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ARTICLE

Cold ion chemistry within Coulomb crystals

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ABSTRACT
Coulomb crystals are ordered structures of spatially-localised ions, held within an ion trap and exhibiting very low translational temperatures. The many advantages of studying the spectroscopic, kinetic and dynamic properties of gas phase ions in Coulomb crystals – such as the ability to manipulate and detect single ions under ultrahigh vacuum conditions – have seen their adoption in an ever-expanding range of fields. This article provides an overview of recent developments, where Coulomb crystals have been utilised for precision measurements, for the study of controlled ion-neutral reactions and in the implementation of quantum information science.
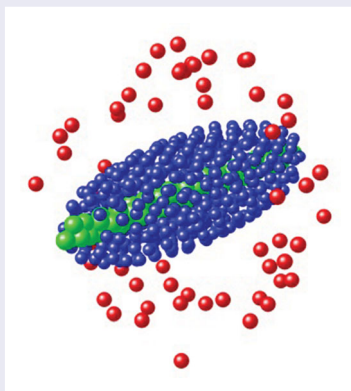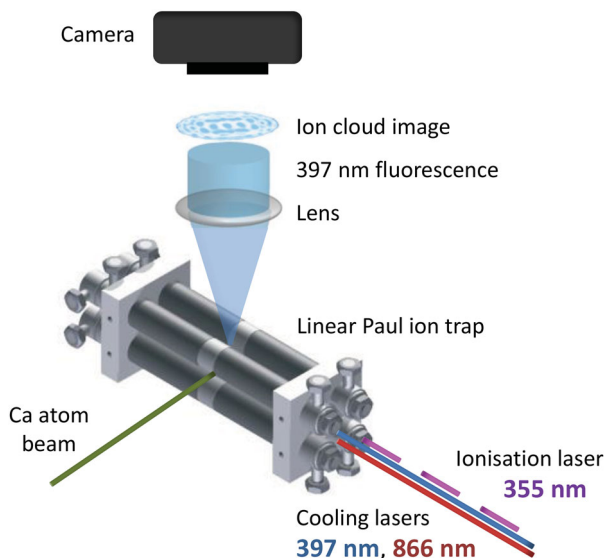
1. Introduction

The term 'Coulomb crystal' refers to an ordered array of translationally cold ions held within a trap. When sufficient kinetic energy is removed from a cloud of trapped ions, the interaction parameter $\Gamma = E_{pot}/E_{kin} = Q^2/(4\pi\epsilon_0 a_{WS} k_B T)$ exceeds a critical point, $\Gamma \gtrsim 160$ [1,2], and a phase transition occurs to a 'crystalline' state.[1] In certain atomic ions, such as the singly charged alkaline earth metals (Be^+, Mg^+, Ca^+, Sr^+ and Ba^+) and species such as Yb^+, kinetic energy can be straightforwardly removed by laser cooling methods [3–5]. Whilst molecular ions cannot usually be laser cooled due to their complex energy level structures, ionic species that are not amenable to laser cooling can be sympathetically cooled by elastic collisions with laser-cooled species. In this way, multi-component Coulomb crystals can be generated – as first experimentally demonstrated in 2000 [6].

