# Ion-Neutral Chemistry in the Cold Regime

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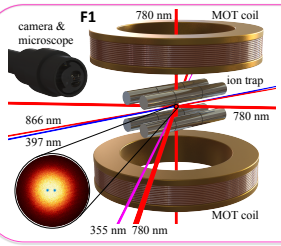
## Abstract and motivation

We present the results of combined experimental and theoretical investigations into cold reactive collisions between laser- or sympathetically cooled ions and Rb atoms in an ion-atom hybrid trap. We compare the collision systems of $Ca^+$ + Rb [1,2] and $Ba^+$ + Rb [3], in which both species are laser cooled, and find that for both systems the rate of reaction is considerably enhanced in electronically excited channels. These observations are rationalised with reference to computed potential energy curves, calculated using high level electronic structure methods. We find that radiative processes play an important role in both systems, verified by the observation of the radative association products $CaRb^+$ and $BaRb^+$, and rationalised using quantum scattering calculations.

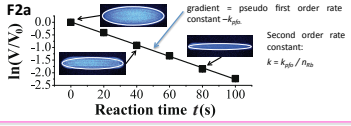
We also compare these results on atomic ion systems with collisions of sympathetically cooled $N_2^+$ molecular ions in their vibrational ground state with ultracold Rb atoms, with average collision energies ($\langle E_{coll}\rangle/k_B$) down to 20 mK [4]. To our knowledge, this is the first time that reactive collisions with molecular ions have been studied at mK energies. We find that the reaction rate is a factor of ≈4 faster than the Langevin rate from the Rb (5p) state, and is two orders of magnitude faster than in the atomic $Ca^+$ + Rb system. The fast rate is explained by a near resonance between entrance and product channels at short range, and the strong charge-quadrupole interaction in the Rb (5p) + $N_2^+$ entrance channel at long range. A classical capture model including these effects reproduces the observed rate.

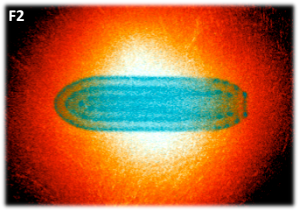
## Hybrid ion-neutral trap



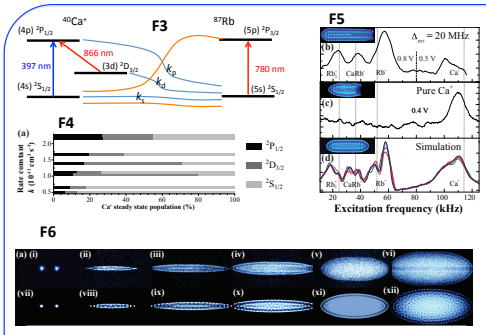

- $Ca^+$ and $Ba^+$ ions are formed by non-resonant multiphoton ionization at 355 nm of atomic beams.
- $Ca^+$ and $Ba^+$ ions are laser cooled in a linear Paul ion trap down to average kinetic energies of $k_B$ • 20 mK, and form Coulomb crystals whose spatially resolved fluorescence (blue in F1 and F2) is collected on a CCD camera.
- Rb atoms are laser cooled and trapped in a magneto-optical trap (red in F1 and F2).
- The two traps are overlaid in space and time to form the hybrid trap (F1).

- Reactions are monitored by observing the decrease in ionic reactant volume following a pseudo-first-order rate law (F2a), and second order rate constants are determined using the average Rb density.

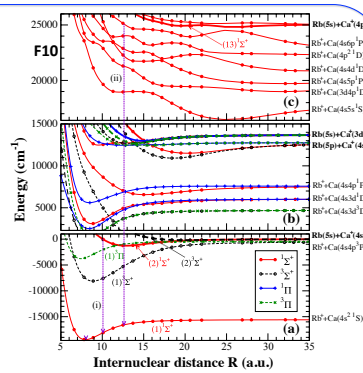


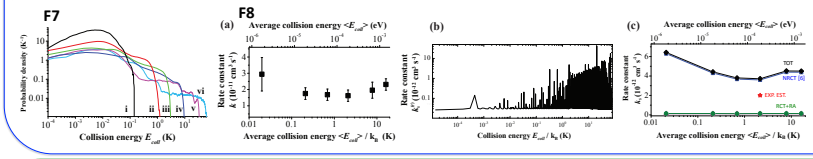




## The $^{40}Ca^+$ + $^{87}Rb$ system [1,2]

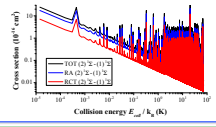



- $Ca^+$ reacts with Rb from four possible entrance channels (F3, bold face in F10).
- $k$ depends strongly on $Ca^+$ $^2P_{1/2}$ population (F4) but not on Rb $^2P_{3/2}$ population.
- Fitting to a rate model gives $k_{s,d} \leq 3\times10^{-12}$ cm$^3$ s$^{-1}$ and $k_p = 1.5(6)\times10^{-10}$ cm$^3$ s$^{-1}$.
- Average collision energy $\langle E_{coll}\rangle/k_B$ (determined from MD simulation energy distributions (F7)) is varied from 20 mK – 20K by changing the shape of the Coulomb crystals (F6), and the rate constant monitored (F8(a)).
- The reaction products are $Rb^+$, $CaRb^+$ and $Rb_2^+$ identified by resonance excitation mass spectrometry (F5).
- Observed rates and products are rationalized with reference to computed potential energy curves (F10)
- Quantum scattering calculations for radiative processes from the lowest entrance channel were conducted and shape resonances found in the cross sections (F9).
- Velocity averaged rate constants were calculated for non-radiative [6] and radiative processes in the ground state channel and compared to an experimental estimate ((F8)(c)).

