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Ion-Atom and Ion-Molecule Hybrid Systems: Ion-Neutral Chemistry at Ultralow Energies

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Abstract. The study of chemical reactions between ions and neutral species at very low energies reveals precise informations about the dynamics of collisions and fine details of intermolecular interactions. Here, we report progress towards the development of next-generation experiments for the investigation of cold ion-neutral reactions. First, we present a new "dynamic" hybrid ion-atom trap which enables the study of collisions with a superior energy resolution accessing a regime in which quantum scattering resonances may become observable. Second, we discuss and numerically characterize the concept and properties of a hybrid trap for cold neutral molecules and molecular ions which paves the way for the study of ion-molecule reactions in the millikelvin regime.

1. Introduction

Driven by recent technological advances in the cooling of atoms and molecules, the study of collisions and chemical reactions at temperatures below 1 K has emerged as a new scientific field over the past few years [1, 2, 3, 4, 5]. One chief motivation for studying chemical reactions at ultralow energies lies in the characterization of elusive quantum phenomena such as collisional resonances and subtle effects of quantum statistics which are often obscured at higher energies [6, 7]. Moreover, at very low collision energies the kinetics and dynamics of reactions become very sensitive to the fine details of the potential energy surface enabling the precise study of intermolecular interactions [8]. In addition, cold-atoms and cold-molecules methods form the basis of new schemes for the control of chemical processes [9, 10]. Ion-neutral reactions form an important class of problems in the context of cold chemistry [2, 5, 11]. Their study at very low temperatures presents a particular challenge as it requires the combination of methods for the cooling and trapping of both species.

2. Ion-atom hybrid systems: ion-neutral chemistry in the cold regime

While early studies combining cold-ion and cold-molecules methods achieved collision energies in the Kelvin range [12], the recent development of experiments for the simultaneous ("hybrid") trapping of cold ions and cold atoms has paved the way for the study of ion-atom interactions, collisions and chemical reactions in the millikelvin ("cold") regime [13,14,15]. These experiments

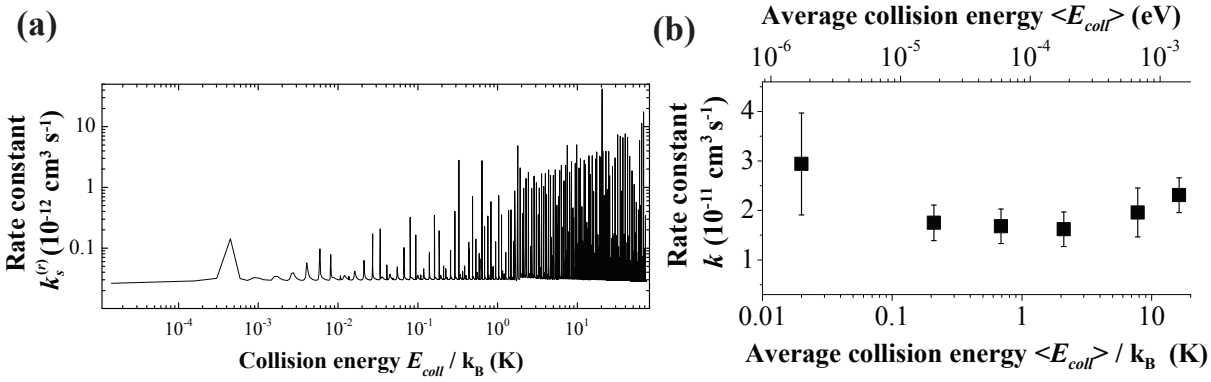

Figure 1. (a) Calculated aggregate rate constant for radiative charge transfer and association in the Ca^+ + Rb system showing a range of scattering resonances at well-defined collision energies superimposed on a constant background. (b) Experimental rate constant averaged over all accessible entrance channels as a function of the collision energy. Resonances were not resolved because of the broad collision-energy distributions in the experiment. Adapted from Ref. [18].

rely on the combination of a trap for cold atoms (such as a magneto-optical trap (MOT), an optical dipole trap or a magnetic trap) with a radiofrequency (RF) trap for cold ions. The species typically used are laser-coolable ions and atoms such as Ca^+, Ba^+, Yb^+ and Rb, Ca, Li, respectively.