Advances in ion trapping and laser cooling methods over the past several decades have been crucial in the preparation of increasingly diverse and complex molecular ions within Coulomb crystals [7–11]. Paul [12] or Penning [13] traps are typically employed to confine the ions, and the fluorescence emitted by the laser-cooled species can be directly imaged using a camera, achieving single-ion resolution (see Figure 1). The balancing of the confining forces of the trap and the repulsive Coulombic forces (arising from neighbouring positively charged ions repelling each other) results in a structure where the ions are separated by some 10–20 μm, with densities on the order of 10^8 ions cm^{-3}. The term 'crystal' as applied to this periodic arrangement of trapped ions is thus perhaps something of a misnomer; ions are not fixed in single lattice positions, the inter-ion spacing is approximately five orders of magnitude greater than the distances between
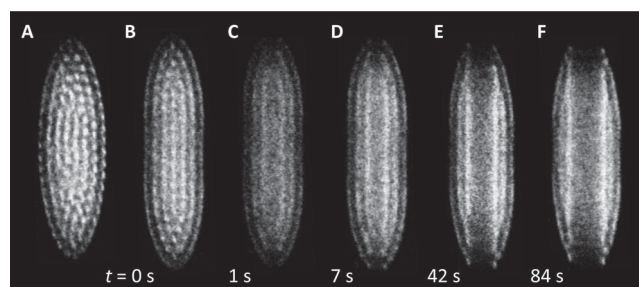
Figure 1. Schematic illustration of a linear Paul radiofrequency ion trap, as used in our experiments. Calcium atoms are non-resonantly ionised by a pulsed 355 nm laser, with two continuous-wave diode lasers (operating at 397 nm and 866 nm) serving to cool the Ca^+ ions. Fluorescence spontaneously emitted by trapped Ca^+ ions during this laser cooling process is imaged using a lens and a camera system.

Figure 2. Fluorescence images of Coulomb crystals showing a central slice through the three dimensional structure; only Ca^+ ions are visible. The charge exchange reaction between Xe^+ ions and neutral ammonia molecules has been followed through observation of the changes in the locations of the fluorescing Ca^+ ions within the Coulomb crystal framework. Panel A shows a Ca^+-only Coulomb crystal; while the laser-cooled Ca^+ ions play no part in the reaction, they sympathetically cool the ionic reactants and products into the Coulomb crystal. In panel B, Xe^+ ions have been sympathetically cooled into the crystal, representing the $t = 0$ reaction conditions. Within 1 s of the introduction of ammonia into the reaction chamber, the beginnings of a dark core could be seen (panel C), with the dark core growing as the charge exchange reaction progressed (panels D–F). In this way, numerous reaction systems can be monitored through the growth (or loss) of the dark product (or reactant) ions in the crystal over time. Reprinted with permission from reference [15]. Copyright 2015 American Chemical Society.
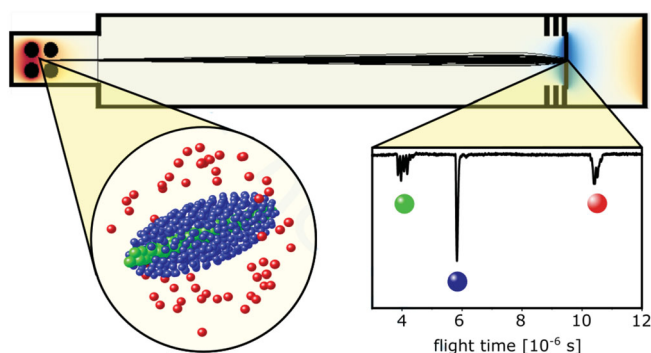
Figure 3. Schematic illustration of the ToF-MS detection of a multi-component Coulomb crystal. The four rods of a linear Paul trap are shown in side view, with a simulated crystal containing Xe^+ (red), Ca^+ (blue) and ammonia ions (green) depicted inset. After the radiofrequency trapping fields are switched off, static repeller and extractor fields are applied to the rods, kicking all ions within the crystal into a free-flight tube and onto multichannel plates (MCPs) for detection. The resulting ToF profile (shown inset) enables the mass-to-charge ratios and abundances of all components of the crystal to be quantitatively established. Reprinted with permission from reference [15]. Copyright 2015 American Chemical Society.

neighbouring atoms in traditional solid crystal structures (with a commensurate difference in density), and long-range order is only evident in large Coulomb crystals containing several thousand ions. The simplest form of a Coulomb crystal is a string of ions positioned along the trap axis; larger Coulomb crystals typically adopt a spheroidal shape (see Figure 2).

