contrast to atoms, molecules can – with a few notable exceptions – not be laser cooled because of their complex energy-level structure. For molecular ions, however, a versatile and efficient method has been developed which allows their cooling to similar temperatures as laser-cooled atomic ions. The principle of "sympathetic cooling" is shown in Figure 3(a). Molecular ions are stored together with laser-cooled atomic ions in the same trap. Through collisions, the two species exchange kinetic energy which is ultimately removed from the atomic ions by laser cooling. As a result, a bi-component or "molecular" Coulomb crystal is obtained (Figure 3(b)) in which the molecular ions (nitrogen ions in this case) are embedded in the atomic Coulomb crystal. The molecular ions are not directly visible in the images in which only the fluorescence from the laser-cooled atomic ions is displayed, but they can be made visible artificially in molecular-dynamics simulations of the cold ions (shown in green in the bottom panel of Figure 3(b)).

One of the chief advantages of Coulomb crystals is the high degree of control which can be achieved over the trapped particles. While cooling freezes their motion and



▶ **FIG. 3:** **(a)** Molecular ions (green) can be sympathetically cooled by collisions with simultaneously trapped laser-cooled atomic ions (orange) leading to the formation of bi-component or molecular Coulomb crystals. **(b)** Top: Experimental image of a bi-component Coulomb crystal containing 25 sympathetically cooled N$_2^+$ ions embedded into ≈ 925 laser-cooled Ca$^+$ ions. The molecular ions are visible as a non-fluorescing region in the center of the crystal. Bottom: Molecular dynamics simulation of the crystal in which the molecular ions have been made visible in green. Adapted from Ref. [1].



◂**FIG. 4:** Illustration of a Coulomb crystal of Ba^+ ions embedded in a cloud of ultracold Rb atoms held in a magnetooptical trap. Cold chemical reactions with the Rb atoms lead to a gradual replacement of the Ba^+ ions in the crystal (blue, green) with product ions (yellow, red).

fixes them in space, their internal quantum state can be manipulated by laser fields. This is fairly straightforward for atoms which only have electronic and nuclear-spin internal degrees of freedom. Achieving full quantum control over molecules, however, is much more challenging as they have additional internal degrees of freedom such as vibrations and rotations. Developing methods for the preparation and manipulation of the internal quantum state of Coulomb crystallised molecular ions has been a major objective of the field over the last years and has only been achieved recently [1].

Applications: From quantum logic ...

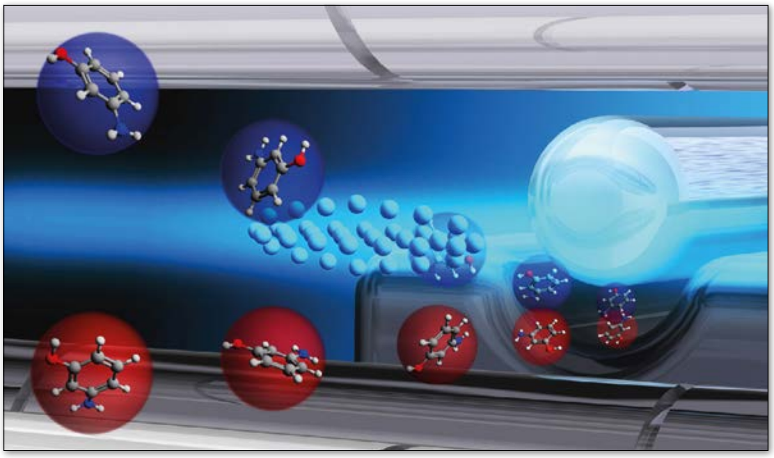
Trapped ions were the first particles in which laser cooling was demonstrated in the 1970s [4]. The scientific breakthrough of cold ions, however, only came in the mid-1990s when Ignacio Cirac and Peter Zoller realized that strings of Coulomb-crystallized ions could form a suitable basis for a quantum computer [5]. Indeed, ion-trap quantum information processing has become a thriving field on its own and experiments relying on Coulomb-crystallized ions count among the most advanced implementations of quantum-information processors to date [6]. Besides conventional quantum-information processing, quantum simulation, *i.e.*, the simulation of the dynamics of a particular Hamiltonian implemented in another system, has become another important application of Coulomb-crystallized ions.

... and precision measurements ...

