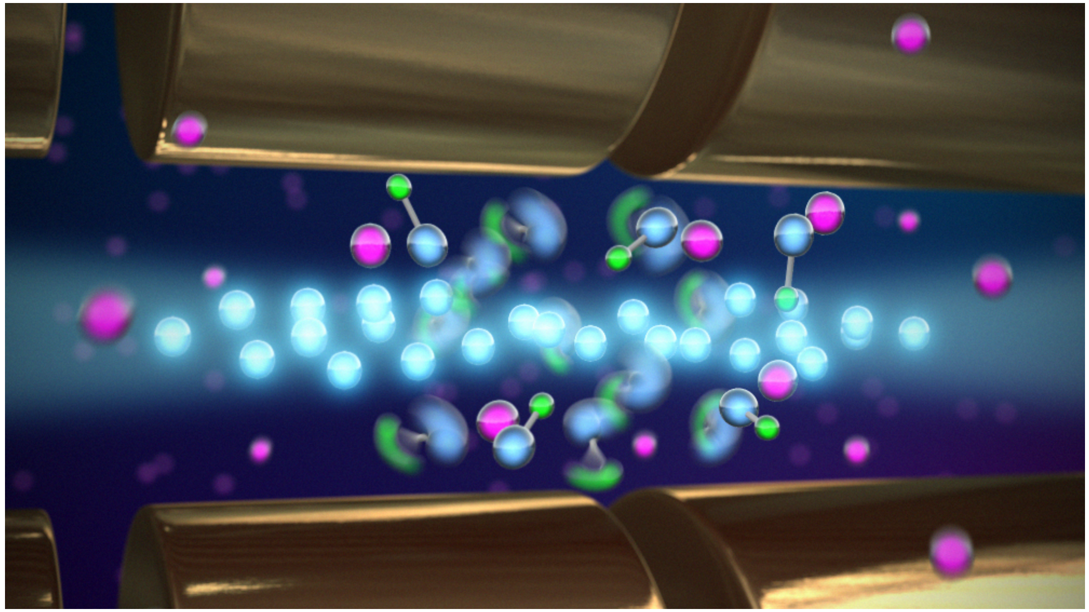
Coulomb-Crystallized Molecular Ions



Michael Drewsen

The Ion Trap Group
Department of Physics and Astronomy
Aarhus University

Physics with Trapped Charged Particles
Les Houches, January 27, 2015

Why conduct experiments with Coulomb-crystallized molecular ions?

- **Cold collisions/reactions**

  Astrophysics (interstellar clouds: ~10 K)
  State specific processes (< 10 K)
  Cold/Ultracold chemistry (~ mK/μK)

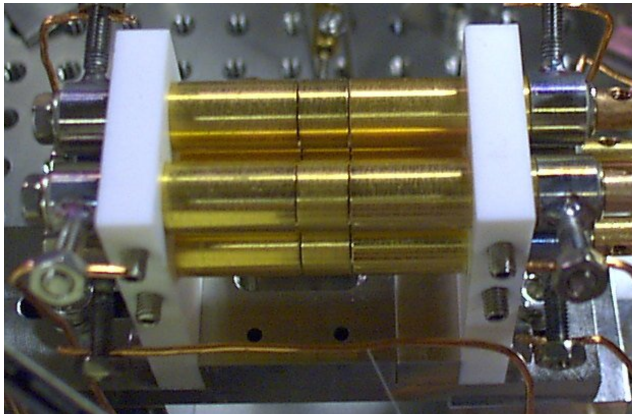
- **High resolution spectroscopy**

  Detailed knowledge of mol. structures
  Frequency standards and molecular clocks
  Determination of natural constants (M_p/m_e, D_e)
  Time variations of nat. const.'s ($d\alpha/dt$) ?

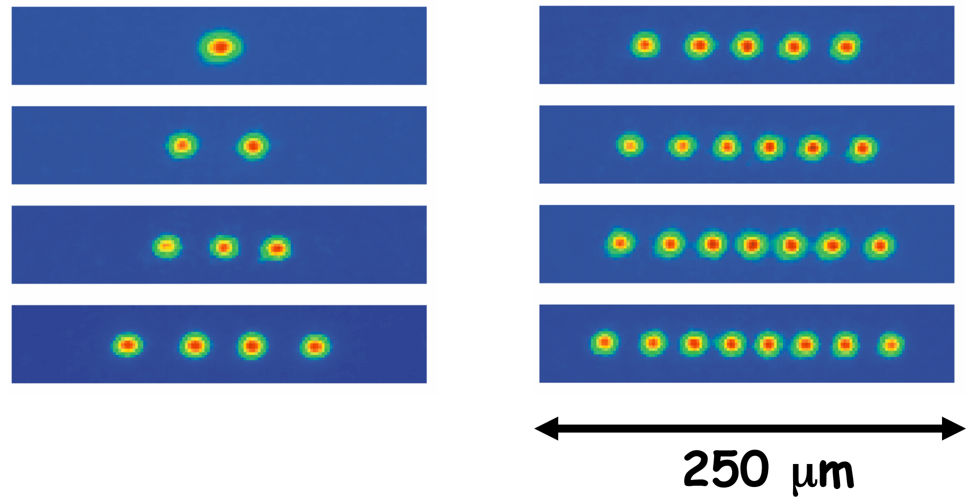
- **Quantum control/optics**

  Coherent control of molecular processes
  Detailed studies of dynamical processes
  Quantum information

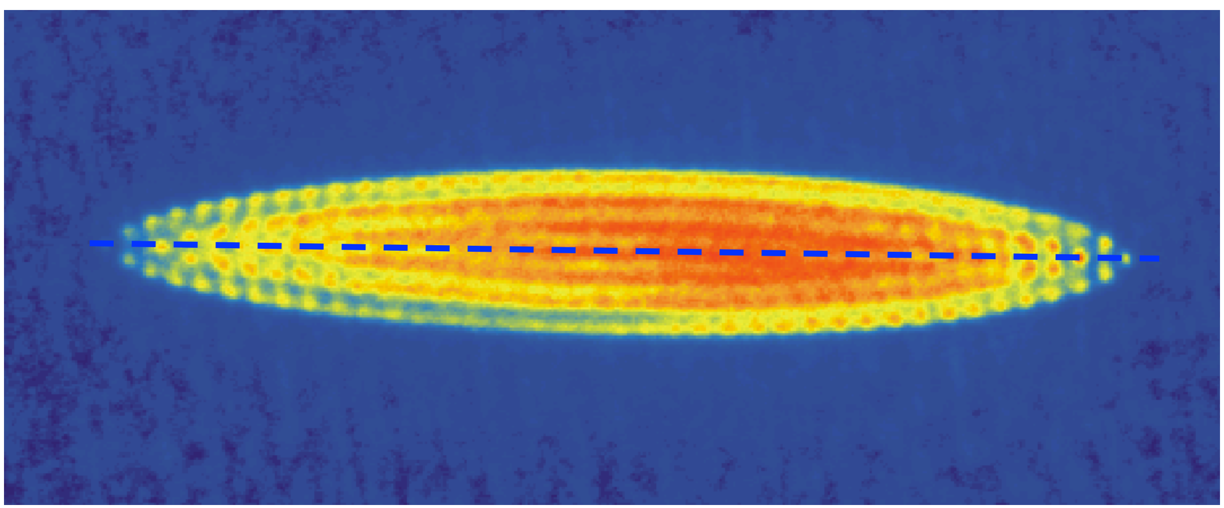
Coulomb-crystallization of laser cooled atomic ions



