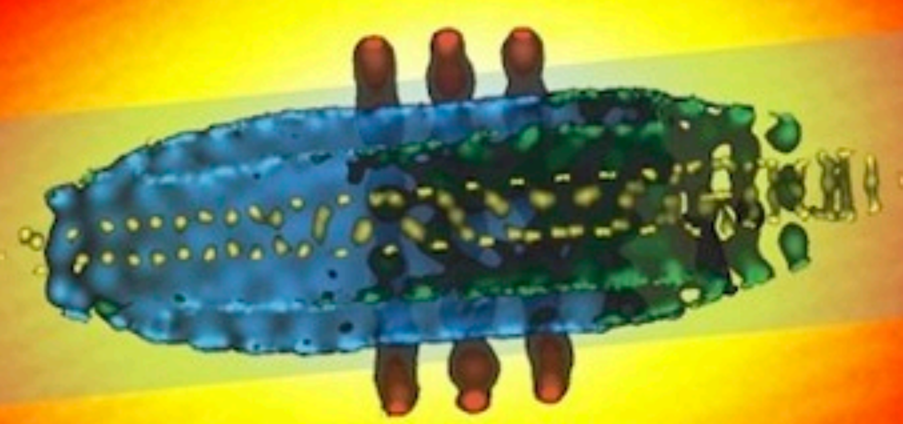
Cold and Controlled Chemistry with Coulomb-crystallized Atomic and Molecular Ions



KITP Conference
New Science with Ultracold Molecules
UCSB, March 11, 2013

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Department of Chemistry
University of Basel, Switzerland

Cold chemistry with ions

Ion chemistry in a new physical regime

- Exotic chemical processes
- Quantum character of ion-neutral collisions

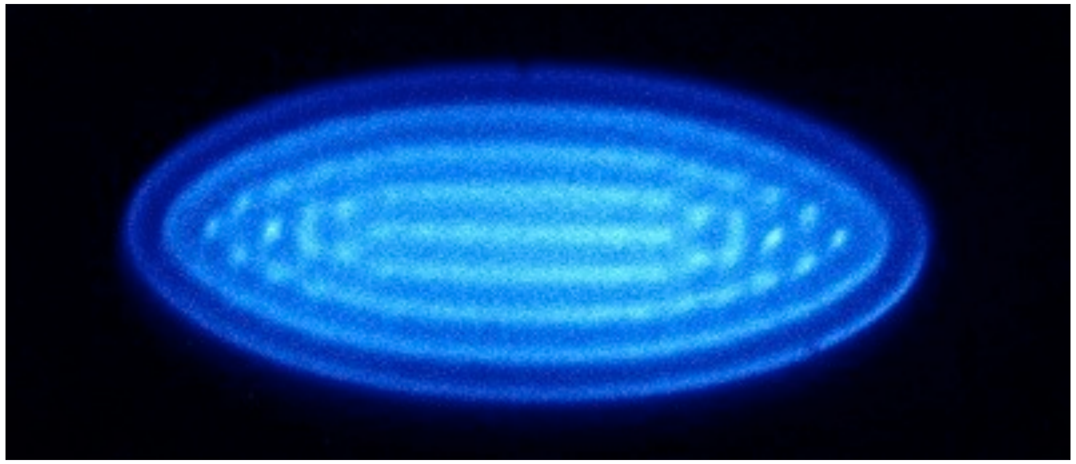
New methods for controlling chemical reactions

- Accurate quantum-state AND collision-energy control
- Chemical reactions with single localised particles

Literature:

- M. Drewsen et al., Int. J. Mass Spectrom. 229 (2003), 83
- B. Roth, S. Schiller, p. 651 in "Cold Molecules", CRC Press (2009)
- SW et al., PCCP 10 (2008), 7200
- SW, Int. Rev. Phys. Chem. 31 (2012), 175
- P.F. Staanum et al., PRL 100 (2008), 243003

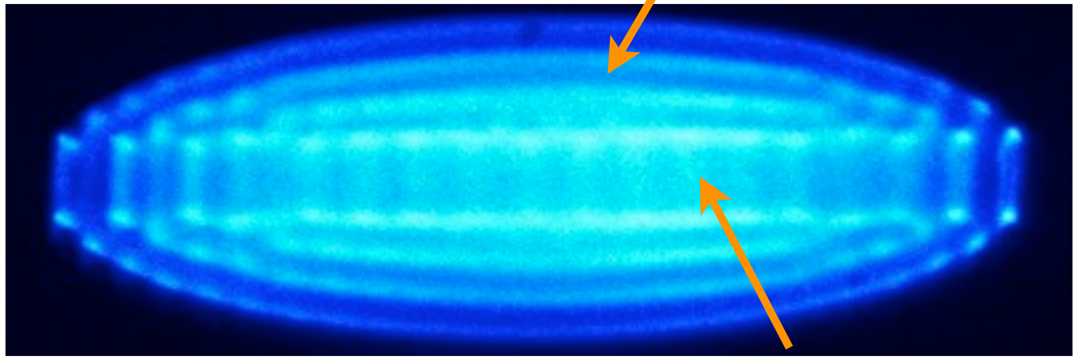
A Coulomb crystal of laser-cooled Ca^+ ions



A bi-component Coulomb crystal with sympathetically-cooled molecular ions

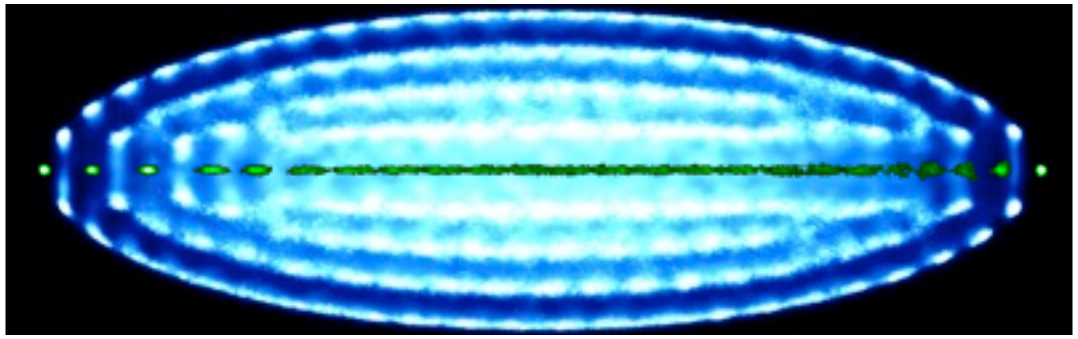
Experiment:

Laser-cooled Ca^+ ions

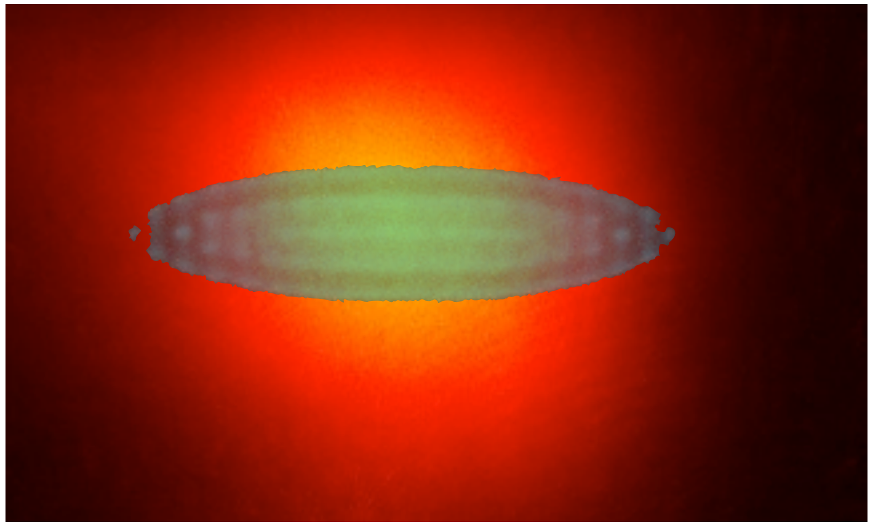


Sympathetically-cooled N_2^+ ions

Simulation:

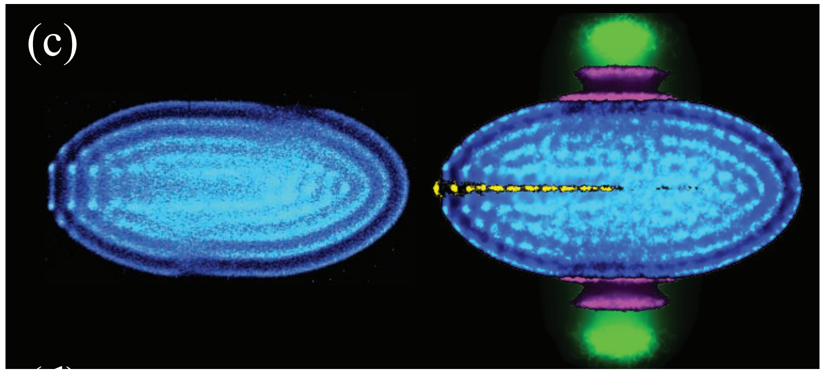


Outline



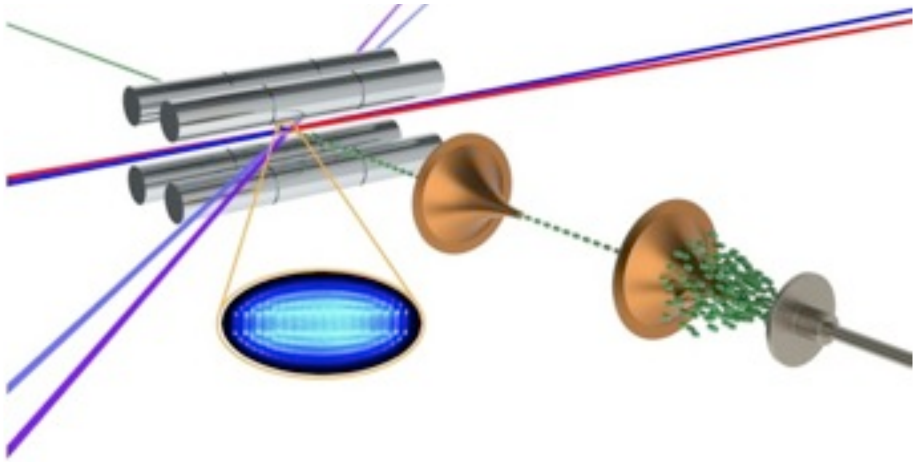
Cold chemistry:

1. Light-assisted processes in the cold regime: Ca^+ + Rb and Ba^+ + Rb
2. Reactions with molecular ions at mK energies: N_2^+ + Rb



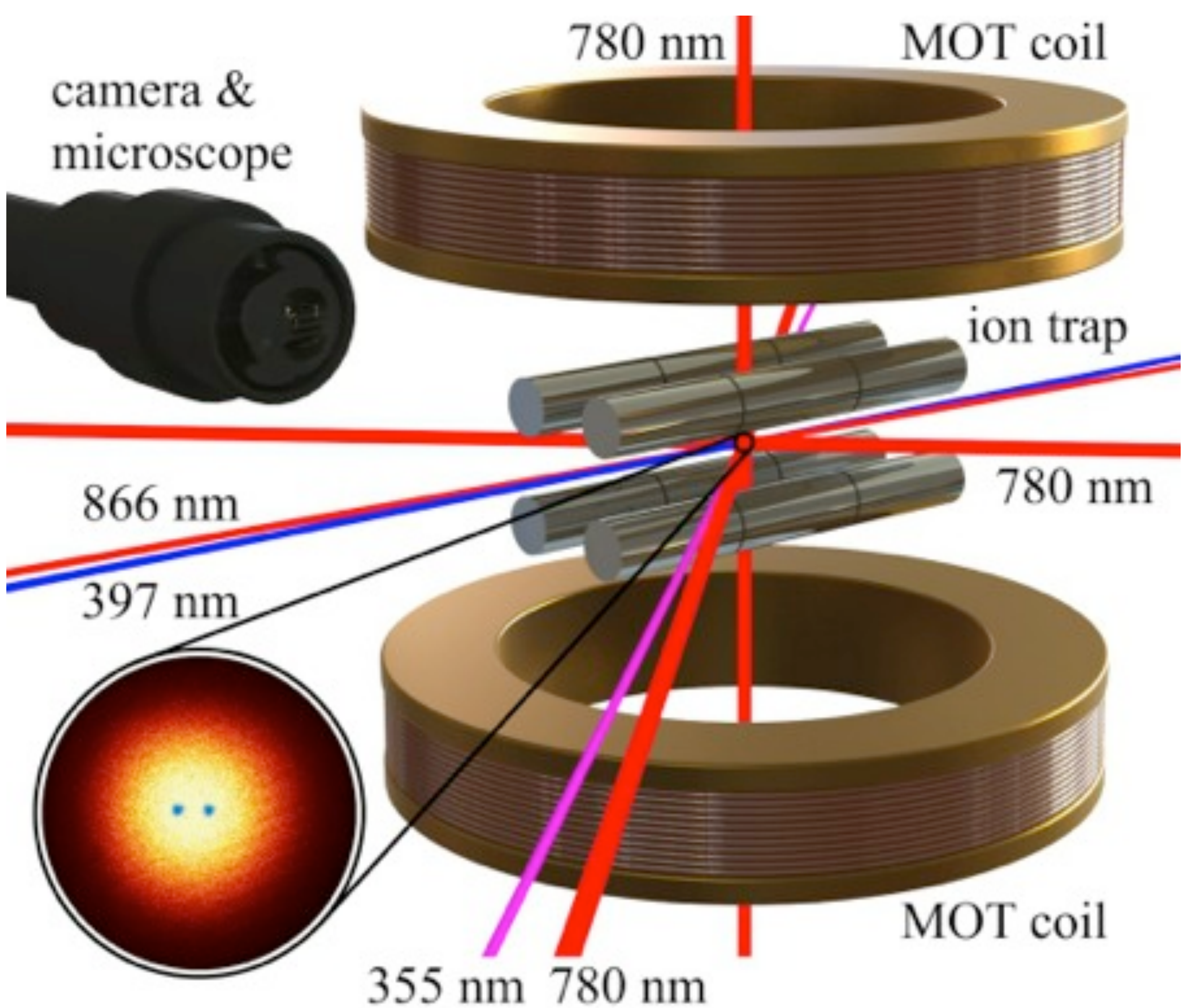
Controlled chemistry:

1. Fully state- and energy-selected reactions with Coulomb-crystallized ions
2. Reactions between Coulomb crystals and selected conformers of complex molecules

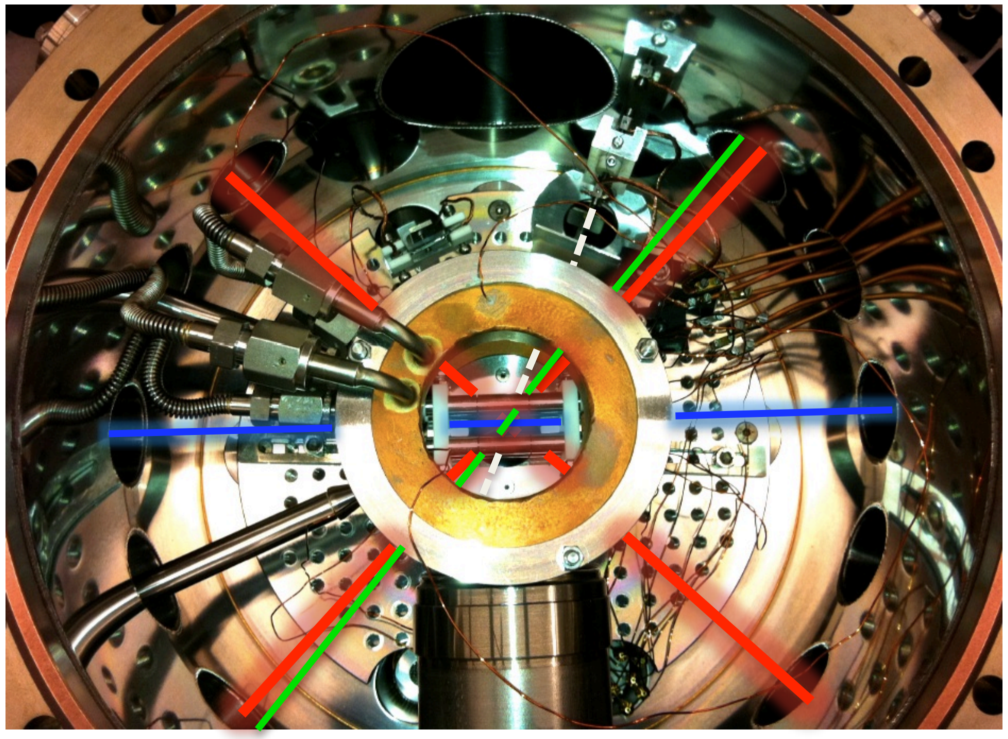


Cold chemistry

- **Hybrid trap:** combination of a trap for ultracold atoms with an ion trap (originally proposed by W.W. Smith 2003)
- **Basel hybrid trap:** ^{87}Rb MOT superimposed on a linear RF ion trap for laser- and sympathetically-cooled ions