Despite the apparent chemical simplicity of these systems in which an atomic ion interacts with a neutral atom, they have been shown to exhibit a rich and complex chemistry in which light-assisted processes play an important role. Charge transfer can occur non-adiabatically or radiatively [16, 17, 18, 19, 20, 21]. Reaction rates can be considerably enhanced by the electronic excitation of the collision partners [8, 16, 22, 23]. Molecular ions can be formed by radiative association [16, 17, 18, 24]. At high atom densities, three-body processes were shown to become dominant [25]. Moreover, reaction rates were shown to strongly depend on the hyperfine state of the atoms in some systems [22].

In the majority of systems studied so far, reactive collisions were characterized by Langevin-type capture dynamics with a non-unit reaction probability yielding a nearly constant dependence of the reaction rate on the collision energy [16, 17, 18, 20, 22]. However, in a range of systems quantum scattering calculations have predicted the occurrence of numerous shape resonances which manifest themselves as pronounced enhancements of the reaction rate within a very small collision-energy interval [17, 18, 24, 26, 27, 28], see Fig. 1 (a) for the example of Ca^+ + Rb. These resonances are a distinct quantum phenomenon and arise when the collision energy matches the energy of a metastable state trapped behind the centrifugal barrier. The positions and widths of these resonances are very sensitive to the interaction potential as well as the collisional angular momentum and thus reveal important details of the scattering dynamics. The observation of scattering resonances has recently been reported in cold collisions of neutral molecules [6, 29, 30]. However, to the best of our knowledge they have thus far not been observed for cold ionic processes.

Although resonances are predicted to occur in the energy window accessible to hybrid ion-atom experiments (see Fig. 1), their observation has thus far been precluded by the low energy resolution of previous studies. Although in a hybrid-trapping experiment both species are translationally cold, it is not straight forward to tune their kinetic energies over a wide interval while preserving a narrow energy distribution. Tuning the collision energies could thus far be achieved by, e.g., imparting a defined amount of micromotion to the ions (the fast oscillating