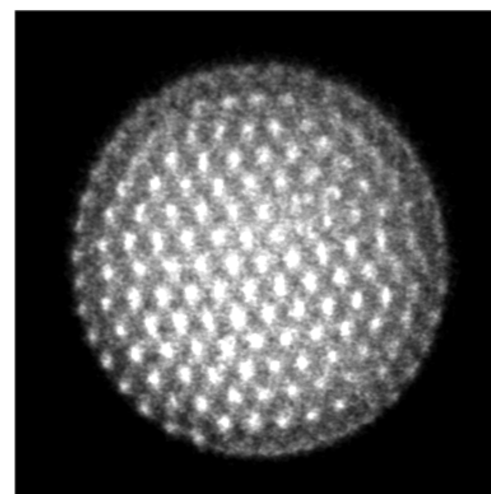
Strings of ions



Larger crystals

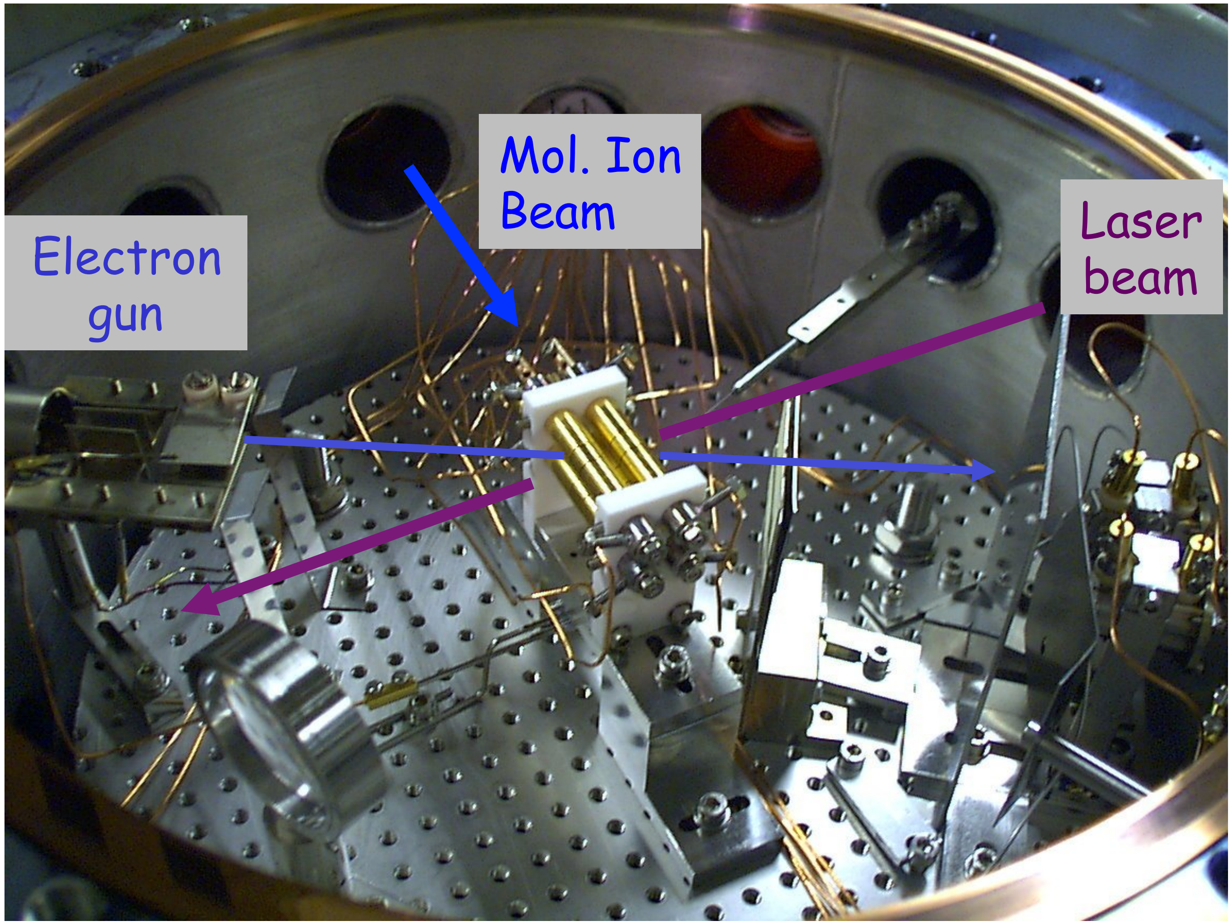


Phys. Rev. Lett. **81**, 2878 (1998)



Phys. Rev. Lett. **96**, 103001 (2006)

Coulomb-crystallization of molecular ions



Gas inlet through leak-valve

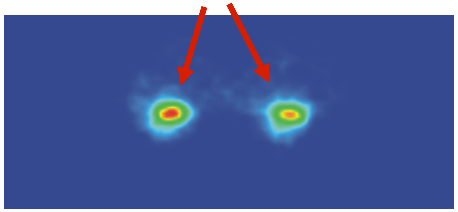
1) Reactions with trapped atomic ions
2) Electron impact ionization of neutral molecules
3) Photoionization of neutral molecules
4) Injecting molecular ions

Coulomb-crystallization of molecular ions

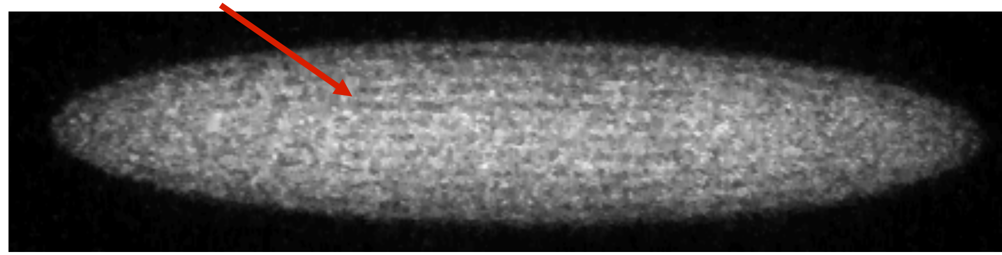
$^{24}Mg^{+}(3p) + H_2 \rightarrow {}^{24}MgH^{+} + H$

Before reaction(s)

$^{24}Mg^{+}$

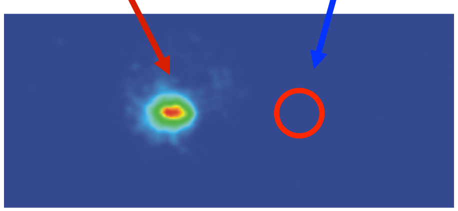


$^{24}Mg^{+}$

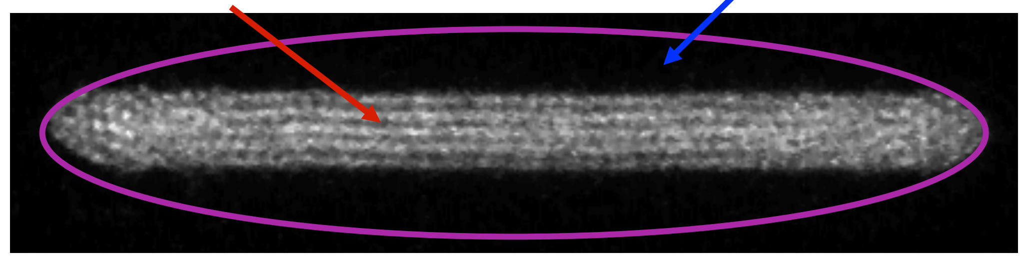


After reaction(s)

$^{24}Mg^{+}$ $^{24}MgH^{+}$



$^{24}Mg^{+}$ $^{24}MgH^{+}$



The translational motion of the $^{24}MgH^{+}$ ions are sympathetically cooled to T~10 mK.