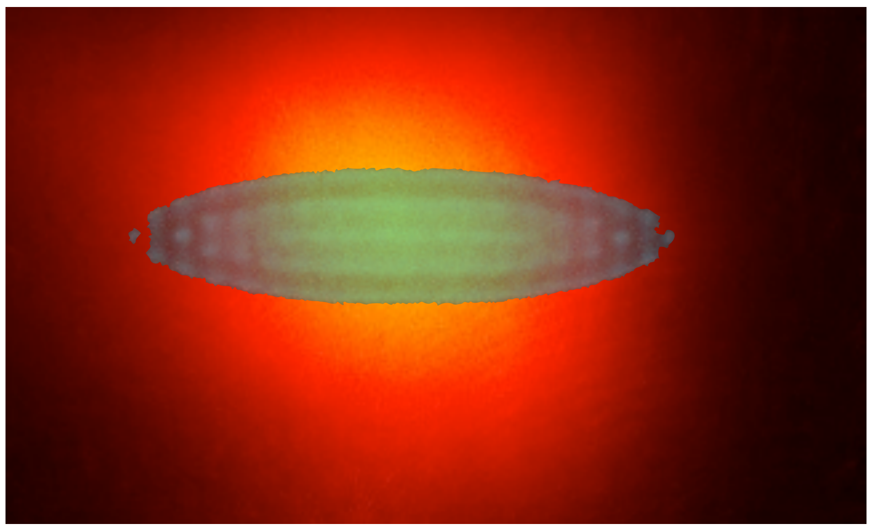
F.H.J. Hall, M. Aymar, N. Bouloufa, O. Dulieu and SW, Phys. Rev. Lett. 107 (2011), 243202



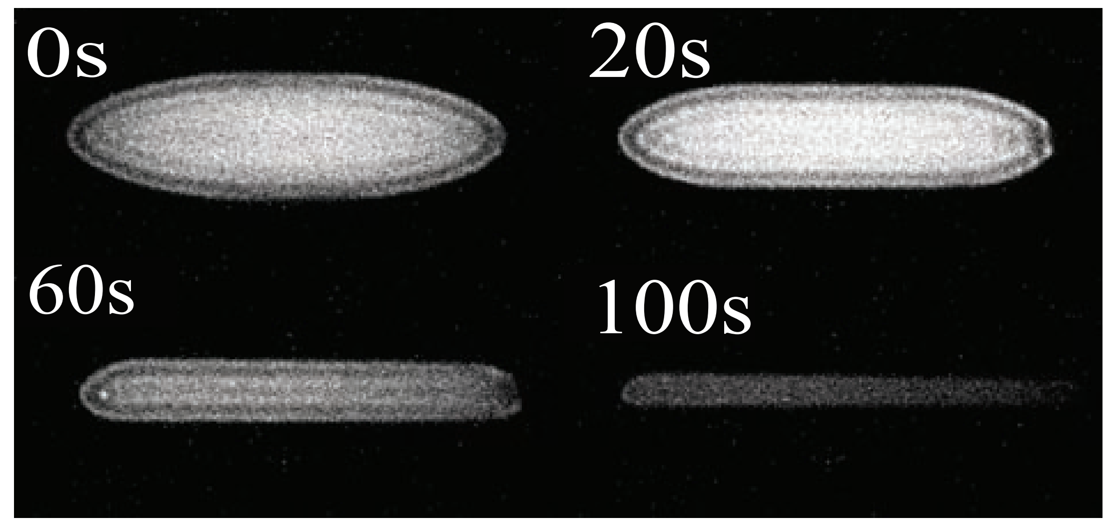
See also experiments by:

- V. Vuletic (MIT)
- M. Köhl (U. Cambridge)
- J. Hecker Denschlag (U. Ulm)
- W. W. Smith (U. Connecticut)
- S. Rangwala (RRI)
- E. Hudson (UCLA)

Cold chemistry: 1. Light-assisted processes in the cold regime: Ca^+ + Rb and Ba^+ + Rb



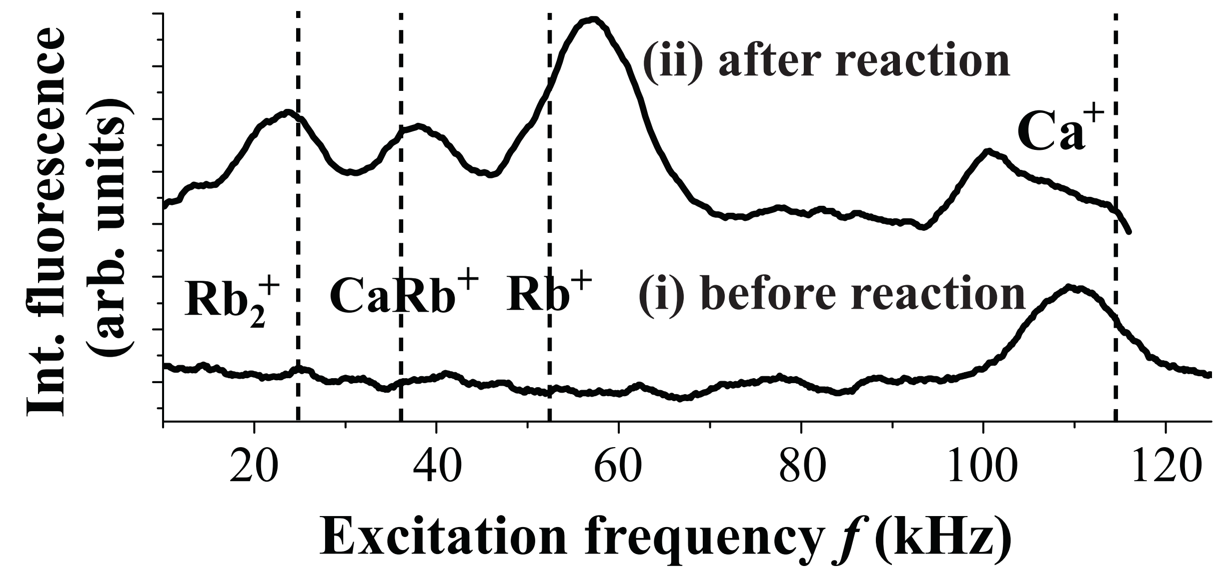
A Ca^+ Coulomb crystal immersed in a cloud of ultracold Rb atoms



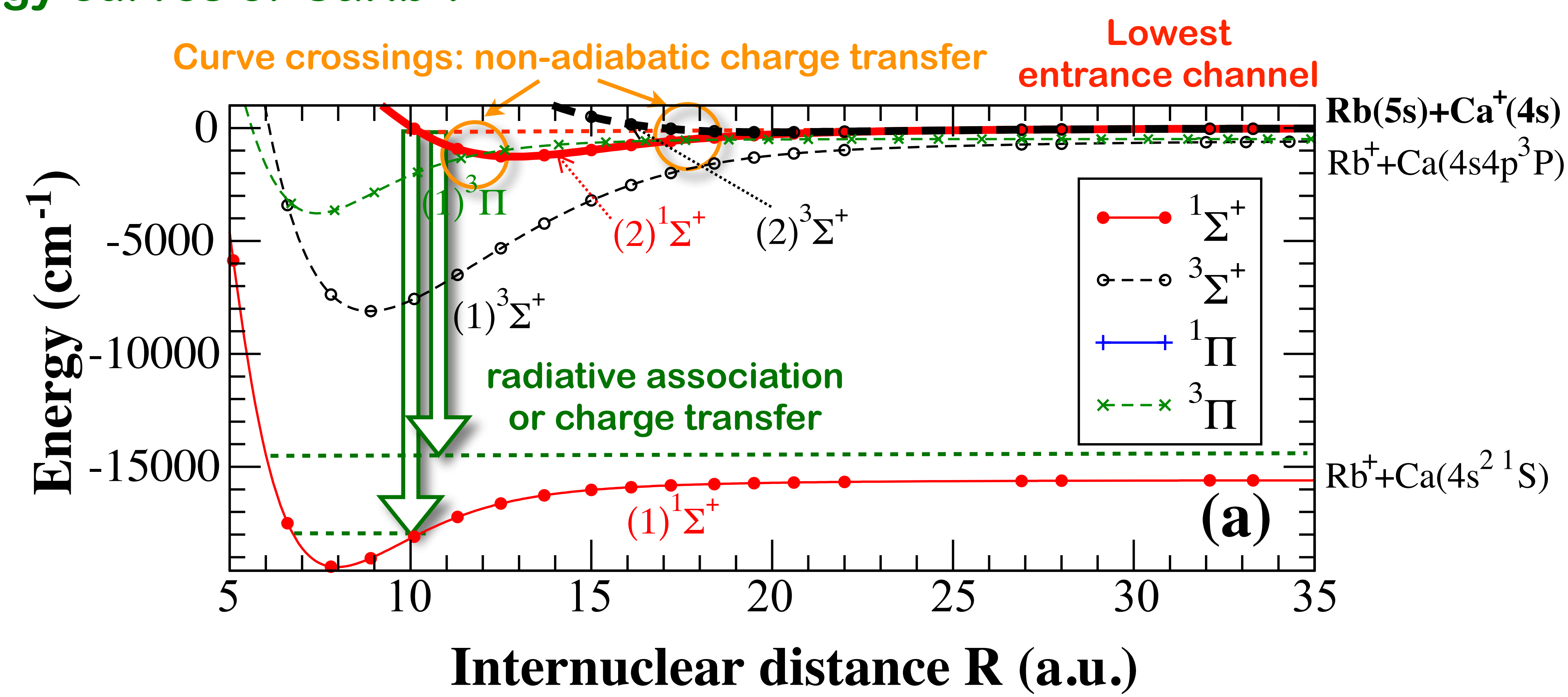
Cold chemical reactions between Ca^+ and Rb
(only Ca^+ fluorescence is shown)

- F.H.J. Hall, M. Aymar, N. Bouloufa, O. Dulieu and SW, Phys. Rev. Lett. 107 (2011), 243202
- F.H.J. Hall, P. Eberle, G. Hegi, M. Aymar, M. Raoult, O. Dulieu, SW, accepted by Mol. Phys. (arXiv:1302.4682)
- F.H.J. Hall,M. Aymar, M. Raoult, O. Dulieu and SW, arXiv 1301.0724 (accepted by Mol. Phys.)

- **Resonant-excitation mass spectra of reaction products:**



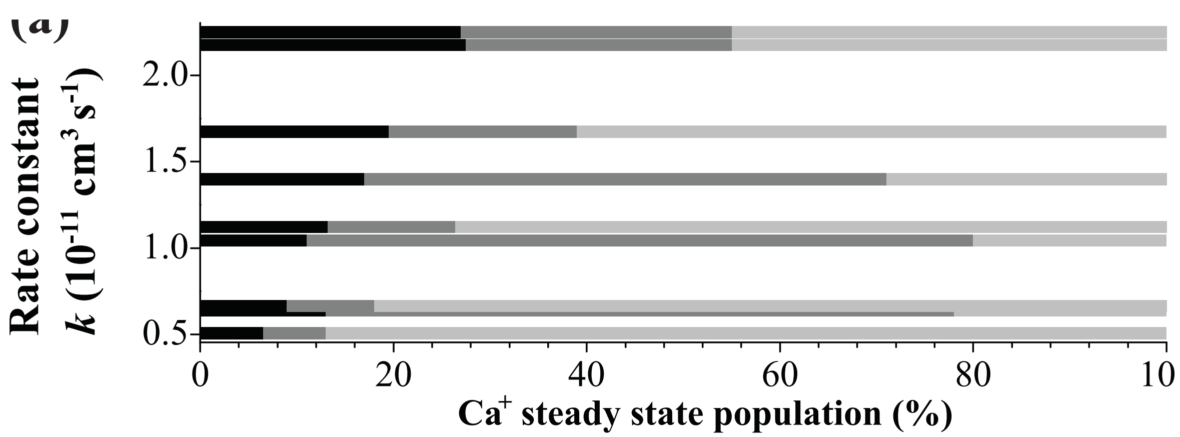
- **Potential-energy curves of $CaRb^+$:**

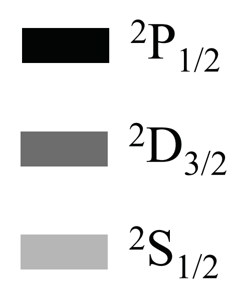


Theory: O. Dulieu, M. Aymar, N. Bouloufa, LAC/CNRS Orsay. See also: M. Tacconi, F. Gianturco, Rome

Cold chemistry: 1. Light-assisted processes in the cold regime

Measured rate constants as a function of Ca^+ level populations:



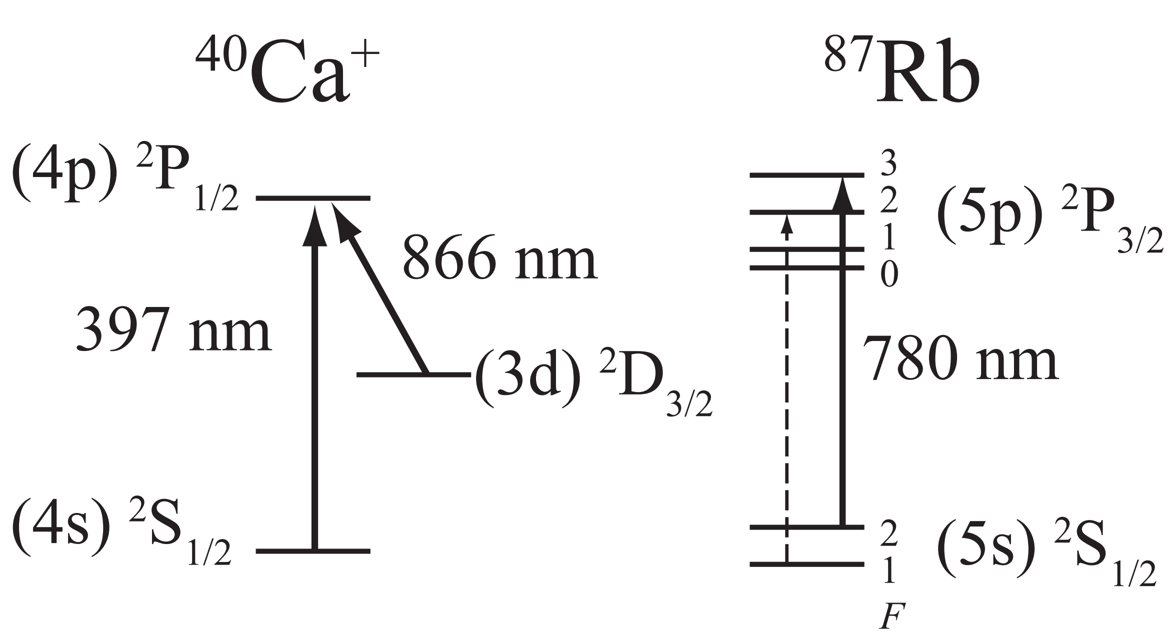


Rate constants:

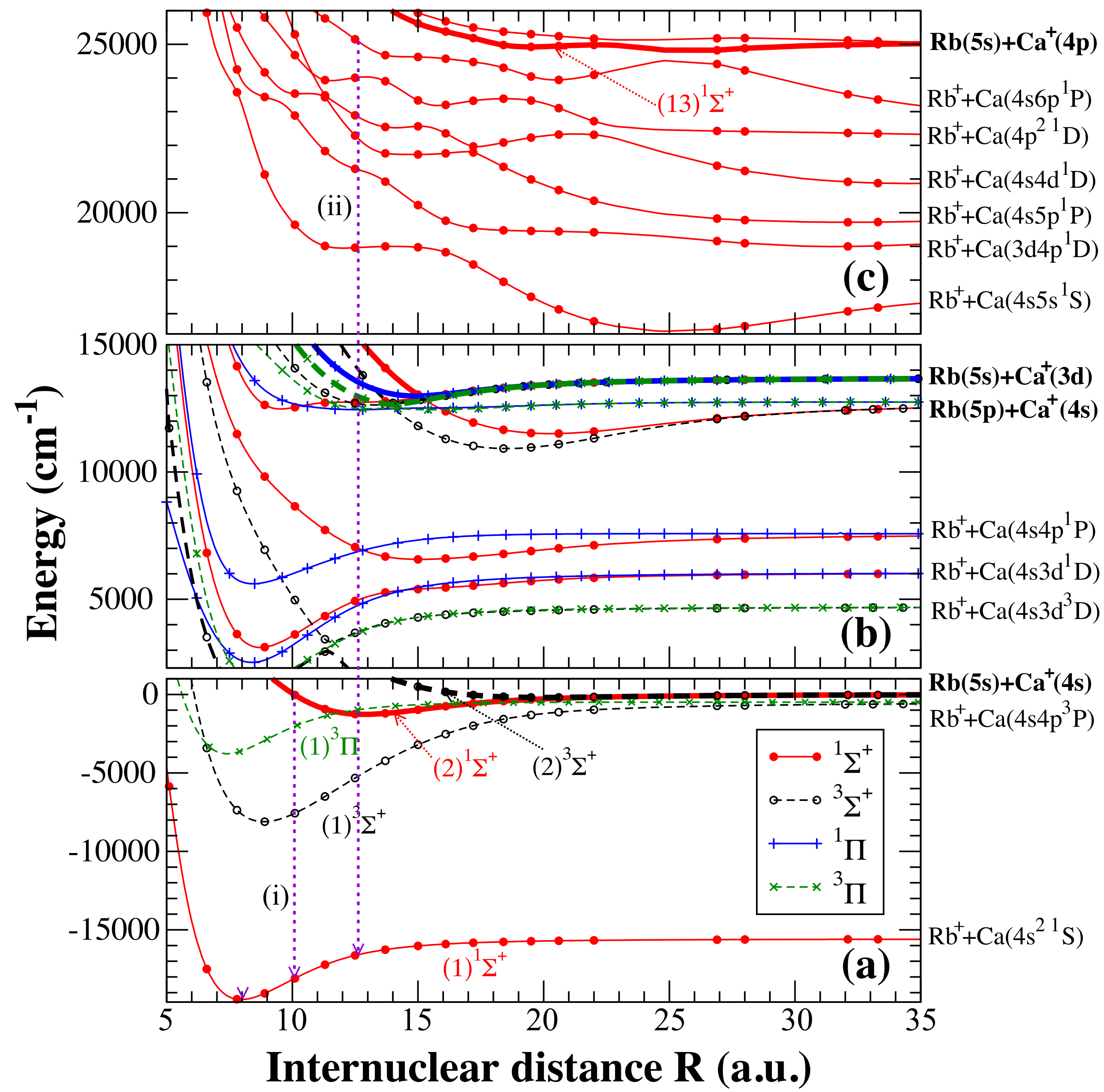
$^2S_{1/2}$: $k_s = 3 \cdot 10^{-12}$ cm^3 s^{-1}

$^2P_{1/2}$: $k_p = 1.5(6) \cdot 10^{-10}$ cm^3 s^{-1}

$^2D_{3/2}$: $k_d < 3 \cdot 10^{-12}$ cm^3 s^{-1}



Potential energy curves of excited states:

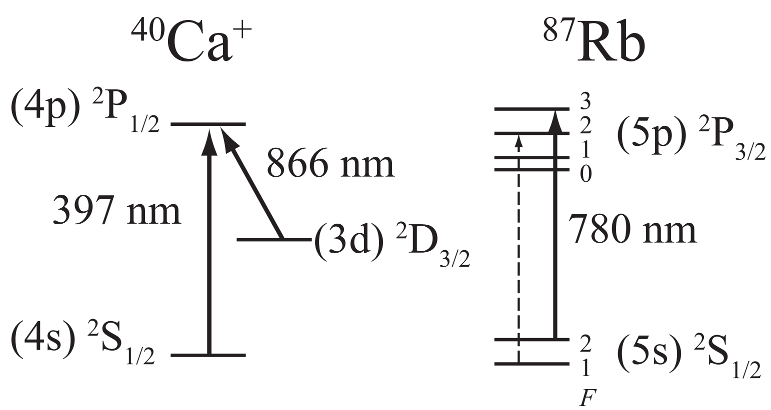


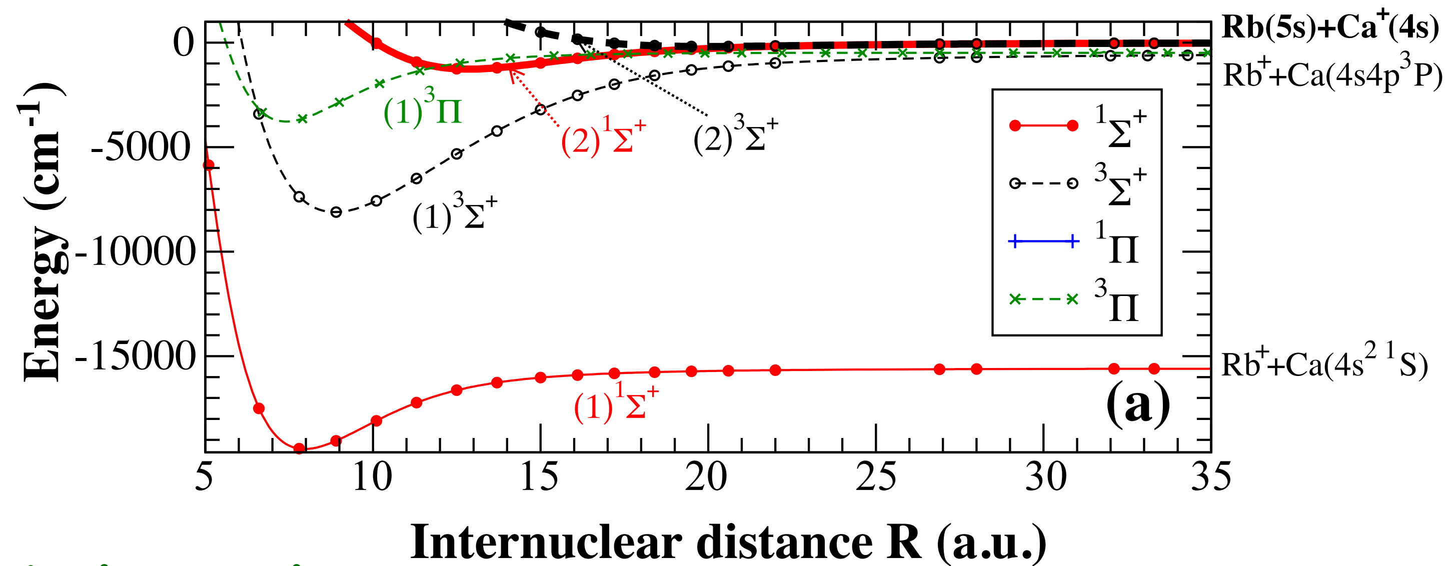
Cold chemistry: 1. Light-assisted processes in the cold regime

Cold reactions of Ba^+ + Rb

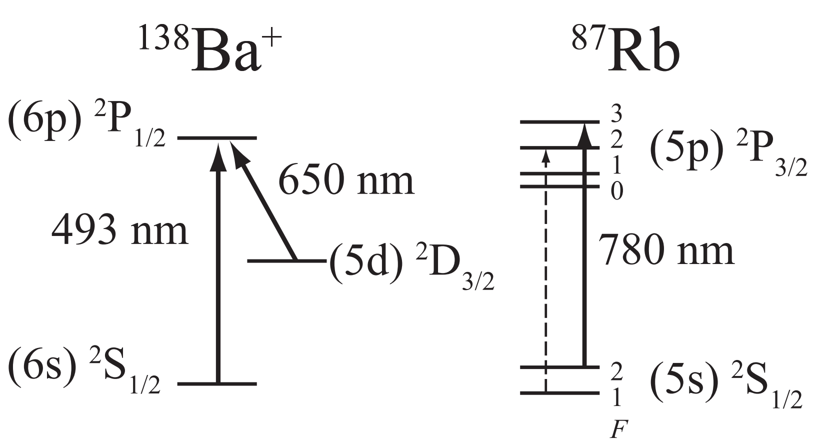
F.H.J. Hall, M. Aymar, M. Raoult, O. Dulieu and SW, arXiv 1301.0724 (accepted by Mol. Phys.)

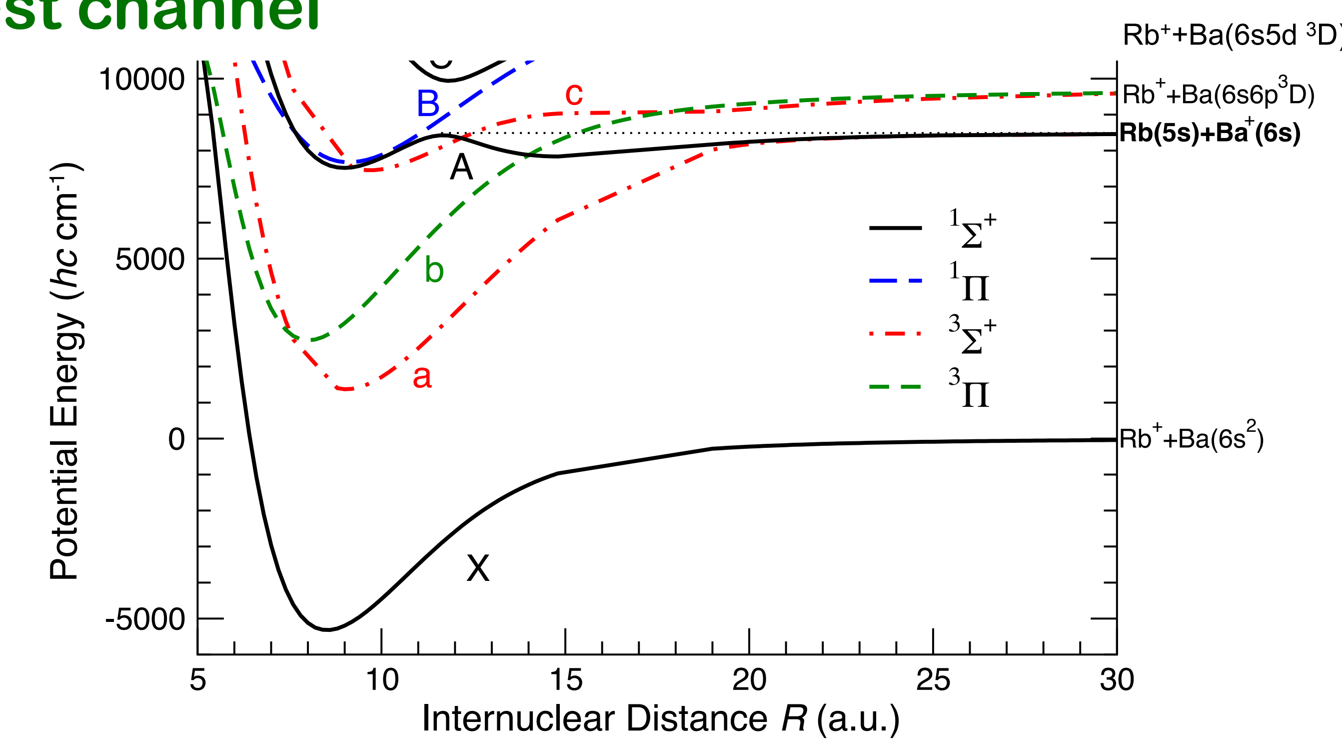
- Ca^+ + Rb: NRCT, RCT and RA in lowest channel





- Ba^+ + Rb: only RCT and RA in lowest channel



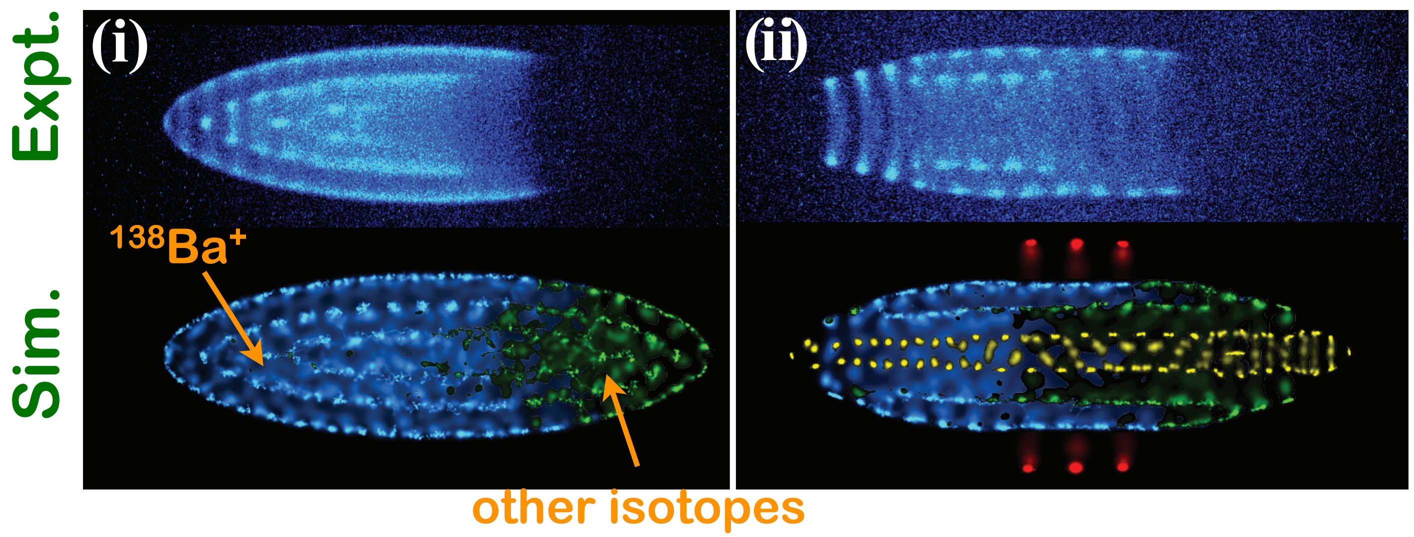


Theory: M. Aymar, M. Raoult, O. Dulieu (Orsay).