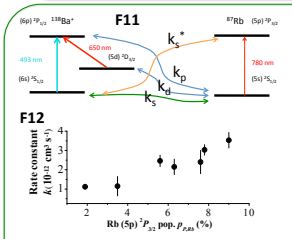



- The rate constant was found to be independent of energy, consistent with a classical charge-induced dipole model, and rationalized in terms of the separability of long range collision dynamics and short range reactive processes [2].

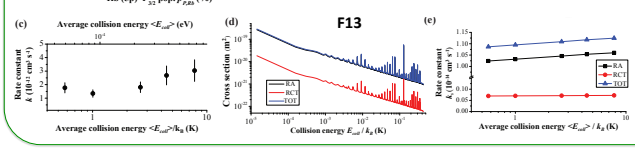


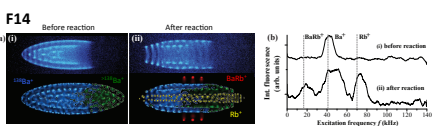

## The $^{138}Ba^+$ + $^{87}Rb$ system [3]

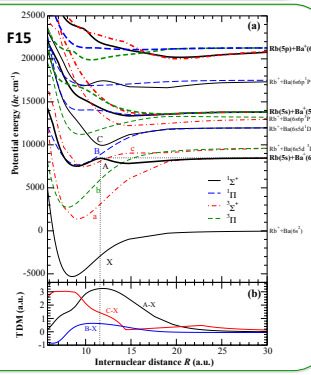



- $Ba^+$ reacts with Rb (F12(b)) from four possible channels (F11).
- $k$ strongly depends on $Ba^+$ $^2P_{1/2}$ and Rb $^2P_{3/2}$ population (F12), with fitting to a rate model yielding $k_s \leq 5\times10^{-13}$ cm$^3$ s$^{-1}$ , $k_d \leq 1\times10^{-12}$ cm$^3$ s$^{-1}$, $k_p = 2(1)\times10^{-11}$ cm$^3$ s$^{-1}$, $k_s^* = 7(2)\times10^{-11}$ cm$^3$ s$^{-1}$ .
- Reaction products are $BaRb^+$ and $Rb^+$ indentified by REMS and the branching ratio (1:2.25) informed by MD simulations (F14).
- Observed rates and products are rationalized using computed potential energy curves (F15).

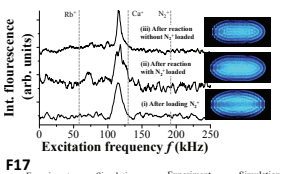
- Cross sections from quantum scattering calculations show RA dominates in the ground state channel (F13(d)), and that shape resonances are predicted, but are not observed experimentally due to low collision energy resolution.
- Collision energy was varied in the same way as for $Ca^+$ + Rb above, and showed a similarly flat dependence (F13(c)), with velocity averaged theoretical rate constants showing a similar dependence (F13(e)).

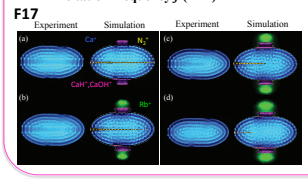


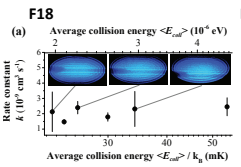

## The $^{28}N_2^+$ + $^{87}Rb$ system [4]



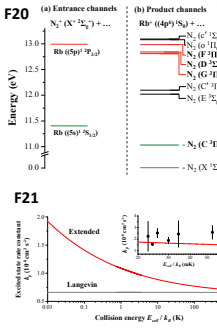

- $N_2^+$ are formed by [2+1] REMPI of $N_2$ [5], and a string of ≈ 25 are sympathetically cooled into a $Ca^+$ Coulomb crystal (F17(a)). The ions are thermalised with background 300 K $N_2$ gas.
- $N_2^+$ reacts with Rb to form $Rb^+$ (F17(a)-(d)), identified by REMS (F16).
- $k$ depends strongly on the Rb $^2P_{3/2}$ population (F19).
- Fitting to a rate model yields a ground state rate constant of $k_s \leq 2\times10^{-10}$ cm$^3$ s$^{-1}$ and an excited state rate constant $k_p = 2.4(13)\times10^{-8}$ cm$^3$ s$^{-1}$, which is four times higher than the Langevin collision rate constant.

- The collision energy was varied by offsetting the ion string from the rf axis, and the rate constant monitored (F18).
- A classical capture model was developed including the charge-permanent quadrupole interaction in the Rb $^2P_{3/2}$ + $N_2^+$ entrance channel (F21) which reproduces the observed rate.
- The implied unit reaction probability from the excited channel was rationalized in terms of a near electronic resonance between entrance and exit channels built on the same electronic core configuration (F20). Efficiency is enhanced in this molecular system due to the release of electronic energy through the translational energy of the predissociated N product fragments.










## References and acknowledgements

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[2] Felix H.J. Hall *et al;* accepted by *Mol. Phys.*(arXiv:1302.4682) (2013)
[3] Felix H.J. Hall *et al;* accepted by *Mol. Phys.*(arXiv:1301.0724) (2013)
[4] Felix H.J. Hall et *al; PRL* **109**, 233202 (2012)
[5] X. Tong, S. Willitsch; *PRL* **105**, 143001 (2010)
[6] M. Tacconi *et al; PCCP* **13**, 19156 (2011)

## Summary and outlook

Laser- and sympathetically- cooled ions show a rich chemistry with laser-cooled atoms dominated by non-adiabatic and radiative effects. Unusual chemical processes such as radiative association, and subtle intermolecular forces like the charge-permanent quadrupole interaction become particularly important at ultralow temperatures. Further experiments will control the rovibrational state of molecular ions [5], and also feature improved energy variation methods which allow a better energy resolution.