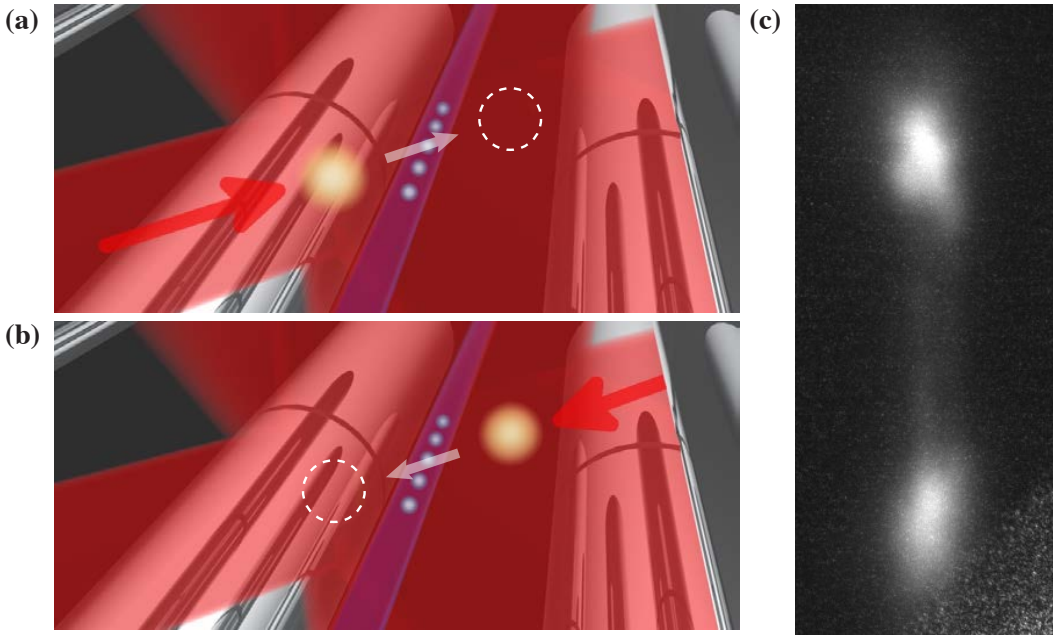

Figure 2. Schematic representation of a "dynamic" hybrid trap in which a cloud of ultracold Rb atoms is alternatingly shuttled back and forth between two magneto-optical trapping (MOT) sites. (a) A cloud of atoms (orange sphere) is cooled and trapped in a MOT site slightly displaced from the center of the setup. Subsequently, the cloud is pushed towards the center of the trap using radiation-pressure forces generated by a near-resonant push laser beam (red arrow). The velocity of the atoms (represented by the white arrow) can be precisely controlled by the intensity and detuning of the push beam. A string of laser-cooled Ca^+ ions (blue spheres) is placed in the center of the setup. Collisions between the Ca^+ ions and the Rb atoms occur when the atom cloud passes through the ion string during transit. The atoms are then re-captured and re-cooled in another off-center MOT site on the opposite site of the ion string (dashed circle). (b) The atoms are subsequently pushed back and recaptured at their original position. The entire scheme is repeated at a frequency of typically 20-50 Hz to increase the duty cycle of the experiment. (b) Fluorescence image of the Rb atoms averaged over two shuttling periods showing the positions of the two off-center MOTs and atoms in transit between them. For the collision experiments, the position of the ions is located in the center of the image halfway between the two MOT sites.

motion driven by the trap's RF fields) [17]. However, because the micromotion is an oscillating motion, the collision-energy distributions achieved in this way were not narrow enough to enable the resolution of resonances, see Fig. 1 (b). To overcome this deficiency, we have recently developed a new "dynamic" hybrid trap which enables experiments with a greatly improved energy resolution which opens up perspectives to resolve the resonance structures.

3. Next-generation hybrid ion-atom experiments

Our new experiment relies on clouds of Rb atoms repeatedly being pushed with a well-defined velocity through a string of laser-cooled Ca^+ ions, see Fig. 2. Ultracold Rb atoms are first prepared in a MOT displaced from the ions. The atoms are then accelerated towards the ions using radiation-pressure forces generated by a "push" laser beam near-resonant with the Rb D II line at 780 nm (Fig. 2 (a)). After passing through the ions, the atoms are captured in a second MOT, re-cooled and then accelerated back towards the first MOT using another laser

beam counter-propagating to the first push beam (Fig. 2 (b)). The cold atoms are constantly shuttled back and forth between the two MOT sites so that collisions and chemical reactions with a well-defined energy can occur each time the cloud passes through the ions. In this scheme, the ions are arranged in a string aligned with the symmetry axis of the linear RF trap where the RF fields vanish (the RF null line). Therefore, the ions exhibit minimal micromotion [2] and possess a minimal translational temperature close to the Doppler cooling limit ($T_{\mathrm{D}} \approx 0.5$ mK for Ca^+). The collision energies are thus entirely dominated by the velocities of the neutral atoms which can accurately be tuned by adjusting the power of the push laser beams.

Fig. 2 (c) shows a fluorescence image of the Rb atoms during shuttling. As the exposure time of the camera (100 ms) is longer than the shuttling period (50 ms), fluorescence can be observed at the positions of both MOT sites from the periods when the atoms are re-cooled in either location, as well as from atoms in transit in between them. The position of the ions (not visible) is located in the center of the image halfway between the two MOT sites.

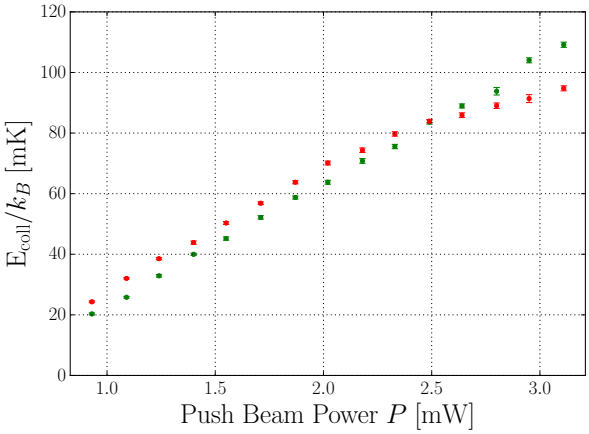

Figure 3. Collision energies of Ca^+ and Rb obtained by varying the velocity of the traveling Rb atom cloud. Red and green symbols indicate the forward and backward pushing directions, respectively.