See also: M. Krych et al., PRA 83 (2011), 032723; S. Knecht et al., JPB 43 (2010), 05501; A. Härter et al., PRL 105 (2010), 133202

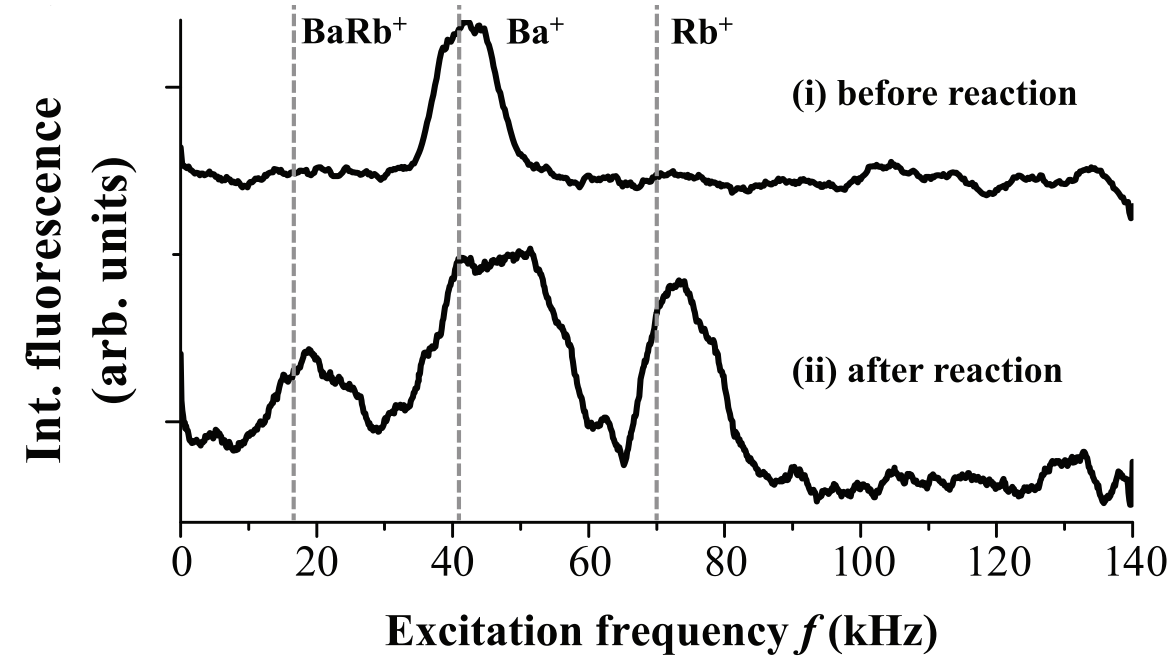
Cold reactions of Ba^+ + Rb

Ba^+ fluorescence images:



before reaction after reaction

Resonant-excitation mass spectra:



Channel-specific rate constants:

Rb(5s) + $Ba^+(6s\ ^2S_{1/2})$: $k_s \leq 5\cdot10^{-13}$ $cm^3\ s^{-1}$

+ $Ba^+(6p\ ^2P_{1/2})$: $k_p = 2(1)\cdot10^{-11}$ $cm^3\ s^{-1}$

+ $Ba^+(5d\ ^2D_{3/2})$: $k_d \leq 1\cdot10^{-12}$ $cm^3\ s^{-1}$

Rb($5p\ ^2P_{3/2}$) + Ba^+ (6s) : $k_s^* = 7.2\cdot10^{-11}$ $cm^3\ s^{-1}$

Compare with Ca^+ + Rb:

$k_s = 3(1)\cdot10^{-12}$ $cm^3\ s^{-1}$

$k_p = 1.5(6)\cdot10^{-10}$ $cm^3\ s^{-1}$

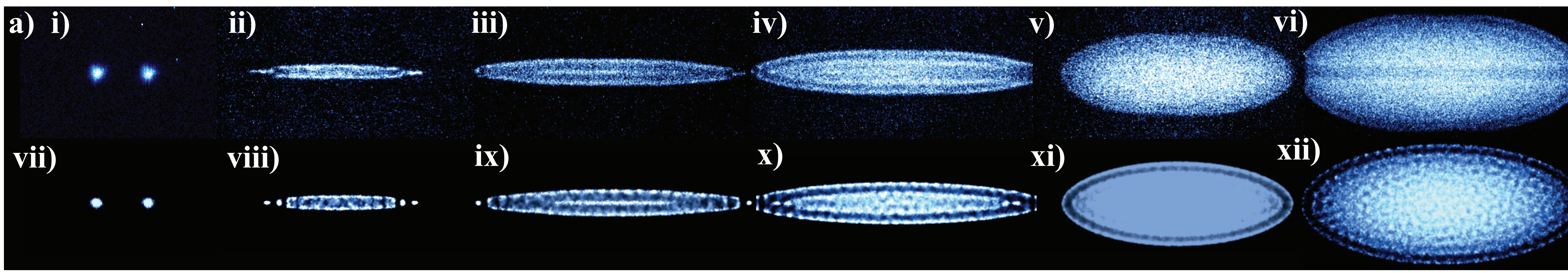
$k_d < 3\cdot10^{-12}$ $cm^3\ s^{-1}$

Collision-energy dependence of reaction rates

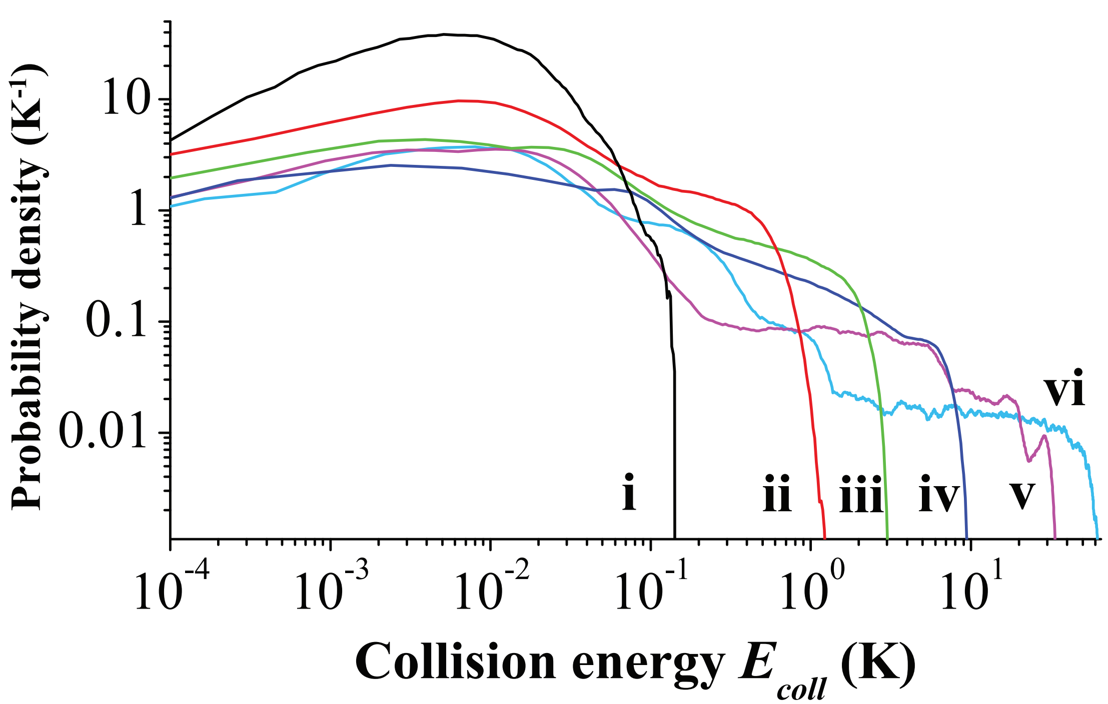
Tuning of collision energies in Ca^+ + Rb: ion kinetic energies as a function of Coulomb crystal size and shape

Experimental image

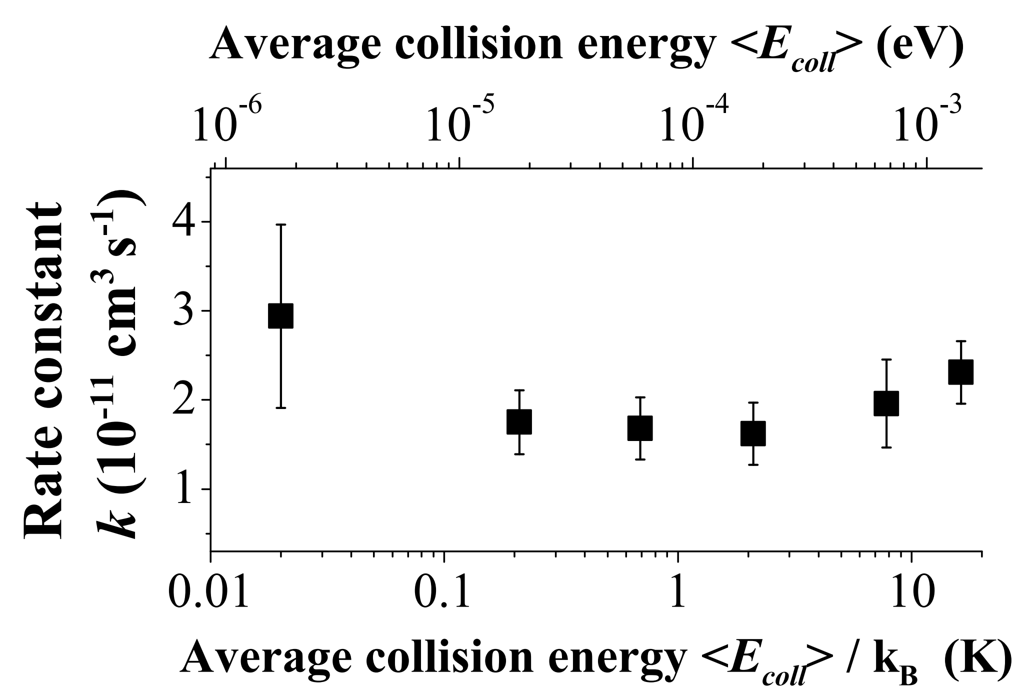
Simulated image



Collision-energy distribution as a function of crystal size/shape:



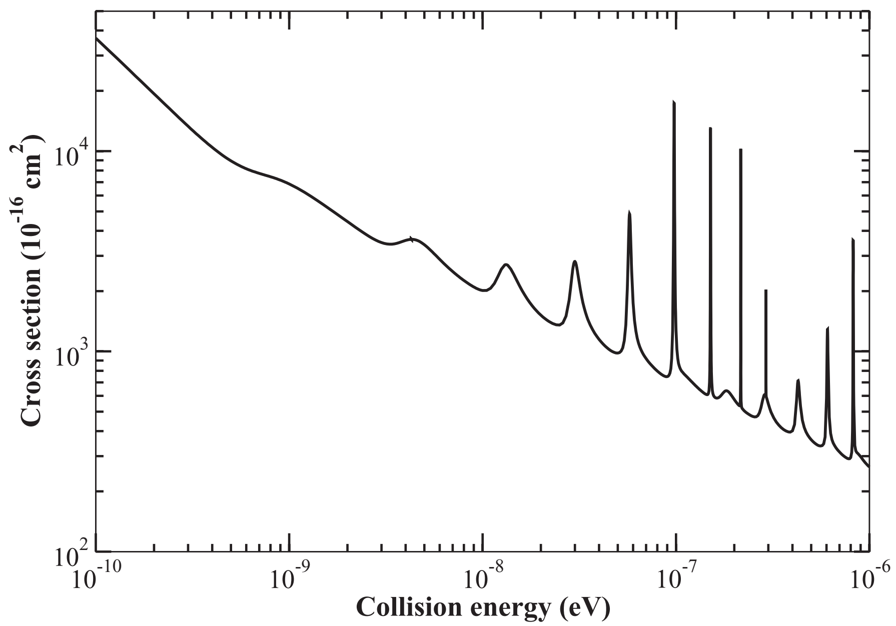
Collision-energy dependence of reaction rates:



Rate constants for Ca^{+} + Rb : comparison with theory

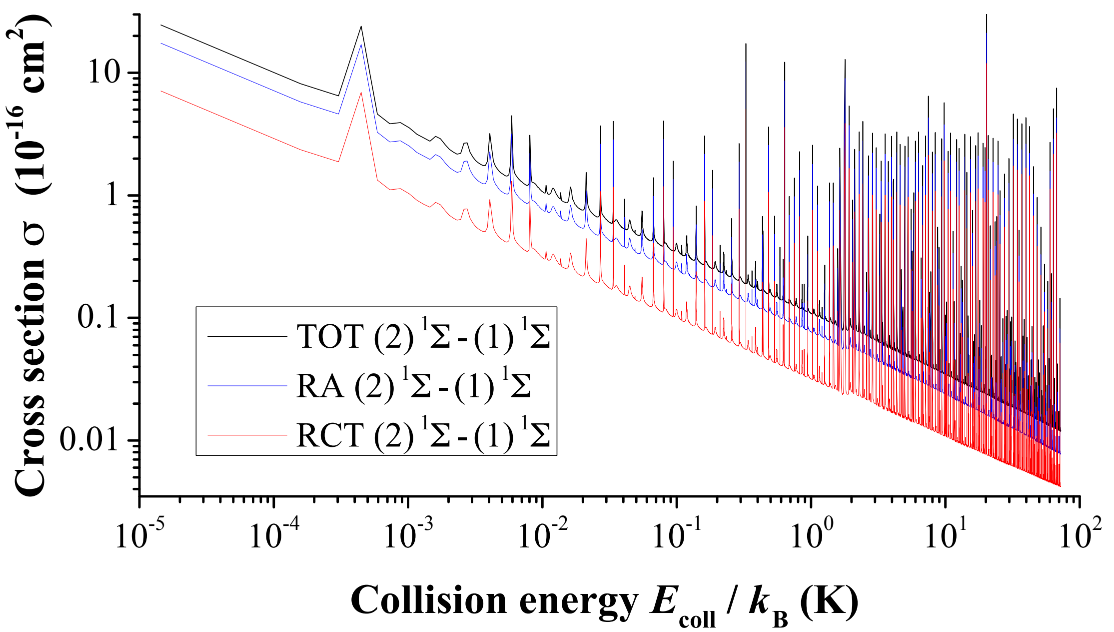
Non-radiative (NR) CT cross sections:

F. Gianturco and co-workers:
PCCP 13(2011), 19156; Phys. Rev. A 85 (2012), 042716

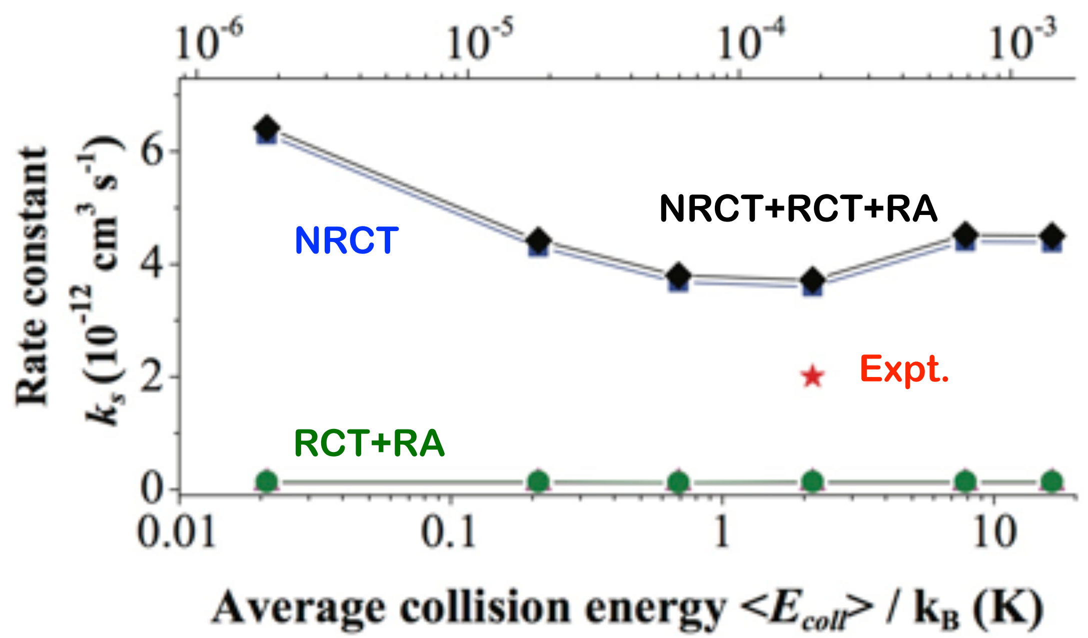


Radiative cross sections (RCT, RA):