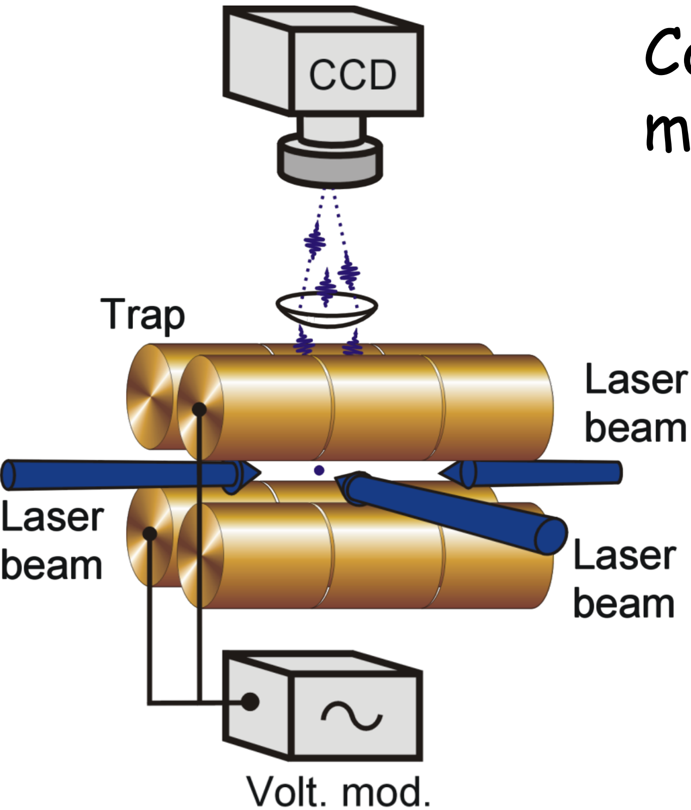
Phys. Rev. A 62, 0011401(R) (2000)

Experiments with single molecular ions

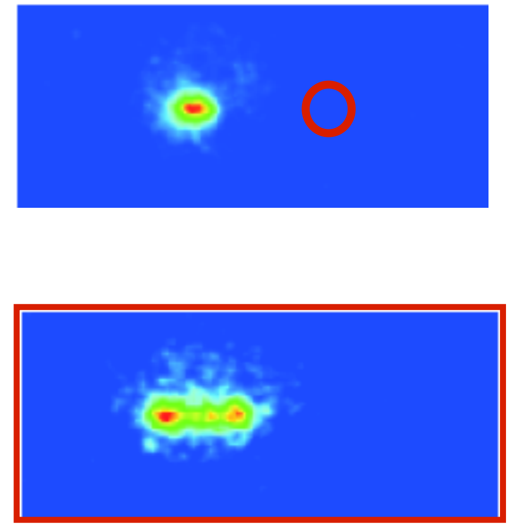
Why *single* molecular ion investigations ?

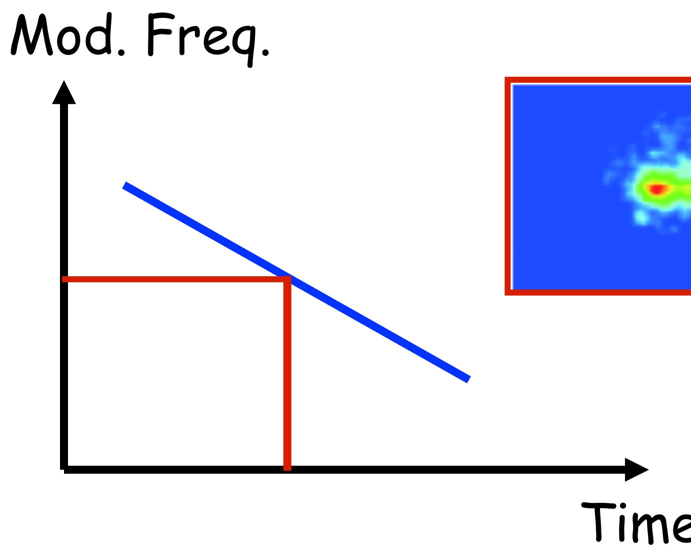
- Ultimate situation for controlling and obtaining knowledge of the molecule under study
- Ultimate situation for reducing unwanted effects from the environment
- Ultimate situation for external and internal state preparation by the use of light fields
- Necessary condition for investigations of ultra-cold ion chemistry
- Necessary condition for investigations of the chemistry of rare isotopes
- Ultimate sensitivity for detections of molecules and their structures
- Ultimate starting point of for studies of light induced processes

Single molecular ion identification



Common motional mode excitations





Mass resolution: $\Delta m/m \sim 10^{-4}$

Phys. Rev. Lett. **93**, 243201 (2004)

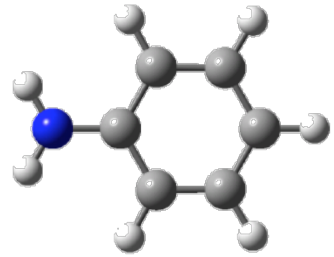
Note:

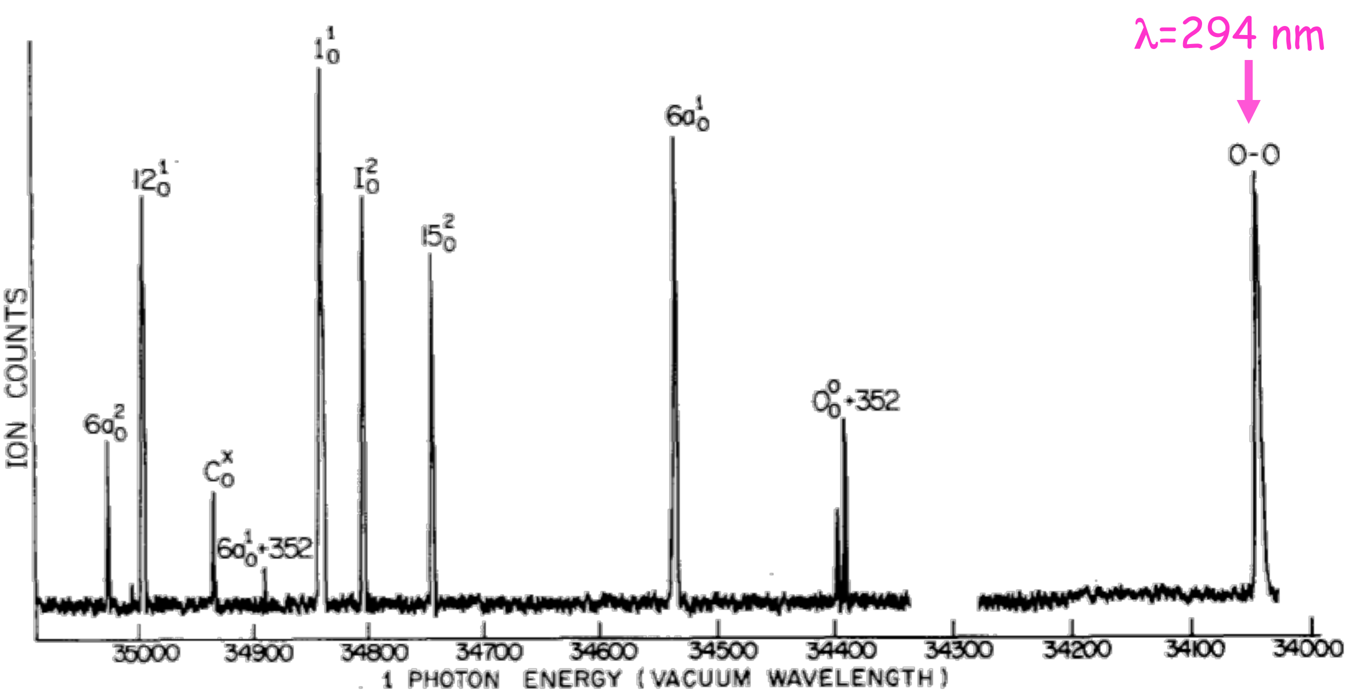
Both the mass ***AND*** charge of the symp. cooled ion can be determined!

