Millikelvin Reactive Collisions between Sympathetically Cooled Molecular Ions and Laser-Cooled Atoms in an Ion-Atom Hybrid Trap

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We report on a study of cold reactive collisions between sympathetically cooled molecular ions and laser-cooled atoms in an ion-atom hybrid trap. Chemical reactions were studied at average collision energies \(E_{\text{col}}/k_B \approx 20 \text{ mK}\), about 2 orders of magnitude lower than has been achieved in previous experiments with molecular ions. Choosing \(\text{N}_2^+ + \text{Rb}\) as a prototypical system, we find that the reaction rate is independent of the collision energy within the range studied, but strongly dependent on the internal state of \(\text{Rb}\). Highly efficient charge exchange four times faster than the Langevin rate was observed with \(\text{Rb}\) in the excited \((5p)^2P_{3/2}\) state. This observation is rationalized by a capture process dominated by the charge-quadrupole interaction and a near resonance between the entrance and exit channels of the system. Our results provide a test of classical models for reactions of molecular ions at the lowest energies reached thus far.

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The combination of radio frequency (rf) ion traps with magneto-optical or optical-dipole traps for the simultaneous confinement of cold ions and atoms has recently enabled the study of ion-neutral interactions at temperatures as low as a few millikelvin [1–7]. Hybrid trapping techniques have opened up perspectives for the exploration of new mesoscopic quantum systems [8], for quantum interfaces between atoms and ions [9], and for new methods to cool ions to ultralow temperatures [6,10]. Moreover, chemical experiments with ions [4,5,7,11] have started to approach an energy regime so far restricted to neutrals [12–15] in which the quantum character of the collision can strongly influence the chemical dynamics [16–18].

Until now, studies of reactive processes in hybrid traps have been restricted to atomic ions and neutral atoms. Despite the apparent simplicity of these collision systems, a diverse range of chemical phenomena has been observed. The effects range from the radiative formation of molecules and charge exchange in \(\text{Ca}^+ + \text{Rb}\) [4], the occurrence of unusually fast reaction rates in \(\text{Yb}^+ + \text{Ca}\) [5] and the influence of the ion’s hyperfine state on the reactivity in \(\text{Yb}^+ + \text{Rb}\) [7]. However, experiments with atomic species can only cover a fraction of the wealth of chemical phenomena, and it is necessary to extend studies to molecules to be able to fully explore the diversity of reactive effects at ultralow energies.

Here, we extend ion-neutral hybrid-trapping techniques to the study of cold reactive collisions with molecular species by sympathetically cooling molecular ions by their interaction with laser-cooled atomic ions [19] and immersing them in a cloud of ultracold atoms in a magneto-optical trap. To our knowledge, this is the first time that chemical reactions with molecular ions have been studied at collision energies down to \(E_{\text{col}}/k_B = 20 \text{ mK}\), about 2 orders of magnitude lower than has been achieved in previous experiments [20–22].

By choosing sympathetically cooled \(\text{N}_2^+\) ions and laser-cooled \(\text{Rb}\) atoms as a prototypical system, we characterize important features of cold reactive collisions between molecular ions and alkali atoms. We observe charge exchange and a strong dependence of the reaction rate on the electronic state of \(\text{Rb}\). Whereas reactions with \(\text{Rb}\) in the \((5p)^2P_{3/2}\) state occur fast, consistent with a classical capture model, reactions with ground state atoms were found to be at least 2 orders of magnitude slower. The fast excited state rate is explained by a long range capture of the atom by the molecular ion dominated by the charge-quadrupole interaction and a near resonance between the entrance and exit channels at short range. Our results highlight the importance of resonant effects in cold ion-neutral collisions and provide a test of classical reaction models for molecular ions at the lowest energies reached thus far.