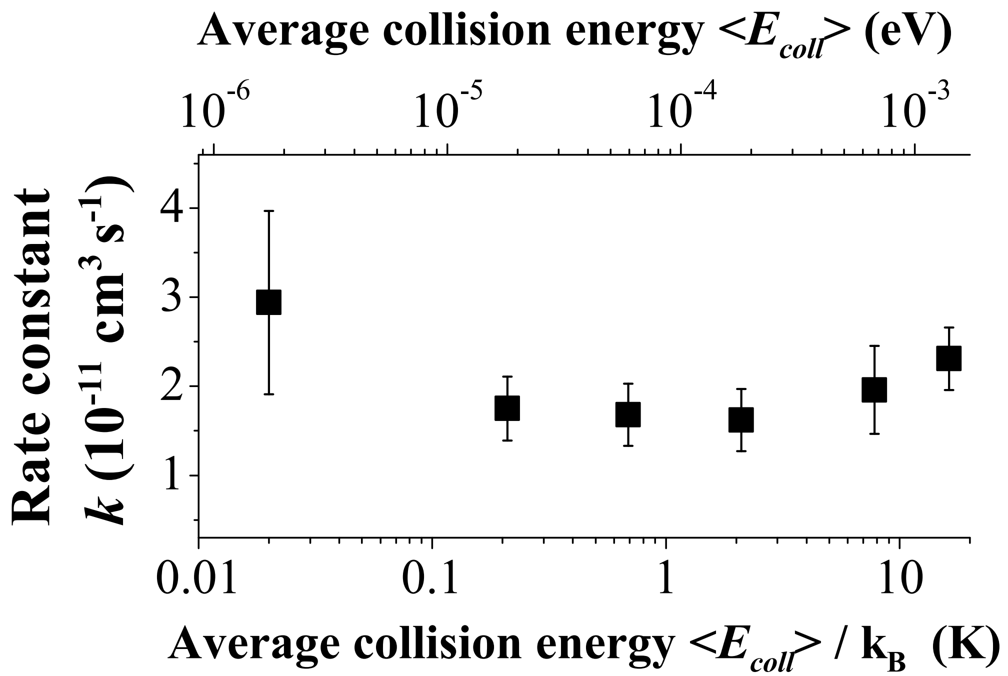
(O. Dulieu, M. Raoult, LAC/CNRS Paris)



Theoretical rate constants (av. over expt. velocity distributions) for lowest channel:

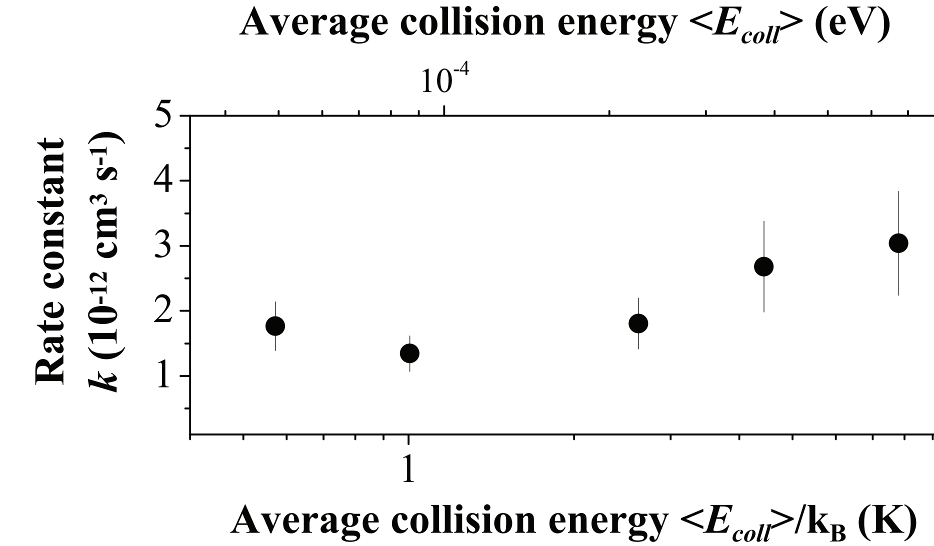


Effective (channel-averaged) expt. rate constants:

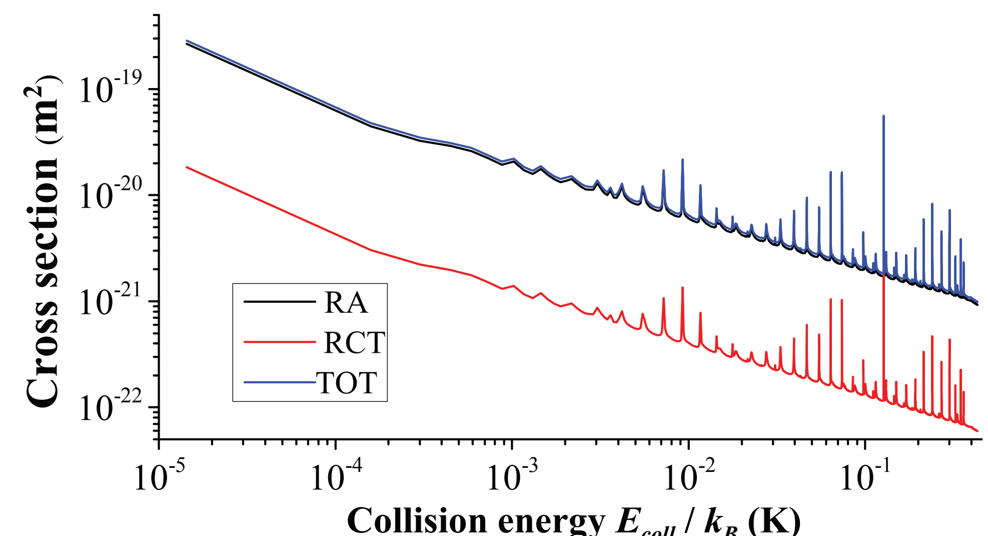


Rate constants for $Ba^+ + Rb$: comparison with theory

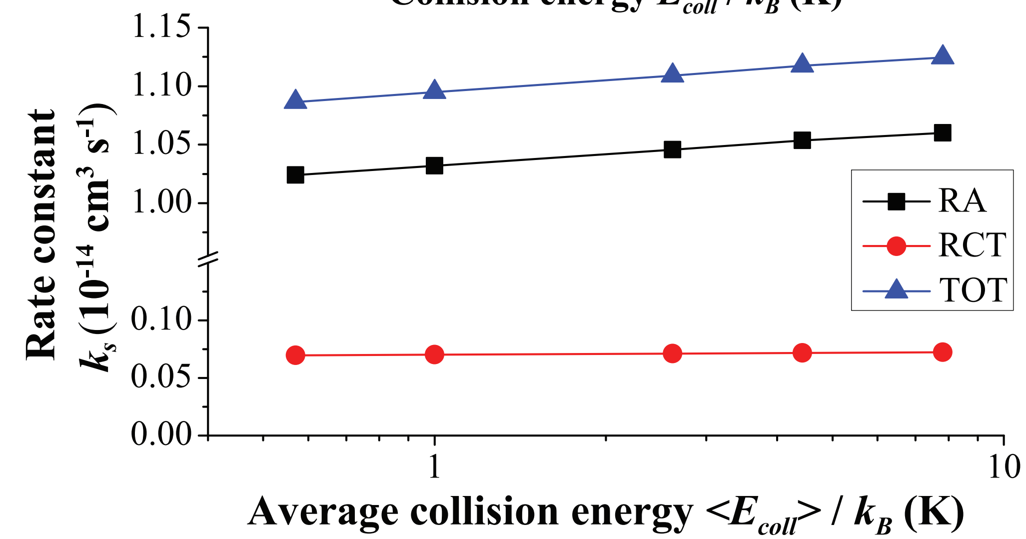
- Expt. channel-averaged rate constants:



- Theoretical radiative cross sections for lowest channel:



- Predicted radiative rate constants for lowest channel:



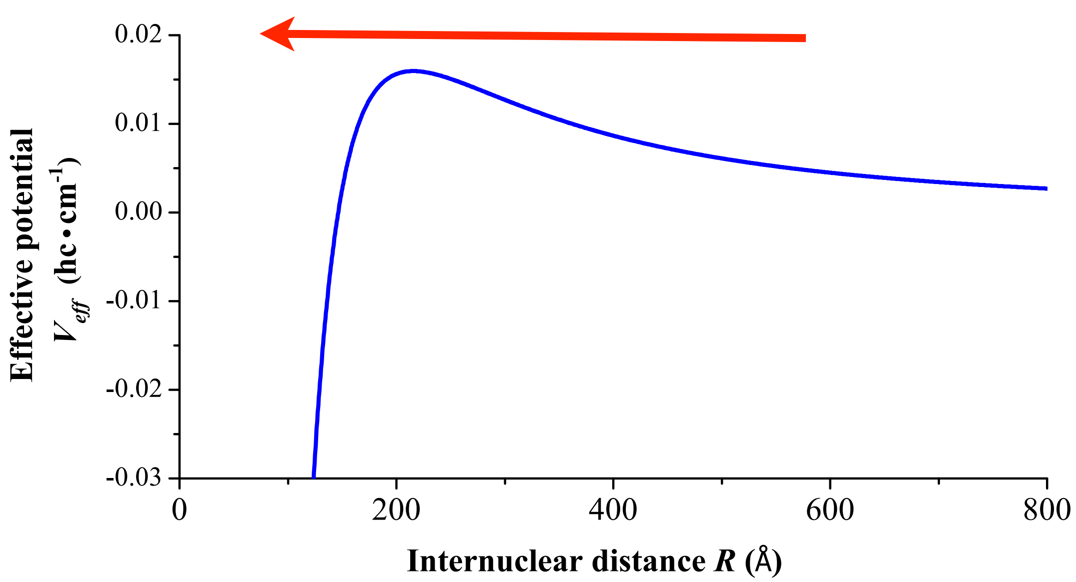
- F.H.J. Hall, M. Aymar, M. Raoult, O. Dulieu and SW, arXiv 1301.0724 (accepted by Mol. Phys.)
- F.H.J. Hall, P. Eberle, G. Hegi, M. Aymar, M. Raoult, O. Dulieu, SW, arXiv:1302.4682 (accepted by Mol. Phys.)

Reaction dynamics: observations

- Rate constants are essentially constant with collision energy
- The energy dependence of the rate constants (but not their magnitude !) seems to be similar across all channels

Interpretation:

- Disregarding the shape resonances, the energy dependence can be described by classical dynamics: the reaction proceeds if the centrifugal barrier is overcome



- For ion-neutral collisions with $V(R) \propto R^{-4}$:

  rate constant k= const.
  (classical Langevin capture)

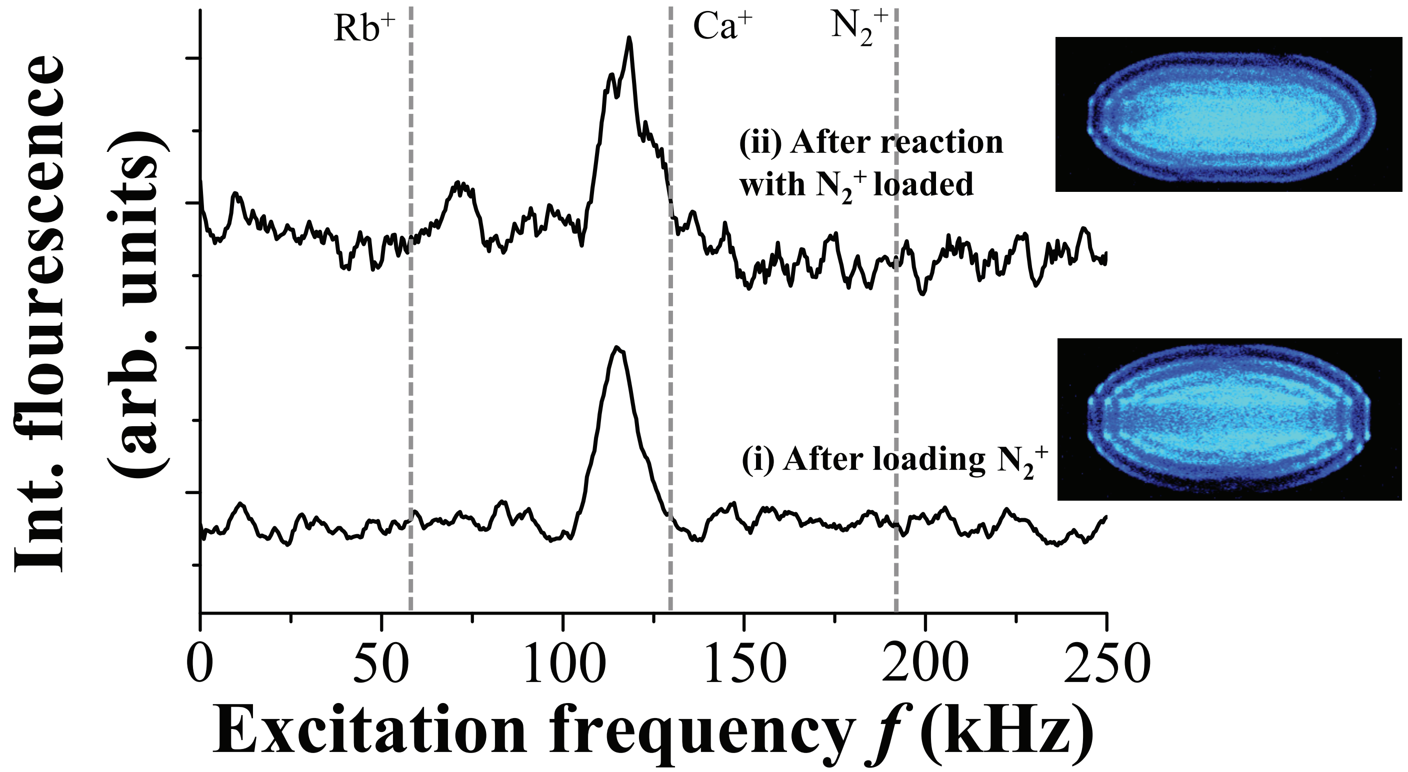
- Magnitude of rate constant is determined by short-range non-adiabatic and radiative couplings
- Short-range coupling matrix elements are independent of the collision energy for low energies

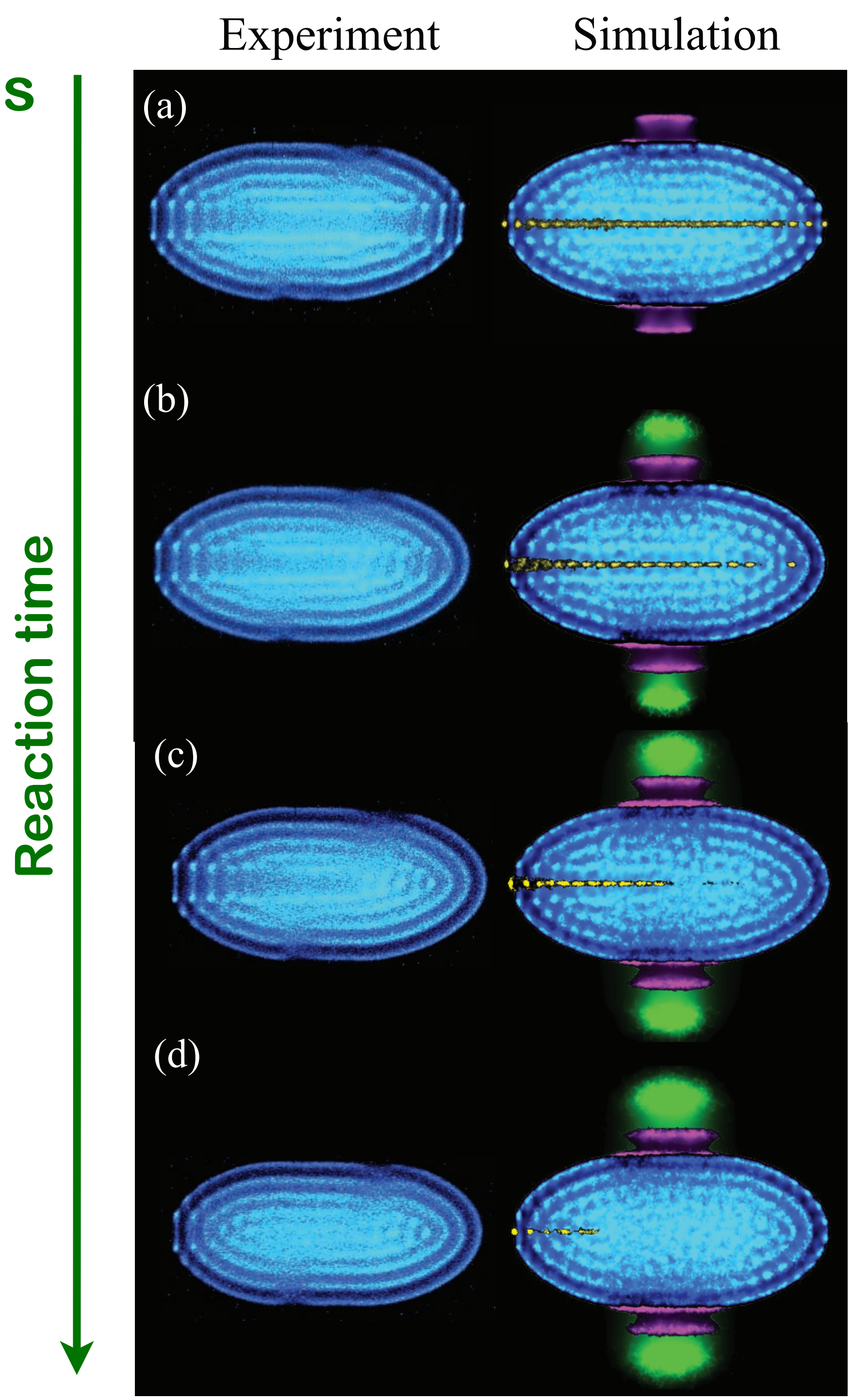
F.H.J. Hall, P. Eberle, G. Hegi, M. Aymar, M. Raoult, O. Dulieu, SW, accepted by Mol. Phys. (arXiv:1302.4682)