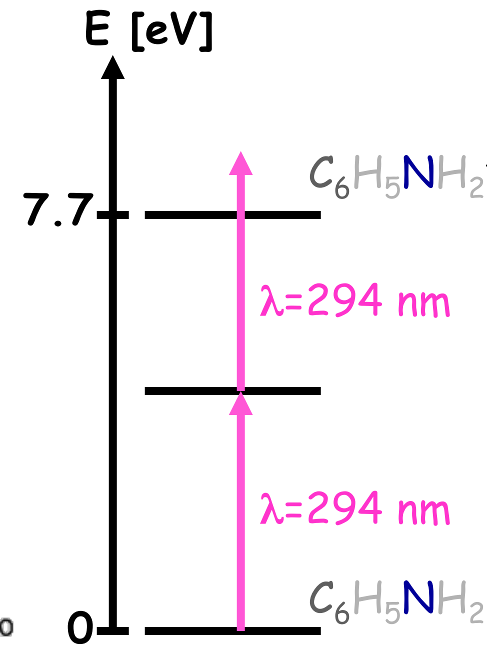
Case study: Photofragmentation of Aniline ions

1+1 REMPI of the Aniline molecule

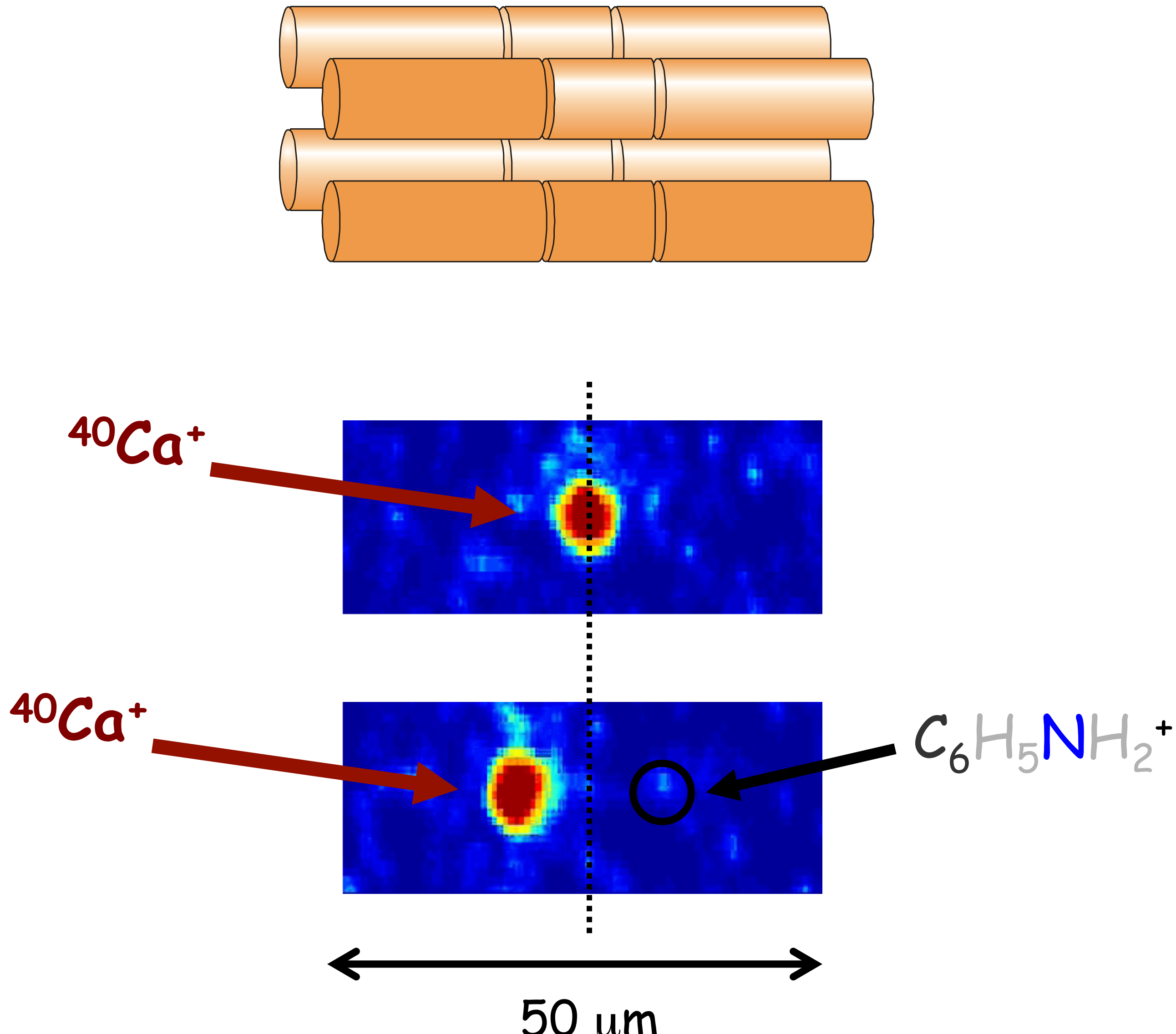
$C_6H_5NH_2$:



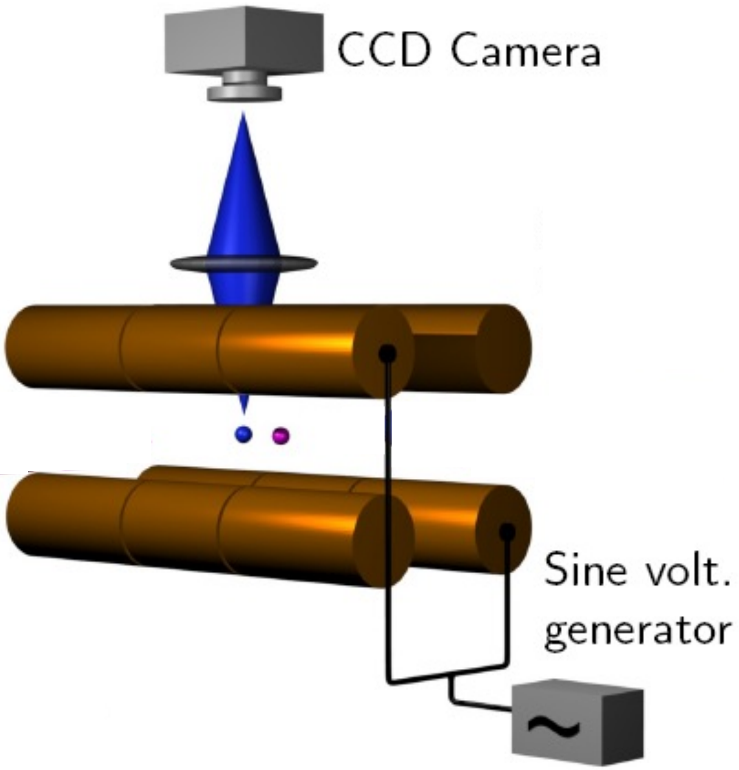




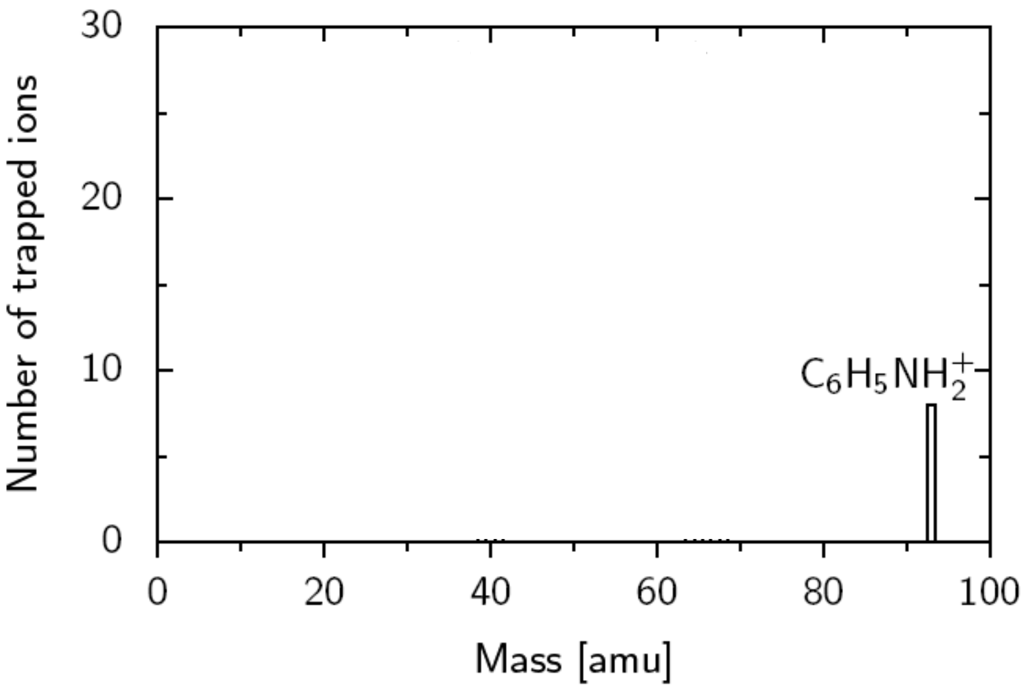
Observation of the production of a single Aniline ion