Our hybrid-trapping apparatus has already been described in Ref. [4]. Here, \(\text{N}_2^+\) ions were generated in a linear rf ion trap from room temperature background nitrogen gas using \([2 + 1]\) resonance-enhanced multiphoton-ionization (REMPI) via the \(Q\) branch of the vibrationless \(X^1\Sigma_g^+ \rightarrow a''\Pi\Sigma_h^+\) transition [23]. The ions were subsequently thermalized through collisions with the background gas [23].

The \(\text{N}_2^+\) ions were sympathetically cooled by the interaction with laser-cooled \(\text{Ca}^+\) ions to form Coulomb crystals [19]. Images of the crystals were obtained by collecting the spatially resolved laser-cooling fluorescence of the \(\text{Ca}^+\) ions using a CCD camera coupled to a microscope. The number of ions in the crystals were determined by comparisons of the experimental images with molecular dynamics (MD) simulations, see Refs. [24,25].

After ion loading, the Coulomb crystals were translated along the axis of the rf trap using a static electric field to be overlapped with the atoms. Ultracold \(\text{Rb}\) atoms at densities \(n_{\text{Rb}} = 4 \times 10^8 \text{ cm}^{-3}\) were generated by laser-cooling in the
The motion of the excited ions couples to the laser-cooled to resonantly excite the radial motion of specific ion species. The motion of the excited ions couples to the laser-cooled Ca$^+$ ions and leads to a modulation of their laser-cooling fluorescence around the resonance frequencies. Figure 2 shows mass spectra of Coulomb crystals (i) before and (ii) after reaction. Additionally, a pure Ca$^+$ crystal (iii) was reacted for the same duration as in (ii) to illustrate the effect of the slow background reaction Ca$^+$ + Rb. The insets show images of the corresponding crystals and the vertical lines indicate the theoretical single-ion resonance frequencies of the relevant species.

Whereas the spectrum recorded before reaction only shows a single resonance corresponding to the excitation of the Ca$^+$ ions, the spectrum after reaction in (ii) shows an additional weak feature around 70 kHz assigned to sympathetically cooled Rb$^+$ product ions. Note that the positions of the resonances in a Coulomb crystal are slightly shifted from the single-ion frequencies because of Coulomb-coupling effects [26]. Resonances for the CaOH$^+$, CaH$^+$, and the reactant N$_2^+$ ions, as well as for the Rb$^+$ ions formed by the background reaction Ca$^+$ + Rb in (iii) could not be observed in the spectra under the present conditions. MD simulations revealed that their numbers were too small to exert any noticeable back action on the Ca$^+$ fluorescence at the excitation amplitudes used. Higher amplitudes would have led to the melting of the crystals around the Ca$^+$ resonance and were therefore precluded.

Figure 3(a) shows the dependence of the rate constant on the collision energy. In the experiments, the Rb kinetic energies $(E_{kin}/k_B = 200 \mu K)$ were much smaller than the ion energies $(\simeq 20 mK)$ so that the collision energies were dominated by the contribution of the ions. Their motion can be separated into two different components, a slow secular motion in the time-averaged pseudopotential of the trap and a fast micromotion driven by the rf fields [19]. The secular $(E_{sec}/k_B = 12 mK$ for Ca$^+$ and 14 mK for N$_2^+$) and micromotion energies were determined from the ion trajectories obtained in the MD simulations of the crystal images [24]. The total kinetic energy $E_{tot}$ of the ions was governed by their micromotion energy which vanishes for
ions located on the central trap axis and increases quadratically with the distance [19]. The lowest achievable energies are limited by the precision with which the N$_2^+$ ions can be localized on the axis. Our present axialization procedures (to be described in detail in Ref. [27]) allowed for a micromotion energy limit corresponding to 17 mK.