Cold chemistry:
2. Reactions with molecular ions at mK energies: N_2^+ + Rb

- Reactions with molecular ions at collision energies down to $E_{coll}/k_B \approx 20$ mK:

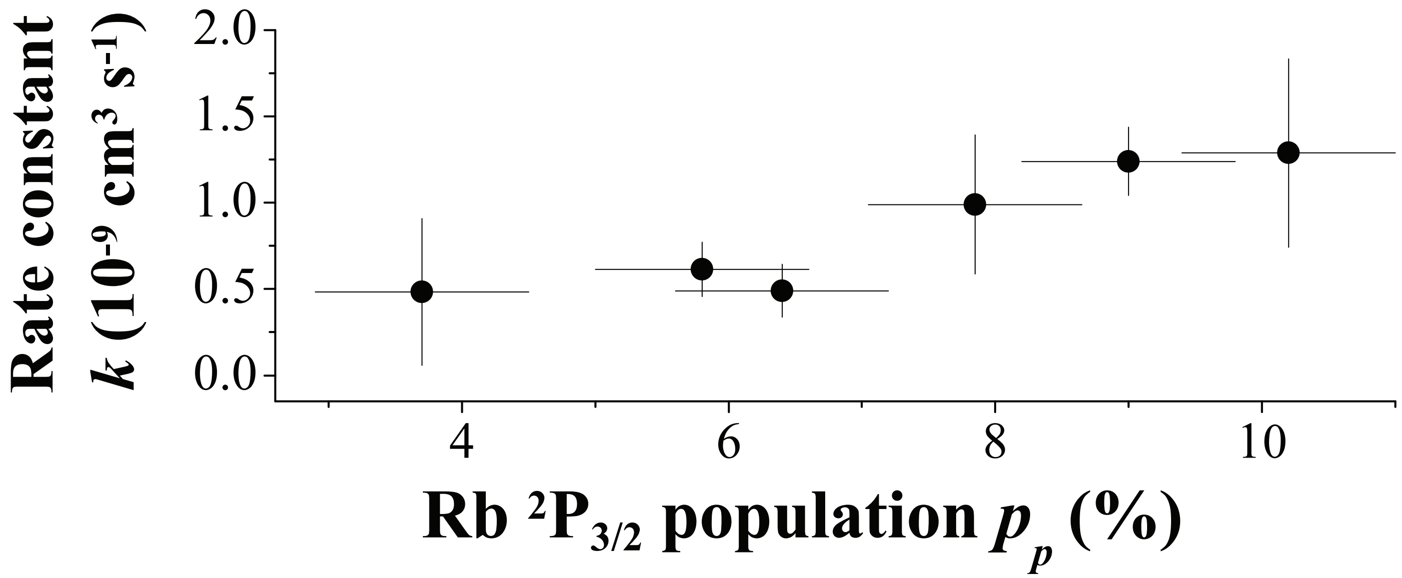
- Reaction products:

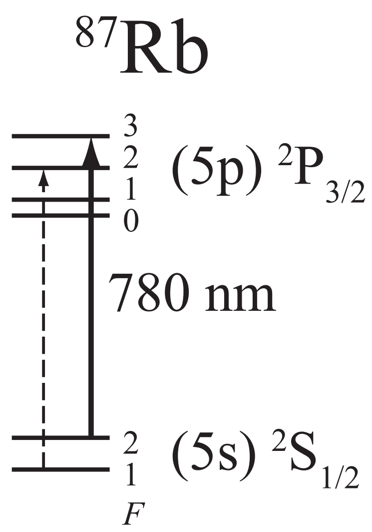




F.H.J. Hall and SW, Phys. Rev. Lett. 109 (2012), 233202

Rate constant vs. Rb excited-state population:





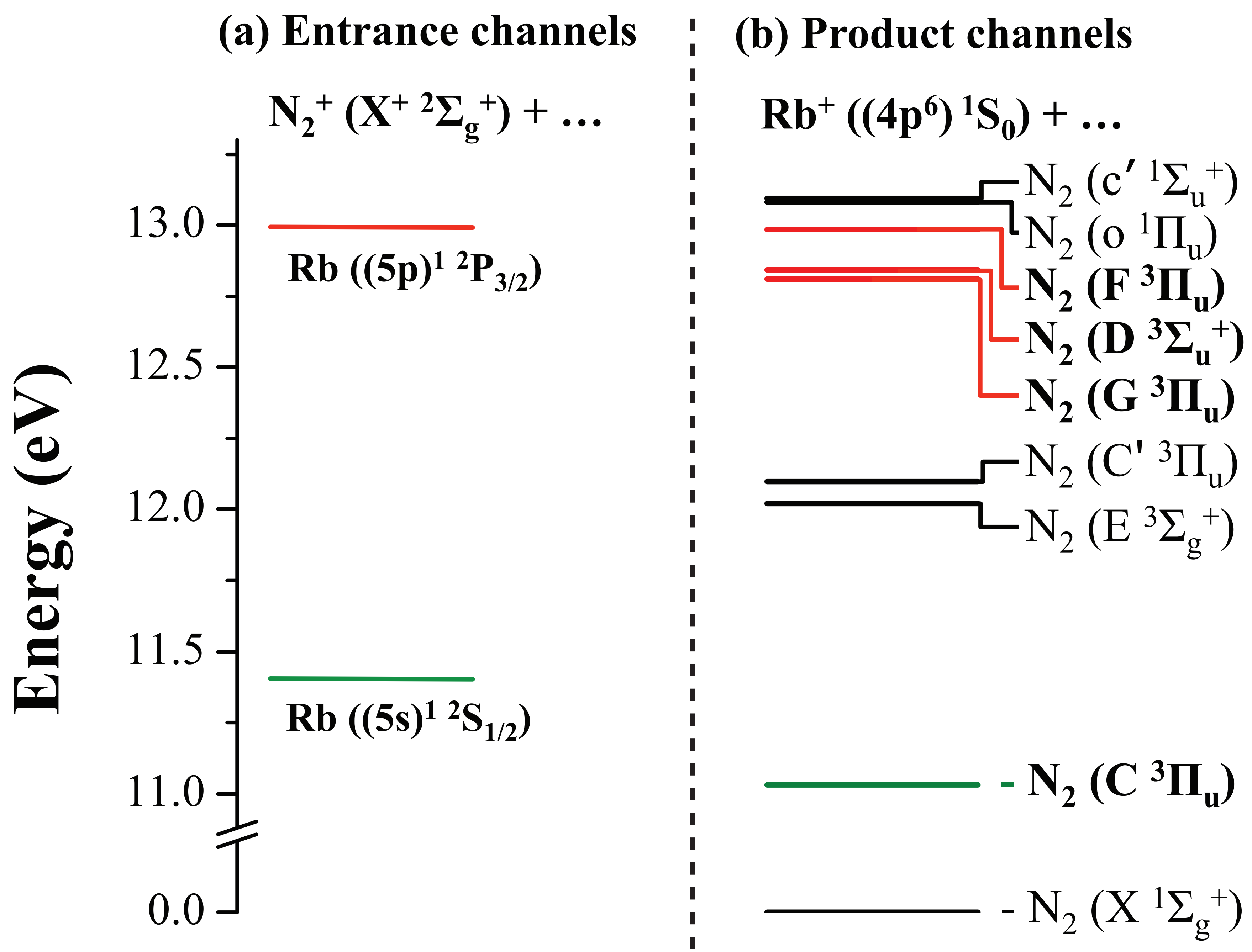
Laser cooling of ^{87}Rb

State-specific rate constants: $N_2^+(X)+Rb(^2S_{1/2})$: $k_S<2\times10^{-10}$ cm^3s^{-1}

$N_2^+(X)+Rb(^2P_{3/2})$: $k_P=2.4(13)\times10^{-8}$ cm^3s^{-1}

Reaction mechanism: electronic energies of entrance and product channels

see A.B. van der Kamp, P.C. Cosby and W.J. van der Zande, Chem. Phys. 184 (1994), 319



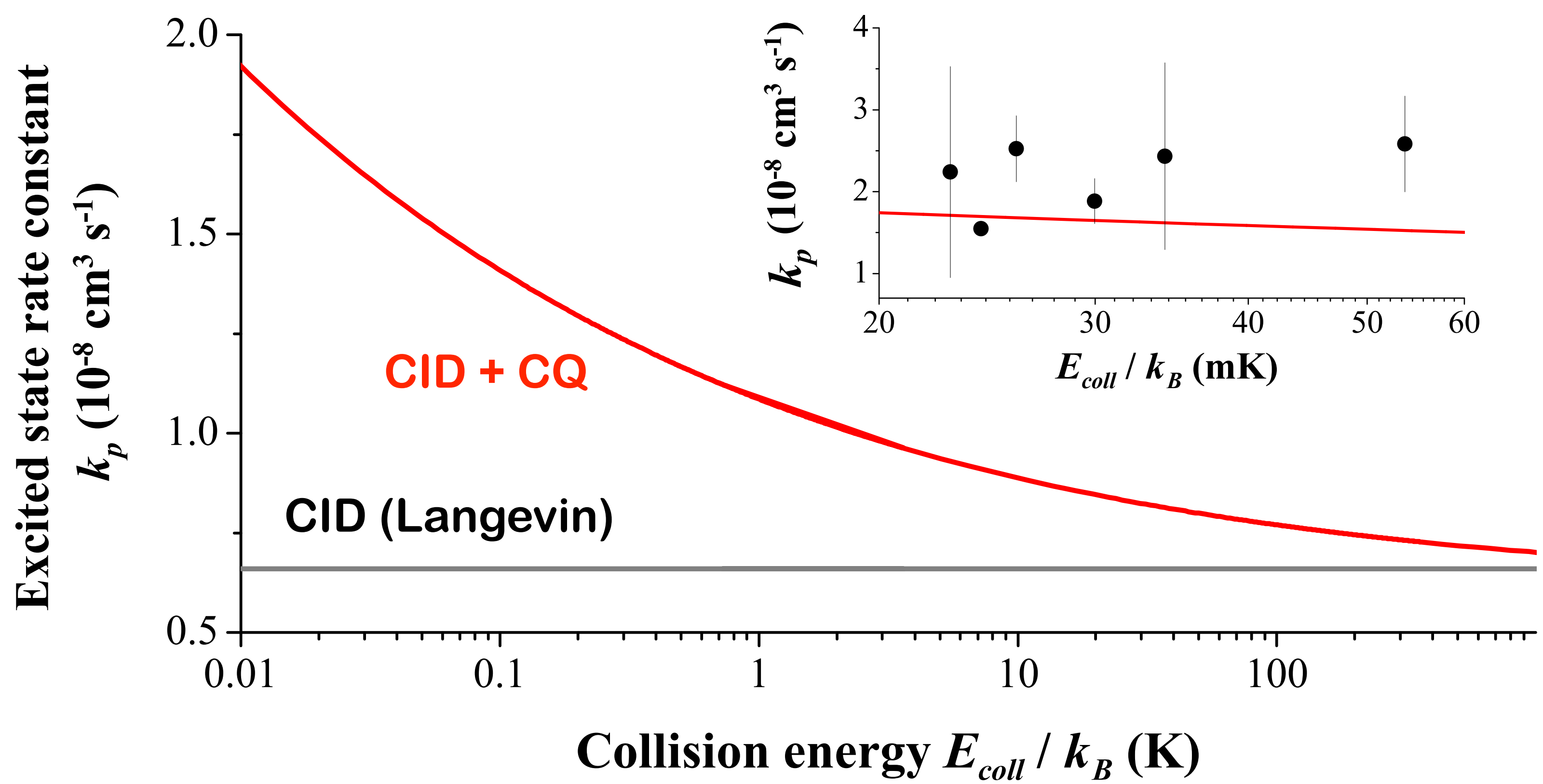
Cold chemistry: 2. Reactions with molecular ions at mK energies

- **Rate constant in excited $N_2^+(X) + Rb(^2P_{3/2})$ channel: k_p=2.4(13)×10^{-8} cm^3s^{-1}**
  - **Compare with Langevin (charge-induced dipole): k_L=6.6×10^{-9} cm^3s^{-1}**
  - **Classical capture model including charge-induced dipole (CID) and charge-quadrupole (CQ) interactions**

Interaction potential: $V(R) = \frac{C_3}{R^3} + \frac{C_4}{R^4}$ $\quad C_3 = (-1)^{\ell+\Lambda} \begin{pmatrix} \ell & 2 & \ell \\ -\Lambda & 0 & \Lambda \end{pmatrix} \langle \ell || Q_2 || \ell \rangle$ $\quad C_4 = \frac{1}{2}\alpha_0$

M. Krych et al., PRA 83 (2011), 032723

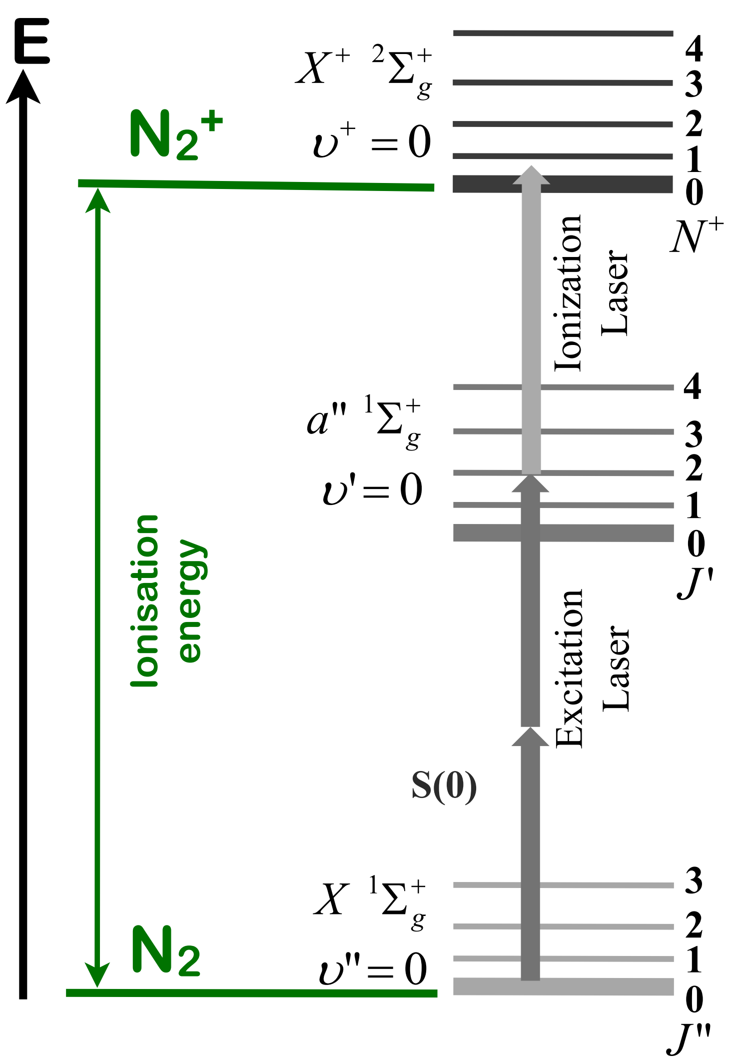
- **Predicted rate constants:**



Controlled chemistry: 1. Fully state- and energy-selected reactions with Coulomb-crystallized ions