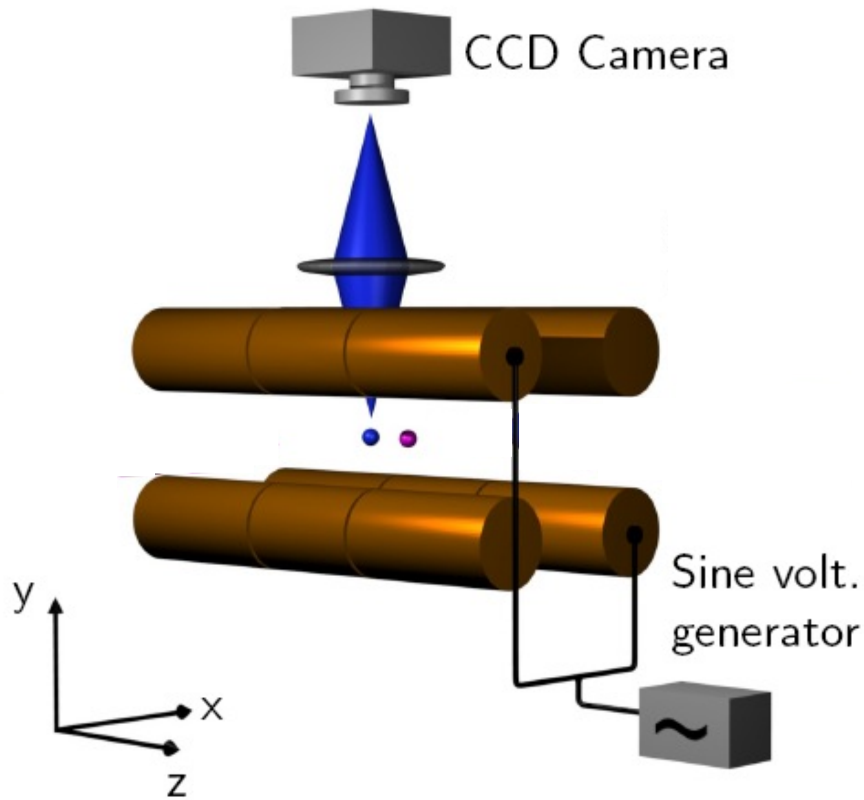
1+1 REMPI experiments with single Aniline molecules