Fig. 3 shows the achievable collision energies of Ca^+ and Rb determined by measurements of the time of flight of the atoms. The red and green symbols indicate the backward and forward shuttling directions, respectively. The error bars are on the order of the size of the symbols illustrating the very good reproducibility of the experiment. The collision energies calculated with this scheme (assuming a negligible contribution from the ion motion) amount to $E_{\mathrm{coll}}/k_{\mathrm{B}} = 20 - 120$ mK. Several shape resonances have been predicted in this energy interval as can be seen in Fig. 1 (a). A preliminary comparison of the experimental data with Monte-Carlo trajectory simulations suggests that a collision-energy resolution down to a few mK can be achieved with the current setup. This should be sufficient in order to resolve broad resonances in collision experiments in the near future [24].

4. Combining cold ions with cold molecules: Towards ion-molecule hybrid systems

Following the exciting experiments that have been performed with cold ion-atom hybrid systems, it is desirable to extend this technique to molecules. Cold molecular ions can readily be produced by sympathetic cooling using the interaction with simultaneously trapped laser-cooled atomic ions [2] and have already been implemented in some hybrid experiments with ultracold atoms [8, 31]. The development of genuine ion-molecule hybrid systems, i.e., the combination of cold neutral molecules with cold molecular ions, is, however, considerably more challenging as it requires elaborate techniques for the cooling and trapping of neutral molecules such as Stark deceleration [32]. An additional complication is constituted by the vastly different time scales for the trapping of the two species. While ions are trapped by electric fields by

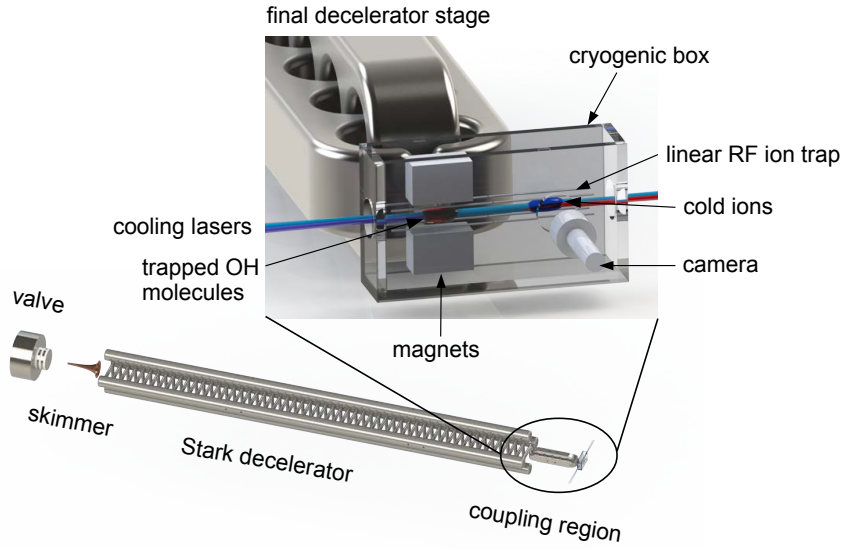

Figure 4. Schematic of the experimental setup for an ion-molecule hybrid trap consisting of a Stark decelerator coupled to a magnetic trap for the generation and trapping of cold OH molecules superimposed on a cryogenic ion trap.

means of their charge and can easily be confined on timescales longer than minutes [2], the trapping of neutral molecules relies on their interaction with electric or magnetic fields, i.e., their Stark or Zeeman effects, respectively, which are dependent on the internal state of the molecules [33, 34]. For strongly polar molecules which are amenable to Stark deceleration, the internal-state populations are redistributed by the ambient room-temperature blackbody-radiation (BBR) field on timescales of seconds which usually leads to their loss from the trap [33]. This effect can be mitigated and trap lifetimes can be prolonged by cooling the trap environment in order to reduce the BBR intensity [35].