The forces experienced by a trapped ion depend on the ion's mass-to-charge ratio. As such, the location of a given ion within a Coulomb crystal is dependent on the mass-to-charge ratios of any other co-trapped species present; the lightest singly charged ions experience a stronger trapping potential and migrate to the trap centre, pushing the heavier singly charged ions into an outer shell. While only the laser-cooled ions fluoresce, and can be directly observed with a camera, the presence of other co-trapped ions can be inferred from their impact on the positions of these fluorescing laser-cooled ions within the crystal framework (see Figure 2). The identity of all ionic species in a crystal can be quantitatively established by, for example, time-of-flight mass spectrometry (ToF-MS) methods [14–17] (see Figure 3), frequently employed alongside imaging analysis – where the observed Coulomb crystal fluorescence patterns are simulated (using molecular dynamics codes) up to the point of crystal ejection.

Ultra-high vacuum conditions provide a near-perturbation free environment for Coulomb-crystallised ions. As such, Coulomb crystals provide us with an ideal medium for studying precision measurements and monitoring slow reaction processes over extended timescales (with ions able to be trapped for hours, or even days). It is this absence of contaminant species, combined with single-ion detection sensitivity, that is enabling

exceptionally accurate experimental measurements to be undertaken on a wide range of ionic systems. Ions are abundant in many naturally occurring gas-phase environments, and the temperatures of these environments can span several hundred Kelvin – from very cold settings (the mesosphere and the interstellar medium) to very hot settings (plasmas, combustion systems and electrical discharges). Consequently, knowledge about the properties of ions under relevant conditions has long been of interest to physical chemists. Coulomb crystals have the potential to provide us with new insights into the chemistry occurring in these important gas-phase environments.

There have been several excellent review articles discussing Coulomb crystals over the past decade [18–26]. The findings presented in these previous publications need no further discussion here; instead of reflecting on what has been done in the past, this article seeks to provide a new perspective – highlighting some of the exciting research that is happening now and proposing what the future of the field might look like.

2. Applications of Coulomb crystals

2.1. Precision measurements

The size of Coulomb crystals can vary considerably, from very small (2 ions) to very large (a few thousand ions) structures. Given the low numbers of ions present – even in very large crystals – it may come as a surprise that one can use a variety of spectroscopic techniques to perform precision measurements on the trapped ions. Employed alongside complementary detection methods, such as imaging, resonance-enhanced multiphoton dissociation (REMPD) has been successfully adopted to probe a range of Coulomb-crystallised ions. Similar in principle to the more commonly encountered resonance-enhanced multiphoton ionisation (REMPI) technique, REMPD serves to resonantly dissociate (rather than ionise) a selected species. REMPD is a powerful, state-selective and broadly applicable spectroscopic analytical tool, provided the species of interest exhibits accessible resonantly-enhanced photodissociation pathways. One can detect the loss of dark ions from the crystal (for example, when the product ion – such as H^+ – is too light to be trapped), or observe the change in the mass of the trapped ions (as occurs when dissociation product ions are subsequently trapped), and these changes can be monitored as a function of the REMPD laser frequency. In this way, REMPD measurements have been successfully performed by Drewsen and co-workers to obtain the rotational state distribution of Coulomb-crystallised MgH^+ ions [27,28]. An alternative to populating an electronically excited intermediate state (as employed by

Drewsen) is to excite vibrational overtones, as demonstrated by Brown and co-workers with their REMPD study of Coulomb-crystallised CaH^+ ions [29]. Doppler-free spectroscopy of sympathetically-cooled molecular ions has seen an almost 50-fold improvement in the resolution of HD^+ rotational transitions, reaching the Lamb-Dicke regime [30]. The approach of Schiller and co-workers takes advantage of the strong confinement of co-trapped molecular ions formed within Coulomb crystals in a linear quadrupole trap, where the molecular ions of interest have a mass-to-charge ratio lower than that of the laser-cooled species.