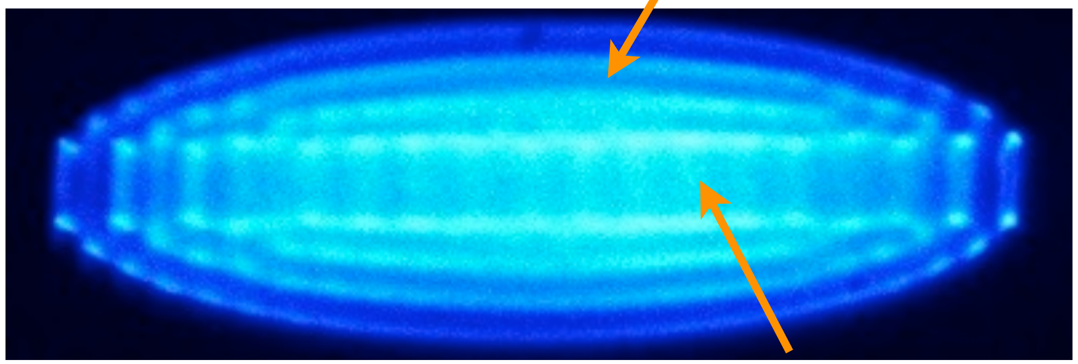
Quantum-state preparation of sympathetically-cooled molecular ions

State-selective threshold-photoionisation scheme for N_2



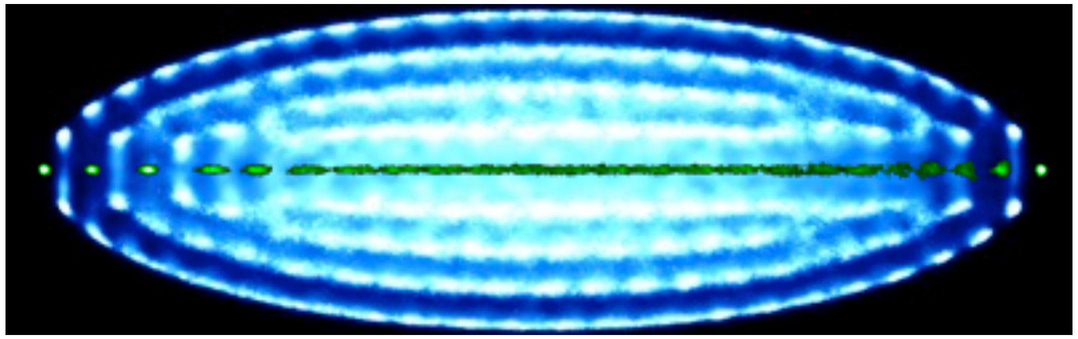
Experiment:

Laser-cooled Ca^+ ions



Sympathetically-cooled, state-selected N_2^+ ions

Simulation:

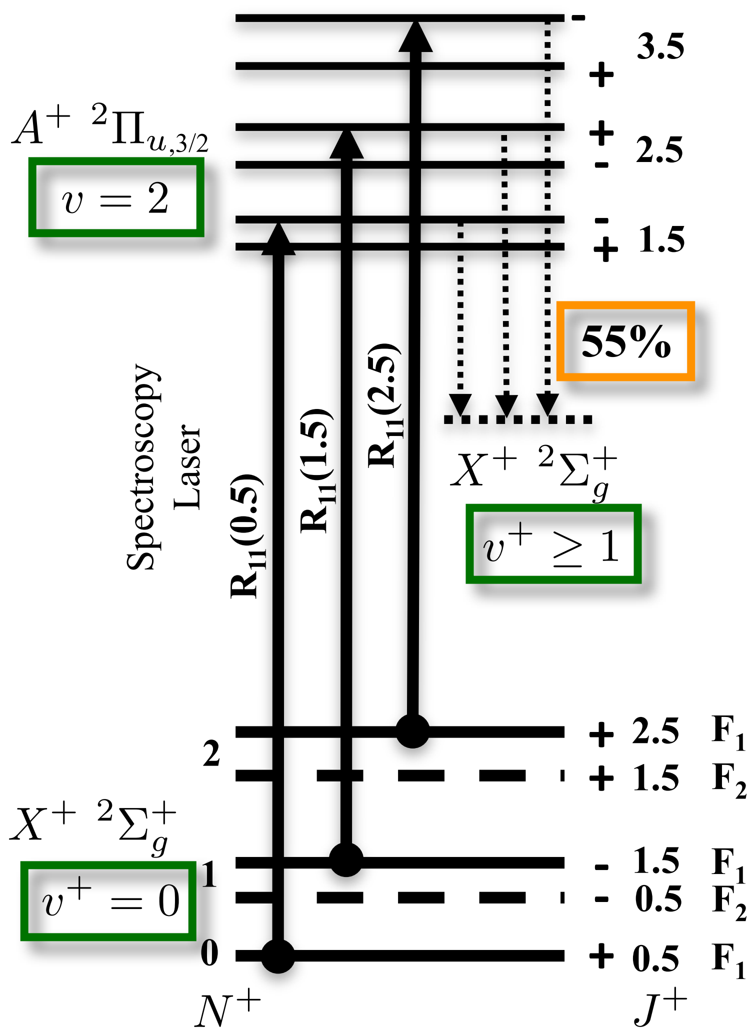


24 N_2^+ ions @ 11 mK

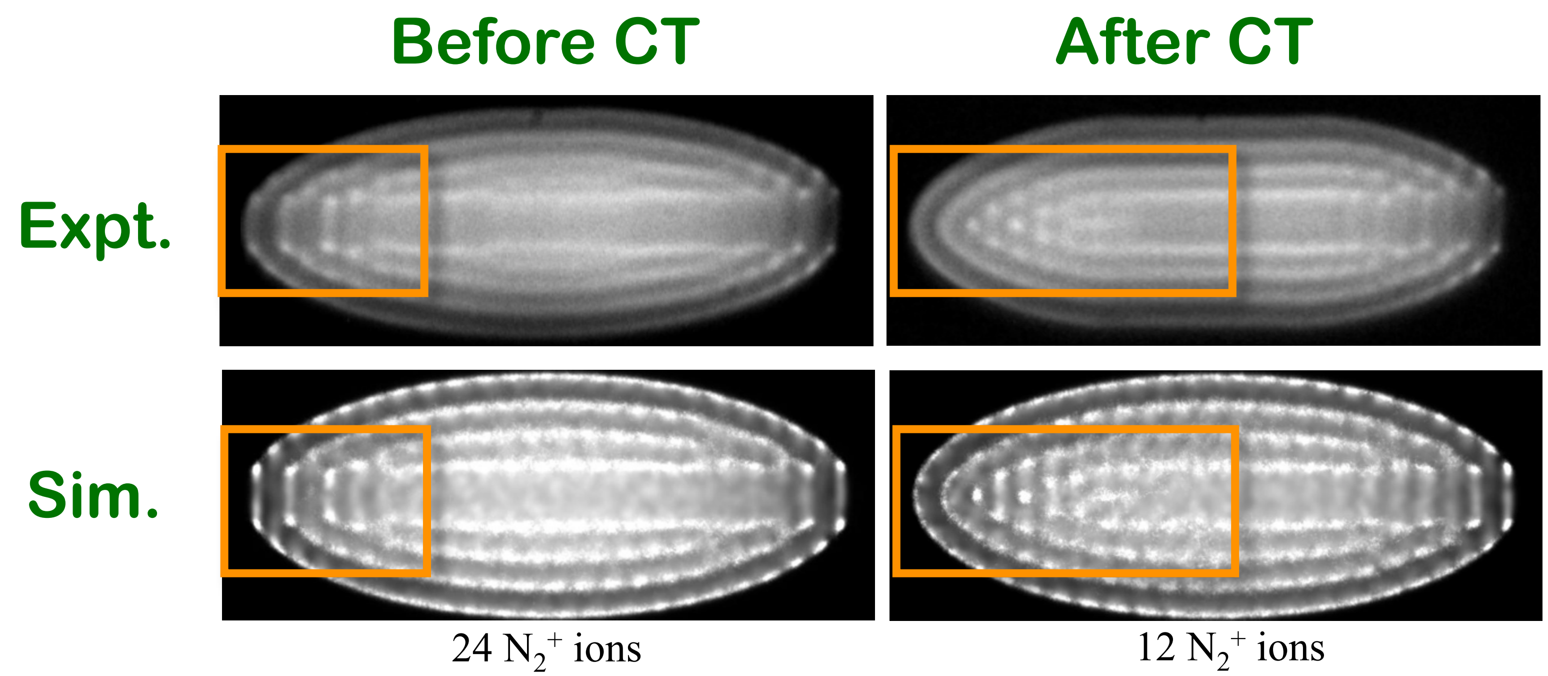
X. Tong, A. H. Winney and SW, Phys. Rev. Lett. 105 (2010), 143001

Population diagnostics

- **Laser-induced charge-transfer (LICT) spectroscopy:** $N_2^+ + Ar \rightarrow N_2 + Ar^+$ ($v^+ \geq 1$)
  $N_2^+ + Ar \not\rightarrow$ ($v^+ = 0$)



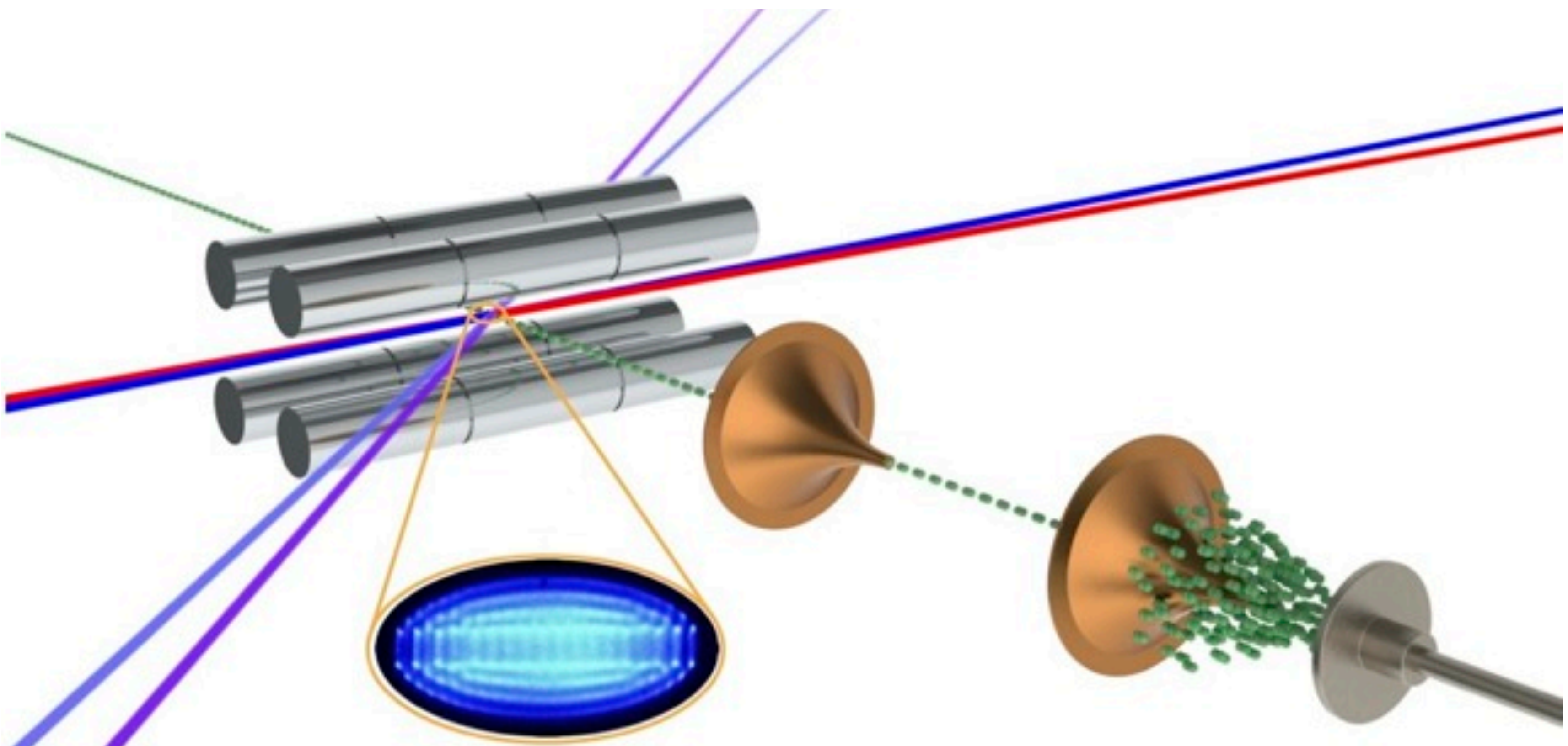
S. Schlemmer et al.,
Int. J. Mass Spectrom. 185 (1999), 589



LICT efficiency out of N^+=0: 50±8 % (max. 55 %)

Total population in N^+=0: 93±11% (averaged over 5 expts.)

The $N_2^+ + N_2 \rightarrow N_2 + N_2^+$ symmetric charge-transfer reaction studied with (almost complete) state and energy control



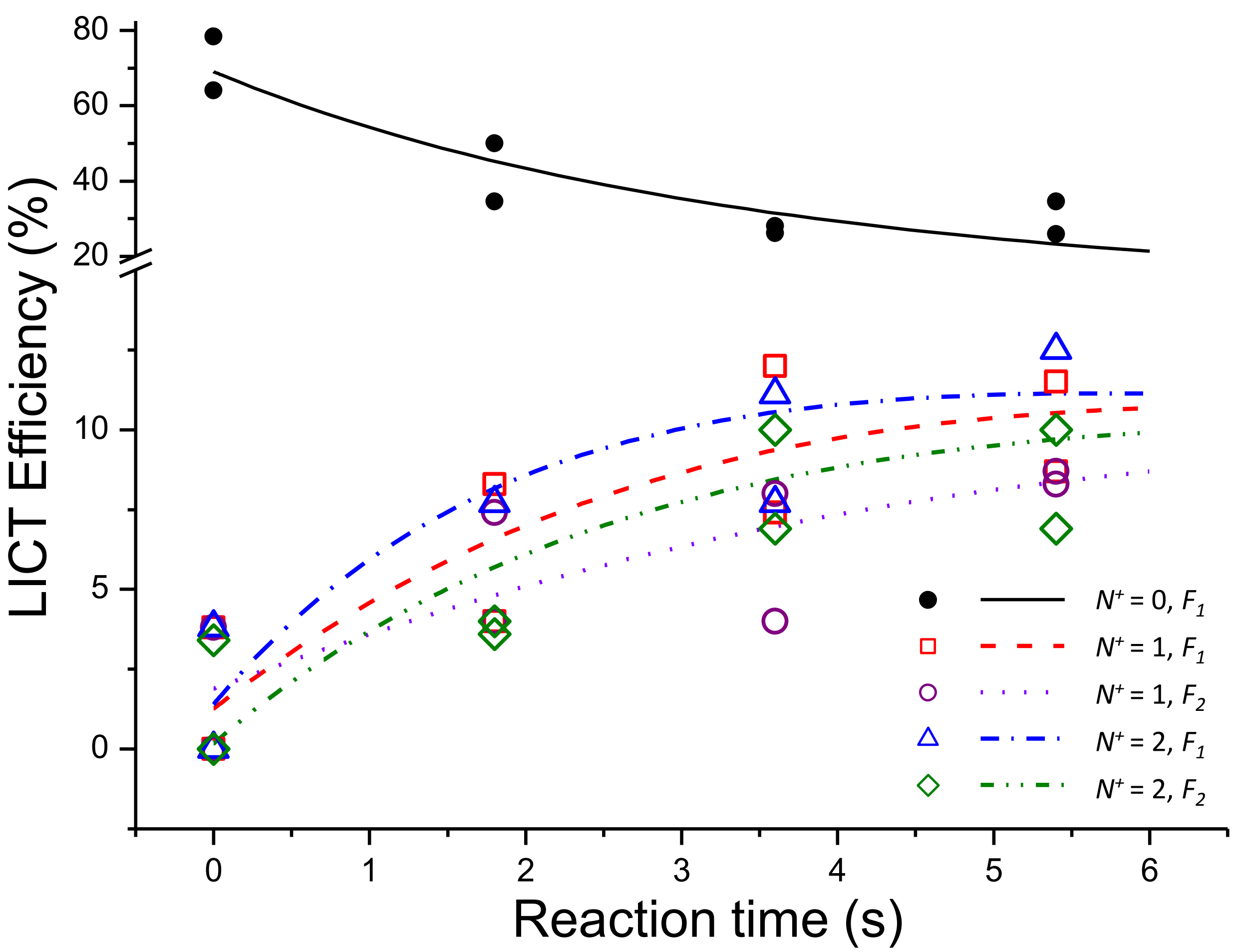
Coulomb crystal with state-selected N_2^+ ions ($N^+=0$)