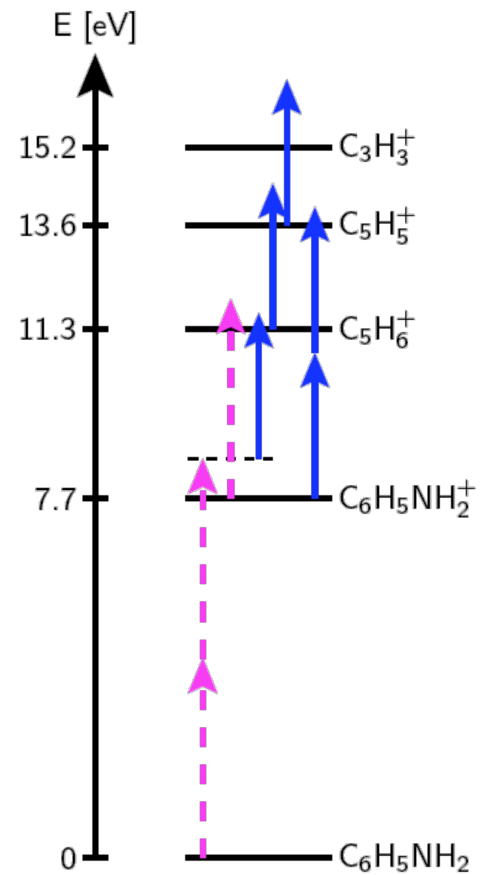


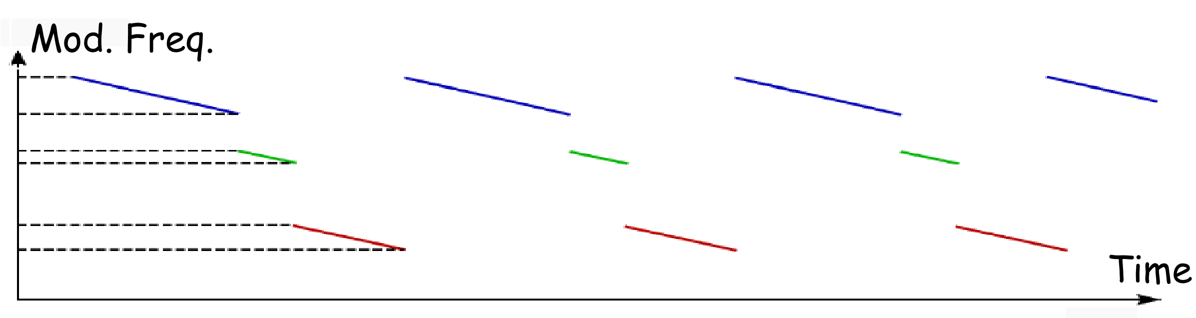
Mass spectrum



Explanation of observed molecular ions

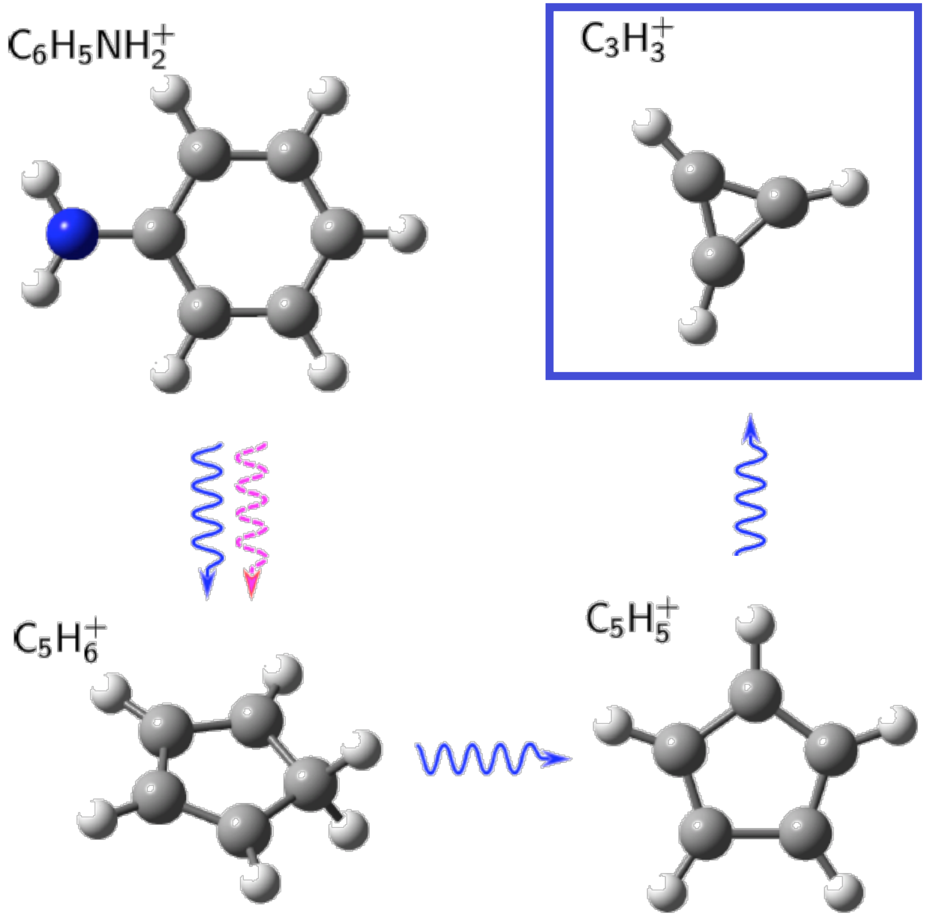


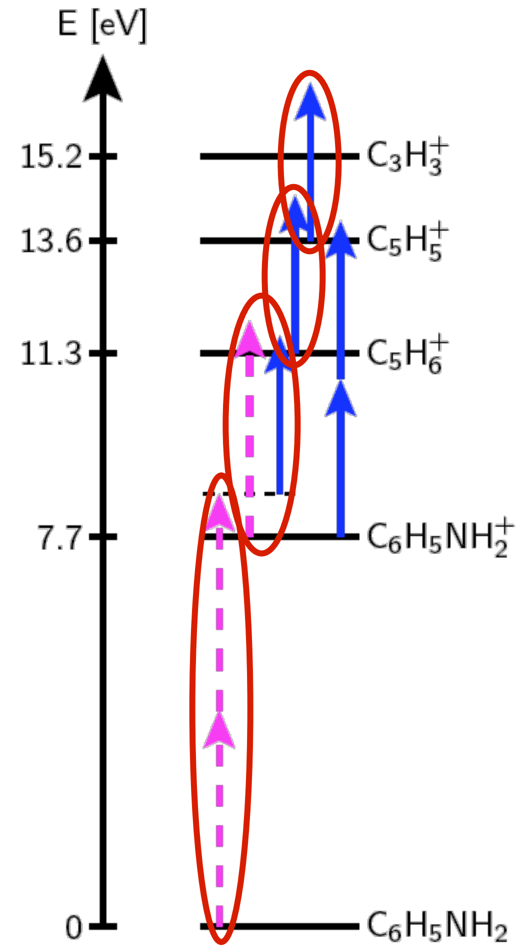




Observation of consecutive photofragmentation:

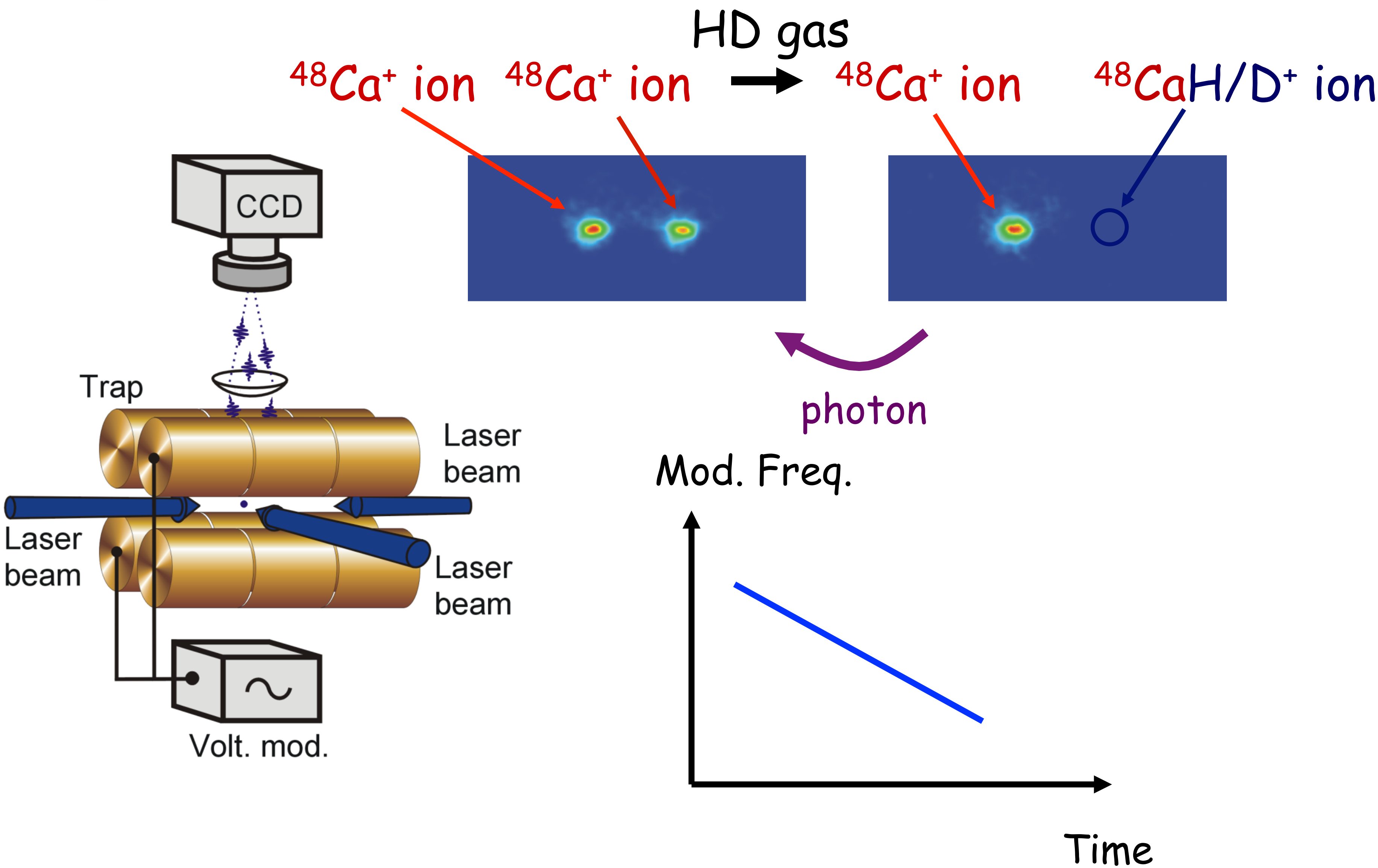
" Stable product"





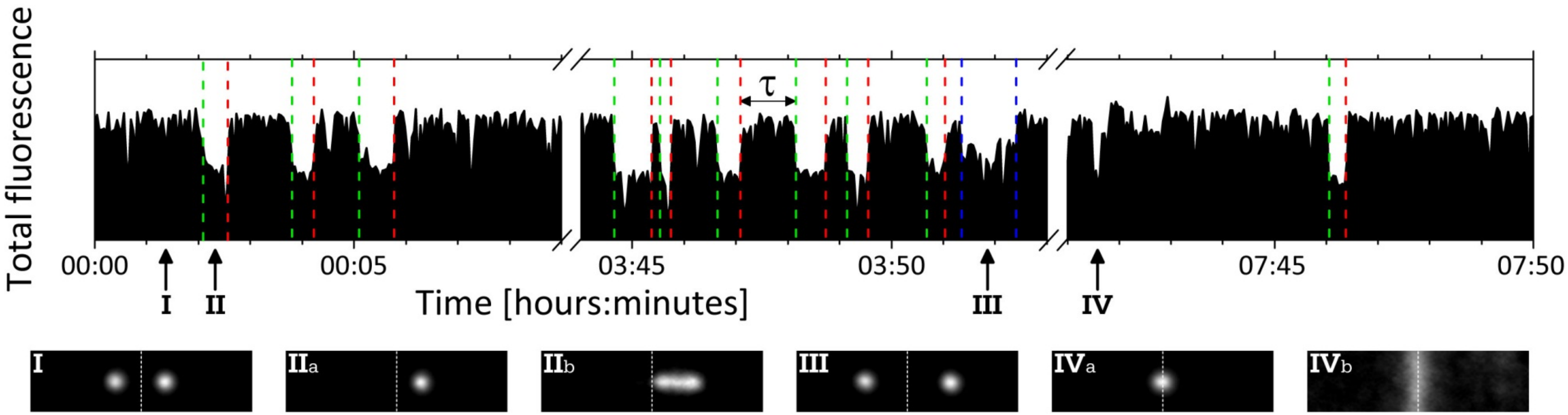
Rev. A 77, 030702(R) (2008)