Beyond REMPD measurements, Willitsch and co-workers have exploited the long interrogation times and almost perturbation-free environment of Coulomb crystals to undertake the most precise vibrational transition measurements to date in N_2^+ ions, exciting a dipole-forbidden electric-quadrupole-allowed transition in the infrared (IR) region [31]. The number of N_2^+ ions excited by a particular laser frequency was established by charge transfer with argon; only vibrationally excited N_2^+ ions possessed sufficient internal energy to charge transfer with Ar atoms, enabling the loss of vibrationally excited N_2^+ ions to be monitored as a function of IR laser wavelength.

There is tremendous potential for extended spectroscopic studies of Coulomb-crystallised molecular ions. However, it is important to remember that, whilst sympathetic cooling is a very useful and widely-applicable method for generating a translationally cold source of ions, it does not affect the internal energy population distribution of the ions. There are no inelastic collisions to internally cool the molecular ions, and the long timescales of many processes studied in Coulomb crystals means that the internal degrees of freedom of (most) molecular ions thermalise with the ambient blackbody radiation (BBR) within tens of seconds [32,33]. One could, of course, choose to study non-polar diatomics, in which case there is no interaction with the BBR field. Another approach has seen ion traps superimposed with magneto-optical traps (MOTs), so-called atom-ion hybrid traps, whereby inelastic collisions between molecular ions and ultracold atoms can cool the ions' internal degrees of freedom [34,35]. Laser-assisted BBR population redistribution has been successfully demonstrated in MgH^+ [36] and H_2^+ [37], and theoretically studied by our own group for several species including $C_2H_2^+$ [32,33], but is impractical for the majority of molecular species owing to their complex energy level landscapes. Trapped AlH^+ molecular ions have, however, been successfully cooled to their rovibrational ground state with a broadband laser, as (undesirable) vibrational excitation was able to be avoided due to vibrational-electronic

decoupling [38]. Cryogenic linear Paul ion traps, such as the CryPTEx instrument [39], have been successfully developed using a cryocooler and nested temperature stages to ensure that the temperature of the innermost ion trap region is minimised whilst maintaining laser and imaging access. Helium buffer gas can also be employed to further cool the internal energy distribution of the molecular ions [28], making this a generally applicable approach to generating a wide range of internally cold Coulomb-crystallised molecular ions.

One significant advantage of cryogenic conditions for spectroscopic studies of complex molecular ions is, of course, that fewer rotational and vibrational states are populated at low temperatures – significantly simplifying the resulting spectra and enhancing the spectral resolution that can be achieved. While such low temperature measurements have been made using 22-pole traps with buffer gas cooling for a number of years [40,41], Coulomb crystals allow new high resolution methods, such as quantum logic spectroscopy [42] (discussed in more detail below) to be explored. With the many added benefits offered by cryogenic conditions, one can envisage the detailed spectroscopic study of a range of complex molecular ions within Coulomb crystals in the near future. The CryPTEx apparatus has already seen the Coulomb crystallisation of highly-charged ions – paving the way for detailed spectroscopic studies and providing a methodology whereby the time dependence of fundamental constants such as the fine structure constant, α, could potentially be measured [43].

2.2. Reaction studies

Non-Arrhenius behaviour, exhibited by many ion-molecule reactions, can complicate the analysis of what initially appear to be simple 'barrierless' processes; ion-molecule rate coefficients – especially those involving the reactions of ions with dipolar molecules – often display a strong negative temperature dependence [44]. As such, ion-molecule reactions play an increasingly important role in low-temperature environments, where most competing processes effectively freeze out. Numerous approximate theories have been proposed to describe capture rate constants for bimolecular ion-molecule reactions, with the simplest of these the Langevin model. However, the Langevin formula is only applicable for reactions between ions and non-polar molecules (i.e. processes occurring on an ion-induced dipole potential) – and even then, breaks down at temperatures $T < 10\,\mathrm{K}$ [45]. The rotationally adiabatic channel model [46] and the statistically adiabatic channel model [47] have successfully extended the applicability and accuracy of ion-molecule capture theories (including the effects of the

rotational quantum states of the colliding neutral partner). And yet, even these more sophisticated treatments start to deviate from available measurements at $T < 10\,\mathrm{K}$ [48].

