Objectives of the RoCMI project

Examine how ion-molecule reactions occur at very low temperatures – providing accurate and precise experimental data on such processes for the first time.

Background information

Coulomb crystals offer a unique medium for experimentally examining state-selected ion-molecule reactions in the cold regime.[1] A Coulomb crystal is formed when atomic ions held within an ion trap are laser cooled, with the ions forming a localised crystal lattice structure. Non-laser-cooled ions can also be incorporated into Coulomb crystals via sympathetic cooling; through elastic collisions, kinetic energy can be transferred from the co-trapped ions to the laser-cooled ions, where it is dissipated by subsequent laser cooling cycles. Sympathetically-cooled ions with appropriate properties can thus be held in ion traps for extended periods of time, allowing us to study a diverse range of ion-molecule reactions with Coulomb-crystallised ion targets.

Key results

(a) Maintaining state selectivity in molecular ions

Sympathetic cooling only affects the external degrees of freedom co-trapped ionic species in Coulomb crystals. In most cases, the internal degrees of freedom of molecular species rapidly thermalize with the ambient blackbody radiation (BBR) field; while trapped molecular ions remain translationally cold, they are not internally cold. There is thus a need to develop methods for preserving state selectivity in trapped molecular ion targets. One way to achieve this is to excite one or more rovibrational transitions with a laser, to drive population (via subsequent fluorescence) into the lowest few internal energy states of the molecular ion. Theoretical work characterising laser-induced BBR-mediated rotational cooling schemes has been undertaken for a number of diatomic (MgH^+, HCl^+, DCl^+, LiH and CsH) and polyatomic ($C_2H_2^+$, with CO_2^+ also discussed) species. A single laser is sufficient to drive 92% of population into the DCl^+ ground state at room temperature.[2] In more complicated polyatomic species such as $C_2H_2^+$, two broadband lasers would be sufficient to drive 78% of population into the two rovibrational ground states (the $^2\Pi$ electronic ground state is split by spin-orbit coupling).[3]

(b) Quantitative detection of Coulomb-crystallised ions

Imaging the fluorescence continuously emitted by the laser-cooled Ca^+ ions enables observation of Coulomb crystals in real time. While species sympathetically cooled into a Coulomb crystal do not fluoresce, their presence can be inferred from changes to the crystal framework. The trapping field is dependent on the mass-to-charge ratio of the ion; species with lower mass-to-charge ratios migrate to the centre, whereas heavier species move to the outer region of the crystal. By monitoring the fluorescing ion framework over time and matching these images with molecular dynamics simulations of the crystal, we can establish the number of sympathetically cooled ions incorporated into the crystal at a given time. However, this requires one to make assumptions about the identity of the dark ions; from the crystal images we can only ascertain whether a (singly charged) co-trapped species is lighter or heavier than 40 u. To this end, we have developed a digital ion trap (DIT) mass spectrometry (MS) technique, enabling precise measurement of the mass-to-charge ratios and relative numbers of each species within a crystal.

A time-dependent trapping potential is typically generated in a linear Paul trap using cosine radiofrequency (RF) trapping fields, with axial confinement achieved using static end cap voltages. To eject crystals from the trap and onto an external detector, the quadrupole RF trapping fields must be switched off and static dipolar fields applied, to create a repeller and extractor pair for Wiley-McLaren style time-of-flight (TOF) MS. It is

difficult to switch off resonantly-driven cosine trapping fields, as ringing noise from the decaying trapping fields is typically superimposed on the ejection pulses – deflecting the ejected ions away from the detector. To overcome this problem, we employ non-resonantly generated digital RF waveforms. Digital fields can be switched off cleanly, resulting in no ringing noise on the ejection pulses. Following the application of repeller and extractor voltages, the crystal is ejected radially from the trap, through a TOF tube and onto a microchannel plate detector, yielding mass-sensitive detection of all ions in the crystal.[4]

However, the DIT has the drawback of a shallower trap depth (under our experimental conditions) compared to that of a conventional linear Paul trap with cosine RF fields. As such, the DIT is not appropriate for all reaction systems. To address this issue, we have also developed a damped cosine trap (DCT), whereby the resonantly-driven cosine trapping fields are actively damped and given time to decay before the application of ejection pulses.[5] Analysis of experimental results, aided by extensive simulations, indicate that the DCT has excellent detection efficiency and mass resolving power comparable to that of the DIT.[5]

(c) Combination of the ion trap with cold molecular sources for to study ion-molecule reactions

Two sources of cold molecules have been developed and independently characterised for the study of cold, controlled ion-molecule reactions.[1,6] The state-selected charge exchange between Xe^+ ($^2P_{3/2}$) and ammonia (J,KM = 1,-1) has been examined, with the presence of an additional reaction channel identified: H-transfer from neutral ammonia in the molecular beam to trapped ammonia ions, $NH_3 + NH_3^+ \rightarrow NH_2 + NH_4^+$.[5]

Future work

Analysis of the dynamics and kinetics of the Xe^+ + ammonia reaction system is ongoing. Once analysis is complete, we will commence a detailed investigation of the influence that collision energy has on reaction rate constants and product formation. This can be achieved with the Stark decelerator; by altering the point at which the electric fields are switched, a selected amount of translational energy is removed at each stage – yielding a molecular beam with tuneable velocity.

Complementing the Stark decelerator-ion trap experiments, another cold molecule source – namely, a buffer gas cell and electrostatic guide (BGCEG) apparatus – has been developed and is in the final stages of combination with an ion trap. Whereas the Stark decelerator is a pulsed source for producing molecules in a single rotational state with variable velocity, the BGCEG is a continuous source for producing molecules with a fixed velocity, but with variable rotational energy. In this way, we can establish the role of J on the reaction rate – enabling the verification of theoretical predictions that the reaction rate of polar molecules with anions increases with decreasing J at low collision energies.

Publications cited
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