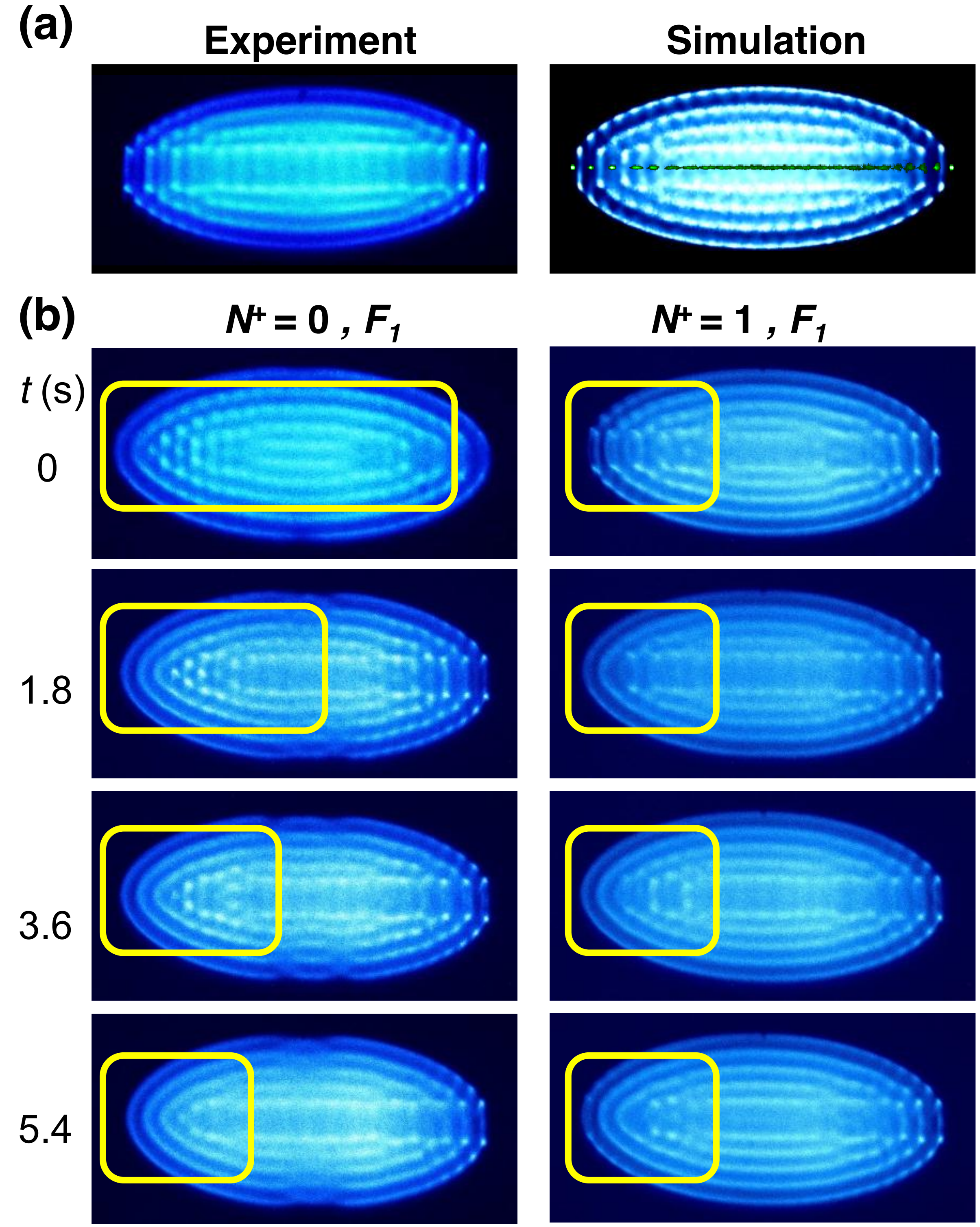
N_2 molecular beam
T_{rot}=8 K: J=0 (1,2)
v=790 m s^{-1}

X. Tong, T. Nagy, J. Yosa, M. Germann, M. Meuwly and SW, Chem. Phys. Lett. 547 (2012), 1

Theory:
T. Nagy, J. Yosa, M. Meuwly
(Uni Basel)

- LICT measurements of N_2^+ ions prepared in $N^+=0$ as a function of the reaction time:
- Time-dependent spin-rotational state populations $N^+=0,1,2$ ($F_{1,2}$):



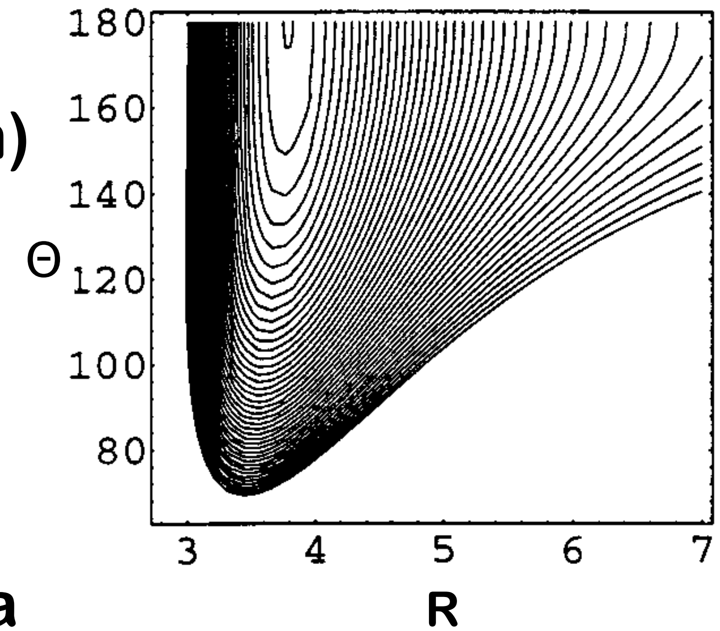


Controlled chemistry: 1. Fully state- and energy selected reactions

Reaction mechanism and translation-to-rotation energy transfer:

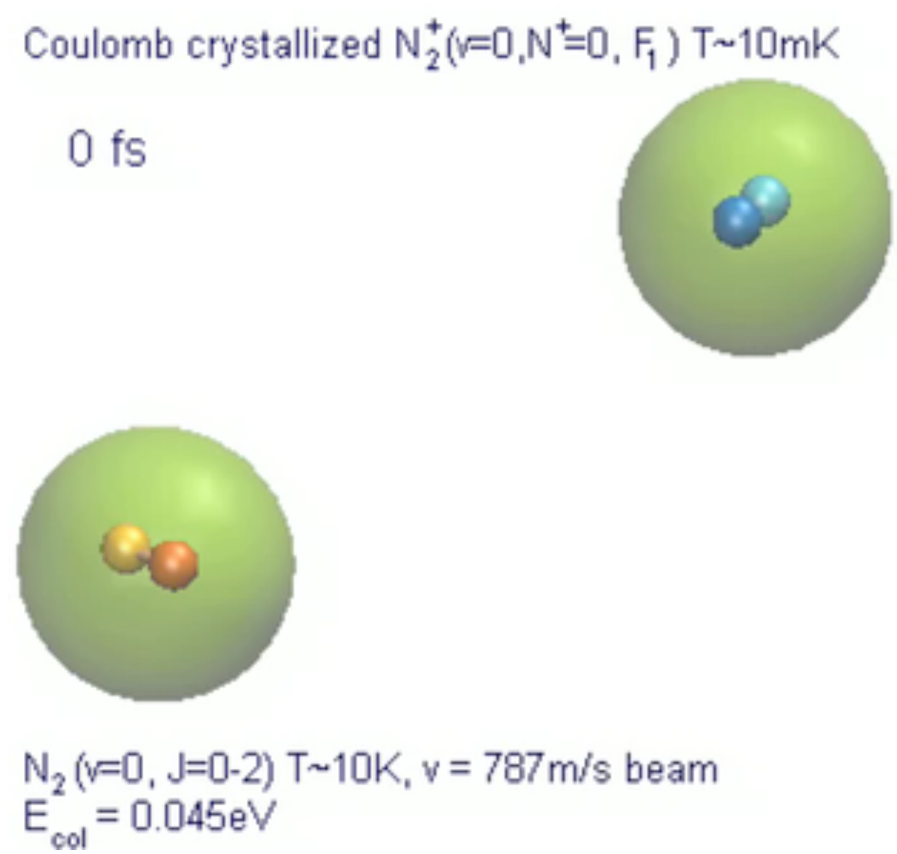
- The reaction proceeds via a linear N_4^+ complex forming at the collision (Langevin) rate: [N≡N ··· N≡N]$^+$

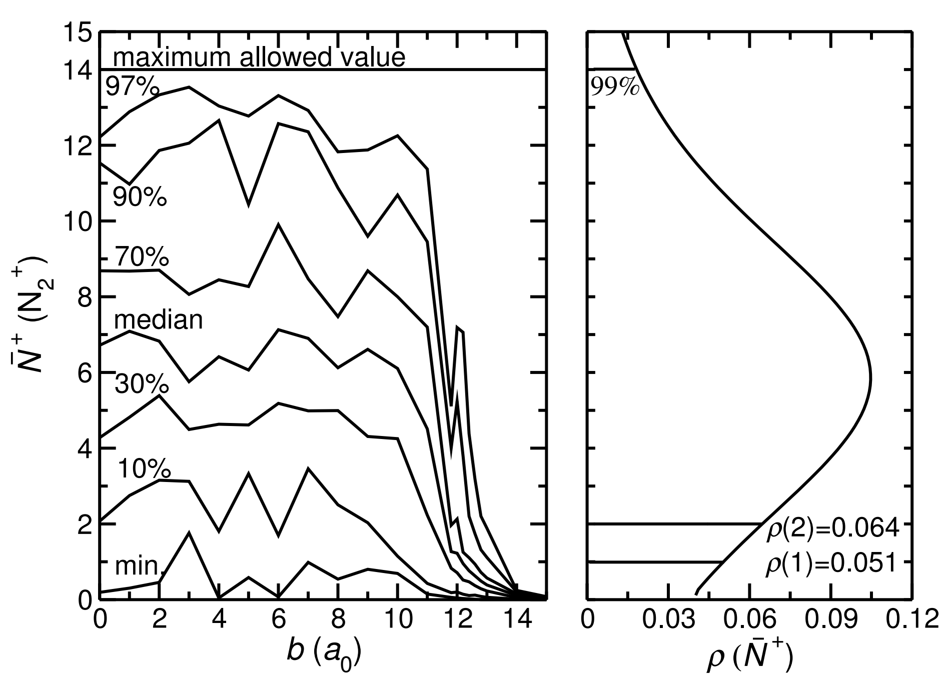
P.A.M. van Koppen et al., J. Chem. Phys. 81 (1984) 288
M. J. Frost et al., J. Chem. Phys. 100 (1994) 6359



C. Leonard et al., J. Phys. Chem. A 103 (1999), 1846

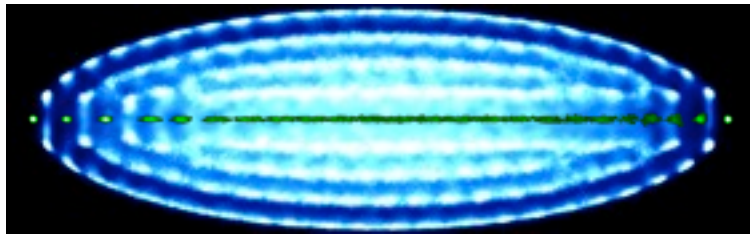
- Translation-to-rotation energy transfer in a long-lived, strongly bound (1.3 eV) reaction complex: Product rotational excitation is produced by bending vibrations upon breakup of the complex



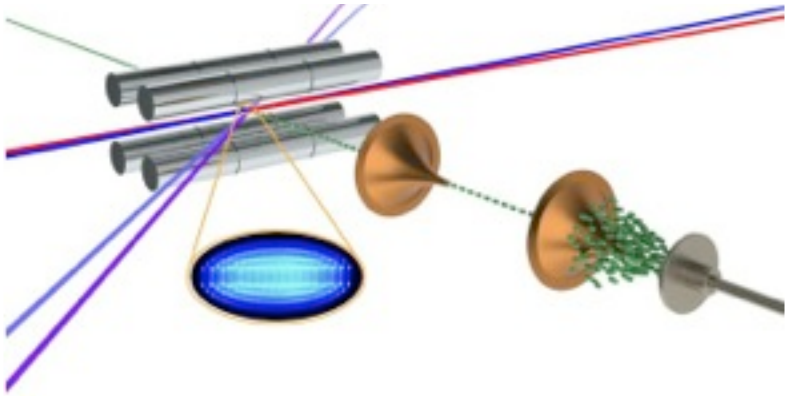


Theory: T. Nagy, J. Yosa, M. Meuwly, Uni Basel

Summary and conclusions

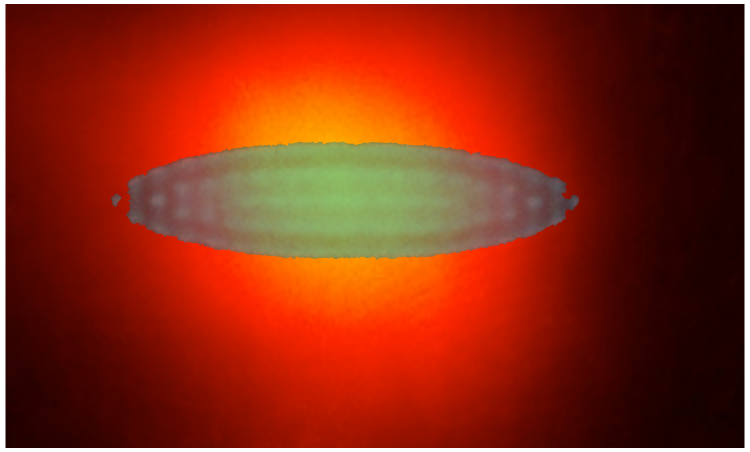


- Ion-neutral reaction experiments at energies down to 20 mK are now feasible, revealing unusual reaction mechanisms at low temperatures and fine details of intermolecular interactions.



- Coulomb-crystal techniques enable chemical-reaction experiments with an energy and state control unprecedented in ion-molecule chemistry.

- State- and energy controlled reaction experiments reveal fine details of the reaction mechanism such as the conversion of energy during chemical change.



- Control of the chemistry of complex molecules is becoming a reality

Acknowledgements

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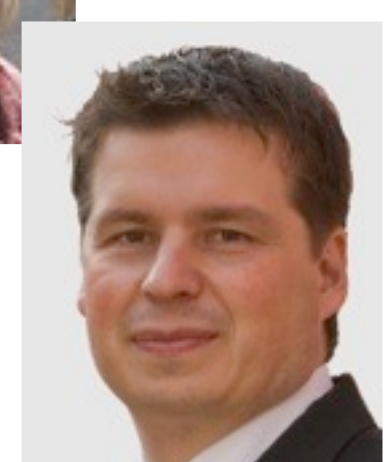
Felix Hall	Daniel Rösch
Anatoly Johnson	Dr Xin Tong

Collaborators:

- Olivier Dulieu, Mireille Aymar, Nadia Bouloufa-Mafaa, Maurice Raoult (LAC/CNRS, Paris)
- Markus Meuwly, Tibor Nagy, Juvenal Yosa Reyes (Uni Basel)
- Jochen Küpper, Yuan-Pin Chang (CFEL & Uni Hamburg)



Funding and support:

FNSNF
Fonds national suisse
Schweizerischer Nationalfonds
Fondo nazionale svizzero
Swiss National Science Foundation

SNI
Swiss Nanoscience Institute
Eine Initiative der Universität Basel und des Kantons Aargau

QSIT Quantum Science and Technology

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