Rate coefficients for exothermic ion-molecule reactions, where the neutral reactant is a non-polar molecule such as H_2, are thought to be largely independent of temperature. In spite of this, unexpected behaviour has been observed at low temperatures in several H-addition reactions [49–51]. One proposed explanation is *'the importance of long lived collision complexes at low collision energies'* [51], with the lifetime of one such van der Waals intermediate calculated to be tens of microseconds in the $C_2H_2^+ + H_2$ system [52]. These van der Waals intermediates are long lived because the energy required for dissociation into products can be sequestered in the numerous internal degrees of freedom rather than the bond-breaking co-ordinate – analogous to what is seen in 'roaming' reaction mechanisms [53,54].

Ion traps are being combined with an increasingly diverse range of molecular sources for the study of ion-molecule systems [22,25], and hybrid traps are enabling the detailed examination of ion-atom reactive collisions [35,55]. Studying reactions in Coulomb crystals also enables one to take advantage of long interrogation times and ultra-high vacuum conditions, meaning that very slow processes can be monitored – something that isn't always possible with the more established reaction kinetics in uniform supersonic flow (CRESU) [56] or selected ion flow tube (SIFT) [57] techniques. As such, as a community, we are now in a position to measure the rate constants of many fundamentally important reaction processes, challenging the accuracy of capture theories and establishing the influence that subtle features on the potential energy surface can have on the reaction mechanism. For example, the first experimental measurement of the rate coefficient for the Be^+ $(^2S_{1/2})$ + H_2O → $BeOH^+$ + H reaction found it to proceed ~ 2 times slower than ion-capture model predictions, owing to the presence of a submerged barrier in the exit channel [58].

In 2013, Küpper, Willitsch and co-workers reported on their successful combination of an electrostatic deflector with an ion trap. By spatially separating the two conformational isomers of 3-aminophenol using a strong inhomogeneous electric field, they were able to study conformer-specific interactions with Ca^+ ions [59,60]. The importance of considering the distinct reactivities of different conformers of the same species was reinforced by their findings; the *cis* conformer of 3-aminophenol was found to have a reaction rate constant that was approximately double that of the *trans* conformer, with these differences in chemical reactivity attributed to subtle changes in the long-range ion-molecule potential.
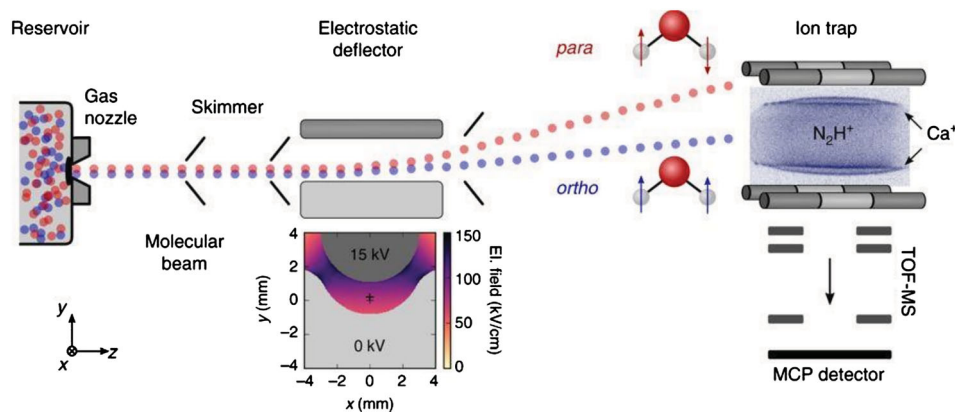
Figure 4. Schematic illustration of the combined electrostatic deflector and linear Paul trap experimental apparatus employed by Willitsch and co-workers. Water molecules seeded in argon were expanded through a pulsed valve, with the *para* and *ortho* components able to be spatially separated by the inhomogeneous fields of the deflector (shown as an inset image) owing to their different dipole moments. The alignment of the various components of the apparatus was altered to direct either the *para* or *ortho* molecules into the ion trap region, where the ionic reactants (N_2H^+) were incorporated into a Ca^+ Coulomb crystal. The reaction kinetics and dynamics were subsequently probed by ejecting the Coulomb crystals onto a detector using a time-of-flight mass spectrometry approach. Reprinted from reference [61]. Creative Commons Attribution 4.0 International License, http://creativecommons.org/licenses/by/4.0/.