"Recycling-chemistry" with Ca^+ ions



“Recycling-chemistry” with Ca^{+} ions

Nearly 100 reactions with the *same* pair of $^{48}Ca^{+}$ ions



= reaction

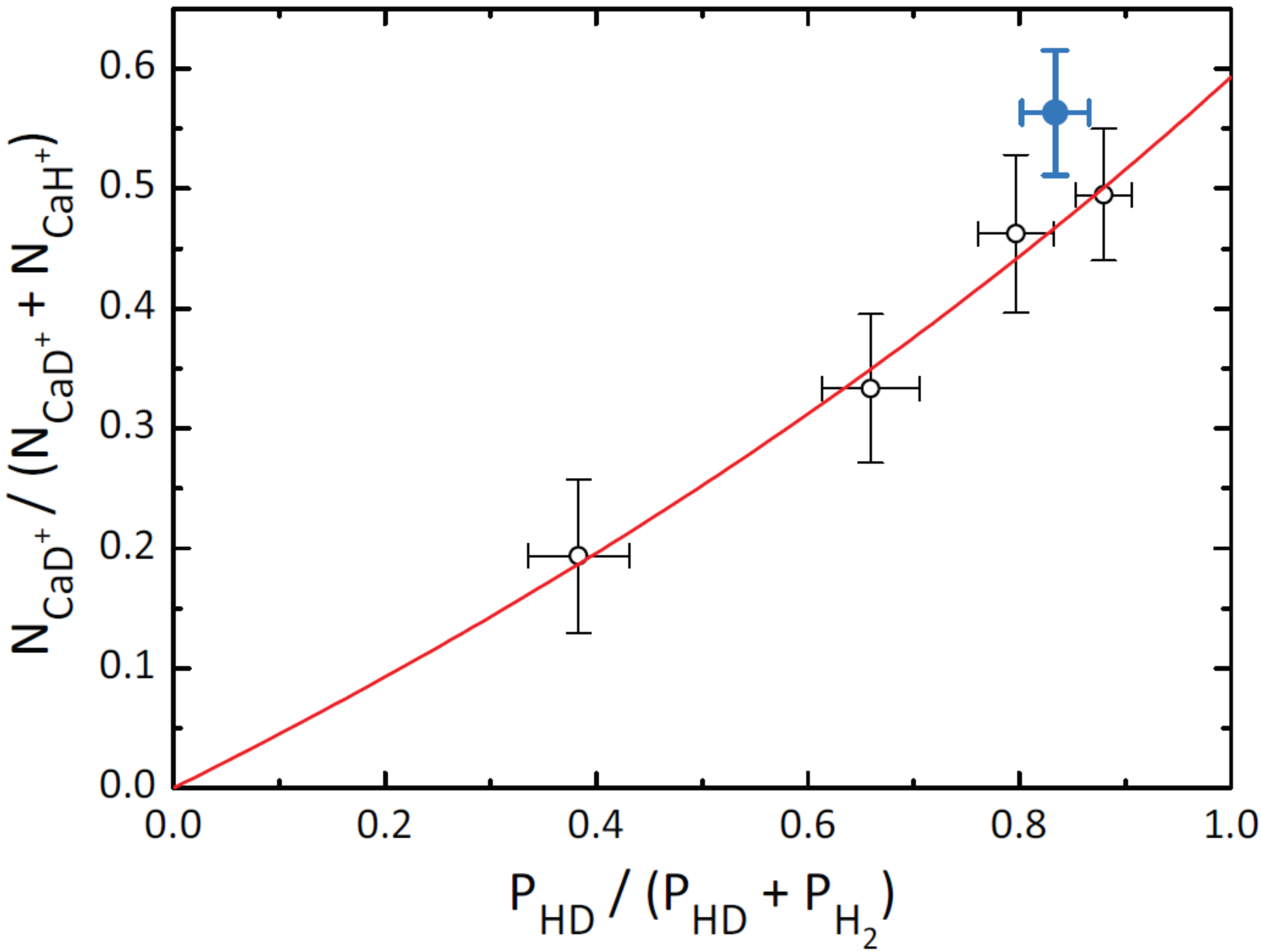
= dissociation

Of those 87 reactions leading to hydride formation:

$\boxed{38\ ^{48}CaH^{+} \text{ and } 49\ ^{48}CaD^{+}}$

Angew. Chem. Int. Ed.: DOI: 10.1002/anie.201203550 (2012)

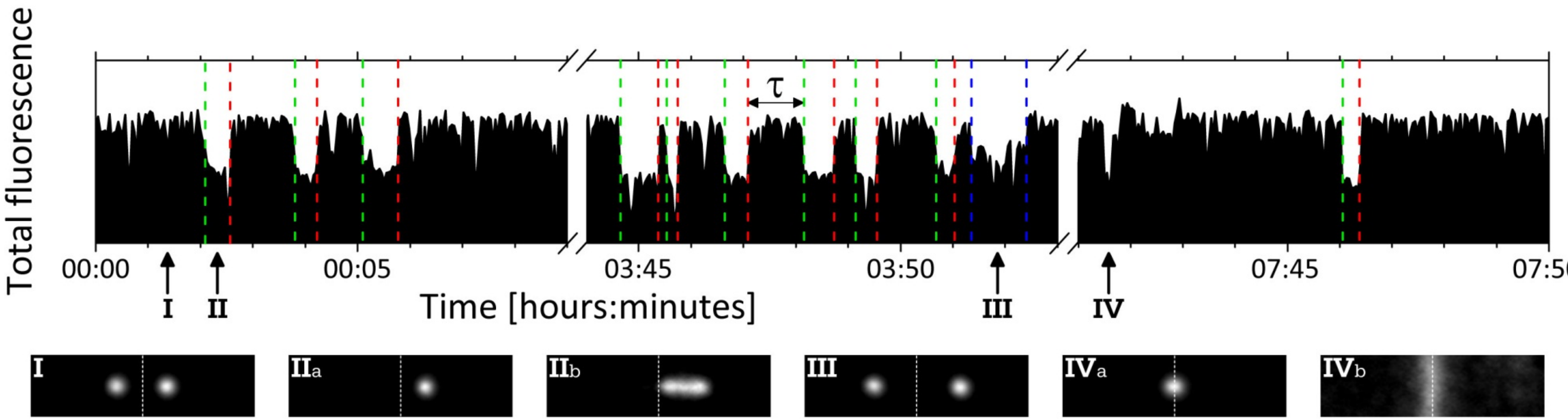
“Recycling-chemistry” with Ca⁺ ions



Angew. Chem. Int. Ed.: DOI: 10.1002/anie.201203550 (2012)