The possibility to isolate single particles in the well-controlled ultrahigh-vacuum environment of an ion trap and to control their motion and internal quantum state has enabled the development of a new generation of ultra-precise atomic clocks which count among the most precise time standards to date [7]. These clocks rely on the measurement of electronic transition frequencies in a single trapped atomic ion. As these atomic transitions typically lie in the visible or ultraviolet region of the electromagnetic spectrum, the accuracy of these clocks far surpasses the one of conventional atomic clocks which relies on the measurement of hyperfine transitions in the radiofrequency domain. Besides providing an extremely accurate frequency (and thereby time) standard, such high-precision spectroscopic measurements also allow one to study fundamental physical problems which thus far have largely been the domain of particle- and astro-physics. These include the question of a possible time variation of fundamental physical constants such as the fine structure constant or the masses of fundamental particles [8]. Another impressive application of these highly precise frequency measurements is the study of the influence of gravitation on atomic transition frequencies [9]. Besides the atomic systems, cold molecular ions have recently also received considerable attention as potential candidates for new, highly precise clocks [10].

.... to cold and controlled chemistry

While the examples discussed thus far belong to the realm of atomic and quantum physics, the development of sympathetic cooling of molecular ions has also made chemists aware of the potential of Coulomb crystals. For instance, Coulomb-crystallised ions are ideal systems to study ion-neutral interactions and chemical reactions at extremely low temperatures. To this end, a range of different experiments has been developed over the past few years which combine ion traps with sources of either cold neutral atoms [11, 12] or cold neutral molecules [13]. Figure 4 shows an illustration of an experiment in which a Coulomb crystal of laser-cooled Ba^+ ions has been overlapped with a cloud of ultracold Rb atoms prepared by laser cooling and magneto-optical trapping [12]. Experiments like this allow the study of exotic chemical processes occurring at extremely low temperatures in dilute environments, *e.g.*, the formation of molecular ions by photon emission during collisions of the cold atomic ions with the cold neutral



▲ FIG. 5: Illustration of a "controlled chemistry" experiment in which two different shapes (highlighted in red and blue) of the organic molecule 3-aminophenol were spatially separated through their interaction with an inhomogeneous electric field and directed at a spatially localised reaction target consisting of a Coulomb crystal of cold ions [14]. Experiments like this enables one to study in detail the influence of the shape of a molecule on its chemical reactivity. Illustration by Y.-P. Chang, DESY.

atoms. Besides the artificial environment created in these experiments, this sort of processes plays an important role in the chemistry of interstellar space. Combined cold-ion-neutral experiments also enable to unravel the detailed dynamics of collisions between three bodies, which are particularly important in dense media like Bose-Einstein condensates [11], and to explore subtle intermolecular interactions which manifest themselves at very low temperatures, but are often obscured at higher temperatures [12]. In this way, they enable a better understanding of the forces that drive chemical processes.

The intriguing properties of Coulomb-crystallised ions have recently also been used in the context of studying the mechanisms of reactions of complex molecules in unprecedented detail [14]. Large molecules can frequently assume different shapes, so-called conformations, which differ only by a rotation of parts of the molecule about a chemical bond. The influence of the specific shape of a molecule on its chemical reactivity is one of the long-standing problems in chemistry, but has been difficult to address experimentally so far because different conformations tend to interconvert into one another through their thermal motion. In a recent study, a mixture of two distinct molecular conformations of the organic molecule 3-aminophenole was entrained in a molecular beam in which their interconversion was suppressed through adiabatic cooling. Because the two different conformations of the molecule possess different electric dipole moments, they could be spatially separated through the interaction with a strong inhomogeneous electric field. This corresponds to an electrostatic, molecular version of the celebrated Stern-Gerlach experiment in which in 1922 the intrinsic angular momentum of electrons, the spin, was first observed experimentally through magnetic deflection. The spatially separated conformers were then directed at a stationary reaction target consisting of a Coulomb crystal of laser-cooled Ca^+ ions (Figure 5). In this way, the distinct chemical reactivities of the two molecular conformations could be characterised individually, shedding new light on shape-specific intermolecular interactions in chemical reactions.

Outlook

The past years have seen impressive progress in the development of the technology of Coulomb-crystallised atomic and molecular ions leading to the emergence of a new scientific field at the interface between quantum science, atomic and molecular physics and chemistry. Exciting future perspectives involve improved atomic clocks which will push the accuracy of frequency measurement to ever further limits, the development of quantum technologies for single molecules which augment and enhance the present capabilities with atoms, and new technologies to precisely study and control chemical reactions. Thus, one could say without exaggerating that cold ions have become a hot topic indeed! ■

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