More recently, the same apparatus has been employed to separate the *para* and *ortho* components of a beam of internally cold water molecules (corresponding to the lowest and first excited rotational states, respectively) to explore the $H_2O + N_2H^+ \rightarrow N_2 + H_3O^+$ proton transfer reaction, facilitating the first experimental measurement of rotational state-specific reaction rate constants in such a system (see Figure 4) [61]. It is the excellent sensitivity that can be achieved when studying reactions in Coulomb crystals – where reactions can be monitored over extended periods of time with a combination of imaging, ToF-MS and laser-based methods – that enables subtle differences in reactivities to be identified. Lewandowski and co-workers have taken advantage of this detection sensitivity and the high control one has over the properties of Coulomb-crystallised ions to study reactive collisions between a molecular radical (NO) and laser-cooled Ca^+ ions, yielding either $CaO^+ + N$ or $Ca + NO^+$ products. The rate of reaction was controlled by altering the quantum state population of the ionic reactants, achieved by changing the detuning of the primary cooling laser [62]. Competition between the two reaction channels was explored, with independent reaction rate constants and branching ratios determined and the findings supported by a mechanistic model.

2.3. Ongoing challenges and outlook

One well-known limitation of using Coulomb crystals is the need for the sympathetically cooled ion to have a similar mass-to-charge ratio to the laser-cooled ion. Ions as small as H_2^+ [63] and as large as protonated glycyrrhetinic acid ($C_{30}H_{47}O_4^+$) [9] have been incorporated into Coulomb crystals with laser-cooled Be^+ and Ba^+ ions (respectively). The simultaneous tight confinement of ions with 'extremely' different mass-to-charge ratios has recently been proposed using a two-frequency Paul ion trap [64]. In the two-frequency mode of operation, the electric quadrupole field oscillates between the optimal trapping frequencies required for each of the species, thereby confining both ions tightly and lifting the upper limit on the mass-to-charge ratio of the sympathetically cooled species.

New and exciting spectroscopic measurements of Coulomb-crystallised ions are already underway. High-resolution spectra have recently been recorded by probing a single CaH^+ ion in a two-ion Coulomb crystal using quantum logic spectroscopy [65]. A frequency comb has been employed to drive Raman transitions in a single trapped $^{40}Ca^+$ ion, achieving unprecedented resolution of the transition frequency [66]. Precision measurements of transitions in cold, trapped ions are increasingly being recognised as a possible way of studying fundamental physical constants. For example, it has been proposed that the constancy of the mass ratio m_e/m_p could be established through precise measurements of vibrational frequencies in Coulomb-crystallised molecular ions – potentially challenging the uncertainty achievable with microwave cold atom clock methods [67,68]. High resolution spectroscopic measurements of isotopic shifts in trapped ions have also been proposed as a potential avenue for exploring new physics beyond the standard model, as such measurements represent experimental observables that are independent of theoretical uncertainties [69].