For the measurements in Fig. 3(a), Coulomb crystals with strings of nitrogen ions [like the ones shown in Fig. 1(a)] were aligned parallel to the trap axis where all ions exhibit approximately the same micromotion energy [24]. The collision energies were varied by displacing the Coulomb crystals from the axis using static electric fields causing the N$_2^+$ ions to move into regions where they acquire an increased micromotion energy (see insets). The dislocated crystals exhibit an asymmetric ion distribution because the heavier Ca$^+$ ions are more strongly displaced than the lighter N$_2^+$ ions as a consequence of the mass dependence of the effective trapping potential [19]. The collision-energy distributions for the data points with the lowest and highest energies in Fig. 3(a) obtained from the MD simulations are displayed in Fig. 3(b) alongside the corresponding simulated images. Within the uncertainty limits, the rate constant was observed to be essentially independent of the collision energy in the interval studied.

Because the ultracold atoms are constantly excited during laser cooling, a fraction of the reactions occurs with Rb atoms in the (5p)$^2P_{3/2}$ state. The population in the excited state was adjusted by varying the intensity of the Rb cooling laser [4]. The rate constant shows an approximately linear increase with the (5p)$^2P_{3/2}$ population [Fig. 3(c)]. Following Ref. [4], a kinetic model $k = \frac{1}{2}(k_s + k_p)$, where $k_s$ and $p$ are rate constants and populations in the Rb (5s, 5p) states, respectively, was fitted to the data. The fit yielded $k_p = 2.4(13) \times 10^{-8}$ cm$^3$ s$^{-1}$ and an upper bound $k_s \leq 2 \times 10^{-10}$ cm$^3$ s$^{-1}$. The uncertainty of $k_p$ is dominated by a systematic error of $\approx 50\%$ in the Rb density.

Because of the large difference between the ionization energies of N$_2$ and Rb, a minimum of 11.4 eV of energy is released in the reaction. By comparison, the rotational-vibrational energy of the N$_2^+$ ions ($\approx 0.025$ eV for a room temperature distribution) as well as the collision energy ($\approx 10^{-6}$ eV) is small, so that the available energy is entirely dominated by the electronic contribution. Figure 4 shows an energy diagram depicting the relevant electronic entrance and product channels (see Ref. [28] for an overview of the electronic states of N$_2$).

Previous studies using keV ion beams showed that charge exchange between alkali atoms and N$_2^+$ is most efficient in a near-resonant transfer of the electron into a Rydberg state of the neutral product molecule which is built on an ion core with the same electronic configuration as the reactant ion [29]. In the present case, the N$_2^+$ ($X^+$) + Rb(5s) entrance channel is closest in energy to a product
channel forming $\text{N}_2$ in the $\text{C}^3\Pi_u$ electronic state (energy mismatch $\Delta E = 372$ meV, see Fig. 4). However, electron capture by $\text{N}_2^+$ in its $X^+ 2\Sigma^+_u^+$ electronic ground state [molecular orbital configuration $(2\sigma_g)^2(2\sigma_u)^3(1\pi_u)^3 \times (3\sigma_g)^1]$ to form $\text{N}_2$ in the $\text{C}$ state $[(2\sigma_g)^2(2\sigma_u)^1(1\pi_u)^3 \times (3\sigma_g)^2(1\pi_u)]$ entails a significant rearrangement of the electronic configuration. This process is, therefore, expected to be inefficient, in line with the observation of a slow reaction rate in this channel. On the other hand, the excited $\text{N}_2^+(X^+) + \text{Rb}(5p)$ entrance channel is near resonant with product channels forming $\text{N}_2$ in the the closely lying $\text{G}^3\Pi_u, \text{D}^3\Sigma^+_u$ and $\text{F}^3\Pi_u$ states (energy mismatches $\Delta E = 183$ meV, 151 meV, and 8 meV). These states are among the lowest Rydberg states of $\text{N}_2$ built on the $\text{N}_2^+ X^+ 2\Sigma^+_u^+$ (in case of the $G, D$ states) and $A^+ 2\Pi_u$ (in case of the $F$ state) ion cores. The $F$ state is heavily mixed with the $G$ state and therefore also contains $X^+$ core character [30]. Thus, capture of the electron into all three states is expected to be efficient, in agreement with the fast rate observed in the excited channel. Moreover, the increased density of states in this region (see Fig. 4) and their short lifetimes (and therefore large resonance widths) [30] also contribute to the enhancement of the reaction probability. The Rydberg molecules subsequently predissociate into the atomic fragments $\text{N}(^4S) + \text{N}(^2D)$ [29] which, however, cannot be detected in the present experiment.