Fig. 4 shows a schematic of an ion-molecule hybrid trap that is currently being developed in our laboratory. Following Ref. [34], cold OH molecules in the $J = 3/2, \pm m_J = 3/2, f$ states are generated by Stark deceleration. Here, J stand for the total angular momentum quantum number, m_J for the quantum number of its space-fixed projection and f is the parity label. After exiting the decelerator, the molecules are stopped by a final electric field ramp centered on a magnetic trap formed by two permanent magnets. Molecules in the the low-field seeking $J = 3/2, m_J = +3/2, f$ Zeeman state (50% of the decelerated ensemble) can be magnetically trapped. The depth of trap has been calculated to be $D \approx 0.14$ cm^{-1} (see Fig. 5 (a)). The

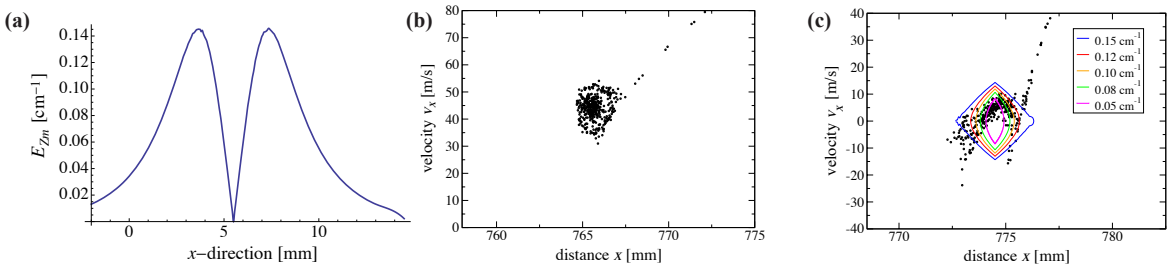

Figure 5. (a) Zeeman energies E_{Zm} for OH molecules in the low-field seeking $J = 3/2, m_J = +3/2, f$ state along the longitudinal (x) direction of the magnetic trap. (b) Phase-space distribution of OH molecules at the exit of the decelerator obtained by Monte-Carlo trajectory simulations. (c) Phase-space distribution of the stopped OH molecules at the position of the magnetic trap. The contour lines indicate the phase-space acceptance of the trap.

magnets are superimposed on a linear RF ion trap in which cold atomic and molecular ions can be produced by laser and sympathetic cooling, respectively, allowing to overlap the cold molecules with the cold molecular ions. The entire trapping zone is encased in a cryogenic shield in order to reduce the BBR intensity.

Because of the comparatively low number densities of cold OH molecules that can be trapped following Stark deceleration ($\approx 10^7 - 10^8$ molecules cm^{-3} [32,33,34]), it is imperative to optimize the trap-loading and trapping efficiencies in order to maximize the number of magnetically trapped molecules. For this purpose, the location of the magnetic trap, the time sequence and the voltages applied to the stopping electrodes were jointly optimized using a mesh-adaptive direct search algorithm [36] implemented in realistic Monte-Carlo trajectory simulations of the molecules in the setup. After optimization, $\approx 42\%$ of the stopped molecules were calculated to match the phase-space acceptance criteria of the trap (Figs. 5 (b) and (c)) so that in total $\approx 21\%$ of the molecules exiting the decelerator can theoretically be trapped. This latter figure is comparable to previous experiments with electrostatic traps [33] which, however, are capable of capturing *all* of the quantum states exiting the decelerator.

Apart from OH, the current scheme is also amenable to other polar and paramagnetic species like NH and CH which can be Stark decelerated and magnetically trapped. Together with the wide range of cold molecular ions that can be generated by sympathetic cooling [2], a variety of cold ion-molecule hybrid systems will be accessible to the current experiment. Whereas the trapped neutral molecules are generically state selected, the cold molecular ions can be produced in specific states by threshold photoionization [37]. Here, the cryogenic environment also helps to conserve the state of the ions for the duration of the experiments (several minutes) [38] so that fully state selected experiments with cold ions and molecules become feasible. Moreover, the capability to apply both electric and magnetic fields to the trapping region will open up further perspectives to influence and control cold collisions.

5. Summary and conclusions

Next-generation experiments for the study of cold ion-neutral reactions will feature a greatly improved energy resolution and will extend hybrid-trapping technology to molecular species. For ionic processes, these advances pave the way for investigating for the first time collisional quantum effects such as scattering resonances and study molecular phenomena in the millikelvin regime. Thus, the new experiments open up new perspectives for the precise characterization of kinetics, dynamics and mechanisms of ionic reactions of interest for chemistry, astrophysics and plasma physics.

Acknowledgements

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