As long ago as 1995, Cirac and Zoller proposed that laser-cooled ions confined within a linear trap satisfied the conditions necessary for quantum computing; transitions between states in a single ion could be precisely driven with lasers and the coupling of ion motion via electrostatic interactions would allow for highly efficient manipulation and measurement with negligible decoherence [70]. In recent years, there has been a groundswell of activity – and significant progress made – in the field of quantum simulation and quantum computing (see, for example, [71–73]). Small Coulomb crystals composed of several $^{40}Ca^+$ ions have very recently seen the realisation of a 'trapped-ion quantum simulator', where a hybrid quantum-classical algorithm was utilised to perform calculations on the ground state energies of molecular hydrogen and lithium hydride [74]. In each $^{40}Ca^+$ ion, a pair of electronic states were labelled as qubit states $|1\rangle$ and $|0\rangle$. Lasers served to both perform operations (encode information) and to read out the final states of the qubits, with fluorescence collected using a CCD camera in the typical fashion. Trapped ions – and, more specifically, strings of Coulomb-crystallised ions – thus represent a promising alternative to superconducting circuits in the quest to perform increasingly complex quantum simulations.

Existing techniques are still limited in their ability to study ion-neutral reactions where atomic hydrogen is the neutral reactant. This is primarily due to the lack of a pure H-atom beam source, as complications arise from H-H recombination and the presence of undissociated molecular hydrogen in the reaction region. Even with a sophisticated atomic beam 22-pole ion trapping apparatus, where atomic hydrogen is preferentially guided and focussed into the reaction chamber by hexapole magnets, the number density of H is only 3 times that of H_2 [75]. For example, despite repeated attempts over several decades, the reaction rate constant for the fundamental ion-radical reaction $N_2^+ + H$ is still unknown [76–78]. SIFT studies have suggested an upper limit of 10^{-11} cm^3/s [76], but no existing methodology has the necessary sensitivity to accurately measure the rate constant. The reaction intermediate for the $N_2^+ + H$ charge exchange process, N_2H^+, was one of the first ions to be detected in the ISM [79,80], nitrogen is the most abundant molecule in our atmosphere and is present in the ISM, and atomic hydrogen is the most abundant species in the universe. A newly introduced radical source [81,82] – where a series of Halbach arrays and blades filter the output of a Zeeman decelerator [83] to generate a pure beam of H atoms – is in the process of being combined with an ion trap. This will facilitate the first precise study of important reaction systems such as $N_2^+ + H$, providing crucial data for inclusion in models of the chemistry of complex gas-phase environments. The new science that will be made possible by instruments that combine ion traps with sources of cold neutral species includes the measurement of very small rate coefficients, the study of processes such as radiative association, and the spectroscopic probing of reactive intermediates.

3. Concluding remarks

In summary, recent years have seen exciting developments in the field of Coulomb crystals. The previous sections have highlighted developments in the state selection of molecular ions and quantum state manipulation, in the combination of Coulomb crystals with cold neutral sources and mass spectrometric methods to study controlled ion molecule collisions, and in precision measurements that take advantage of the long lifetime of ions in Coulomb crystals. These are just some of the exciting current areas of research that are ongoing in the field. Coulomb crystals offer a promising medium for the refinement of fundamental constants and in quantum computing applications. Decades-old theories of reactivity are also beginning to be experimentally verified and challenged for the first time. As ion traps become combined with an increasingly diverse range of cold neutral sources, one might even go so far as to say that the prospect of attaining full control over ion-neutral reactive collisions is almost within reach. In order to achieve complete control at the 'state-to-state' level, all the way through to product formation, we require new developments to sensitively detect the quantum states of product ions. Such methods are most likely to be feasible for very small (two ion) Coulomb crystals, where quantum logic spectroscopy could be most readily applied.

Note

1. Q is the charge on the ions and a_{WS}, known as the Wigner-Seitz radius, is the average distance between ions, $a_{WS} = (3/(4\pi\rho))^{1/3}$, where ρ is the ion density.

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