In previous studies on cold ion-neutral collisions in hybrid traps [1,7], the rates were found to be in agreement with a limiting value set by the classical Langevin theory which only takes into account the interaction between the charge of the ion and the induced dipole of the neutral [31]. The rate constant for the excited channel determined above $[k_p = 2.4(13) \times 10^{-8}$ cm$^3$ s$^{-1}$], however, is about four times larger than the value for the Langevin collision rate constant $[k^{(L)} = 6.6 \times 10^{-9}$ cm$^3$ s$^{-1}]$. This finding indicates that additional long range intermolecular forces must be effective. The most likely candidate is the interaction of the charge of the ion with the permanent electric quadropole moment of Rb generated by the anisotropic charge distribution in the $(5p)^2P_{3/2}$ state [32].

To quantify this effect, the rate constant was calculated with a classical model based on an interaction potential [33] incorporating the Langevin and charge-quadropole interactions. The quadropole moment of Rb $(5p)^2P_{3/2}$ was computed within the single-electron approximation following Ref. [34]. A capture approximation [35] was adopted; i.e., the reaction was assumed to be governed by the long range interactions and to occur with unit probability once the reaction complex was formed. The classical reaction cross section $\sigma^{(c)} = \pi b^2$ was calculated from the maximum possible impact parameter $b$ for which the height of the barrier in the centrifugally corrected potential does not exceed the collision energy [36]. From $\sigma^{(c)}$, the corresponding rate constant at $E_{\text{coll}}/k_B = 23$ mK was obtained to be $k_p^{(c)} = 1.7 \times 10^{-8}$ cm$^3$ s$^{-1}$, which agrees with the experimental value within its uncertainty limits. The agreement supports the conclusion that the reaction rate is close to the collision rate and that the short range charge-transfer probability is near unity, in line with the mechanism discussed above. Note that the charge-quadropole interaction leads to a rate constant weakly dependent on the energy ($k \propto E^{1/6}_{\text{coll}}$) which, however, was not observable over the limited energy interval studied in Fig. 3(a) within the experimental error boundaries.

Notwithstanding the approximations inherent in the model, the result underlines the necessity to reach beyond the Langevin picture to explain the dynamics in the present system. It also suggests that—at least for the present case—a classical capture model seems to adequately reproduce the kinetics in the millikelvin regime. This conclusion is consistent with the theoretical results of Refs. [18,35] which predict a robust performance of these models down to ultracold (< mK) temperatures for all but the lightest systems. This behavior was rationalized by a cancellation of tunneling and reflection effects at the centrifugal barrier [35].

In conclusion, we have studied reactions between sympathetically cooled $\text{N}_2^+$ ions and ultracold Rb atoms at average collision energies down to $\approx$20 mK in an ion-atom hybrid trap. Our results highlight the importance of resonant electronic effects in electron-transfer processes between ultracold alkali atoms and cold molecular ions. The opportunities for resonant charge transfer are markedly enhanced by the dense structure of rotational-vibrational levels [29,30], a unique property of molecular systems compared to the atomic species previously studied in hybrid traps [4,5,7]. A classical capture model was found to adequately describe the kinetics down to the lowest collision energies in cases in which the short range electron-transfer probability is close to unity. Short range effects, such as the rotational-vibrational state of the molecular ion which are not accounted for in the capture picture, could, in principle, modify the reaction probabilities. Because the present experiments were performed with rotationally thermalized ions, we plan further experiments with rotationally and vibrationally state-selected nitrogen ions to characterize the possible role of these effects [25].

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