"Recycling-chemistry" with Ca^+ ions

Nearly 100 reactions with the *same* pair of $^{48}Ca^+$ ions



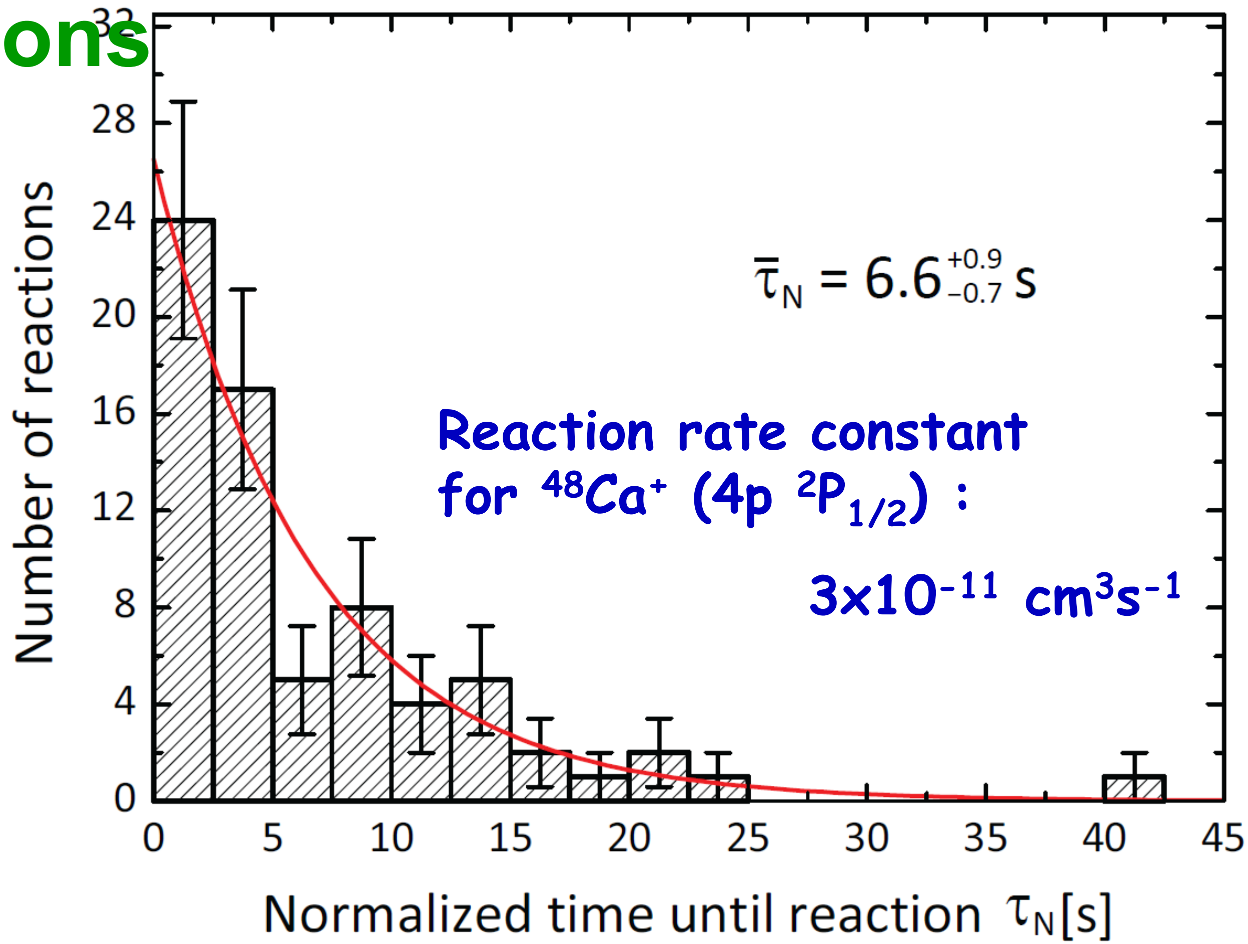
= reaction

= dissociation

Of those 87 reactions leading to hydride formation:

38 $^{48}CaH^+$ and 49 $^{48}CaD^+$

"Recycling-chemistry" with Ca^+ ions



Other recycling reactions:

$Ca^+ + H_2O \rightarrow CaOH^+ \xrightarrow{UV} Ca^+$

$Ca^+ + O_2 \rightarrow CaO^+ \xrightarrow{UV} Ca^+$

Angew. Chem. Int. Ed.: DOI: 10.1002/anie.201203550 (2012)

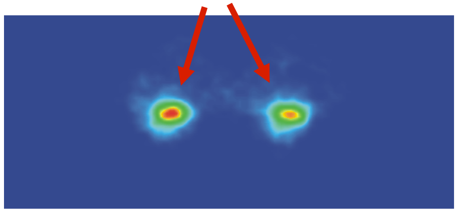
Rovibrational cooling of Coulomb-crystallized Molecular ions

Coulomb-crystallization of molecular ions

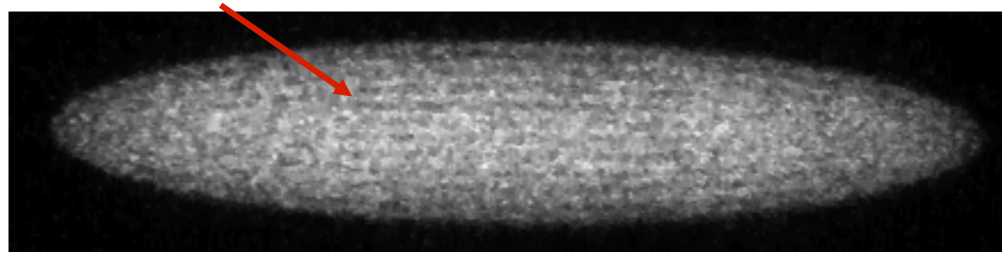
$\boxed{^{24}Mg^+(3p) + H_2 \rightarrow {}^{24}MgH^+ + H}$

Before reaction(s)

$^{24}Mg^+$

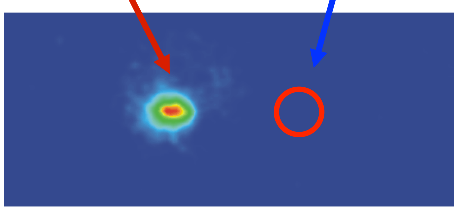


$^{24}Mg^+$

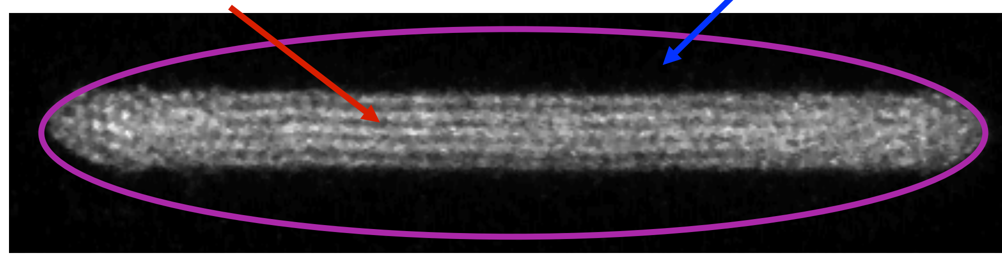


After reaction(s)

$^{24}Mg^+$ $^{24}MgH^+$



$^{24}Mg^+$ $^{24}MgH^+$



The translational motion of the $^{24}MgH^+$ ions are sympathetically cooled to T~10 mK.

Phys. Rev. A 62, 0011401(R) (2000)

How cold are the rovibrational degrees of freedom ?

Vibrational constant of the $^{24}MgH^+$ ion:

$\sim 1600\ cm^{-1} \sim 8 \times k_b T_{room}$

$\Downarrow$

$P(\nu=0) > 99.9\ \%$

$\Downarrow$

Vibrationally cold !

Rotational state selective 1+1 Resonance Enhanced Multi-Photon Dissociation (REMPD) have previously shown

$T_{rot} > \sim 100$ Kelvin $\gg T_{mol,\ trans}$ J. Phys. B **39** L83 (2006)

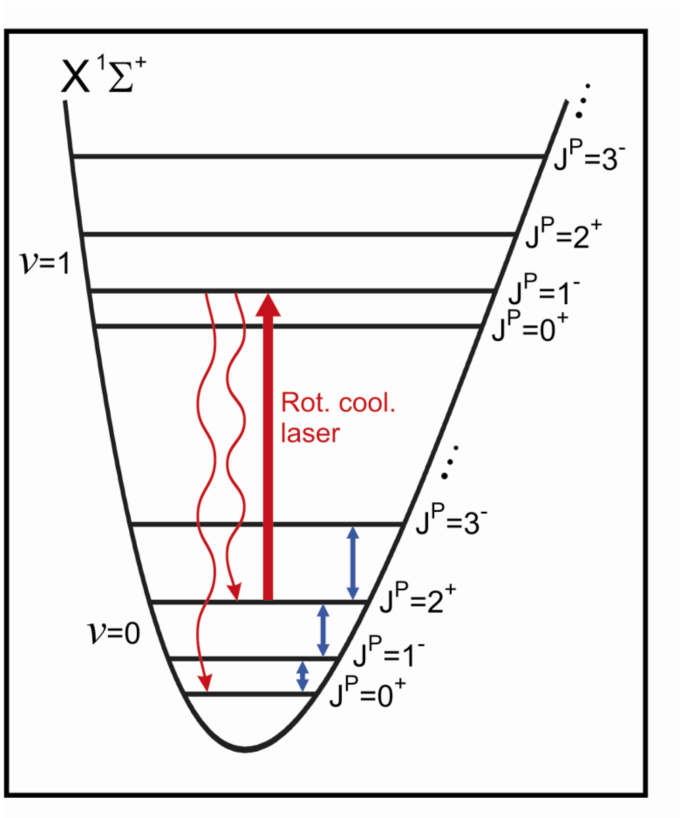
Rot. constant: $B \approx 9$ K

$\Downarrow$

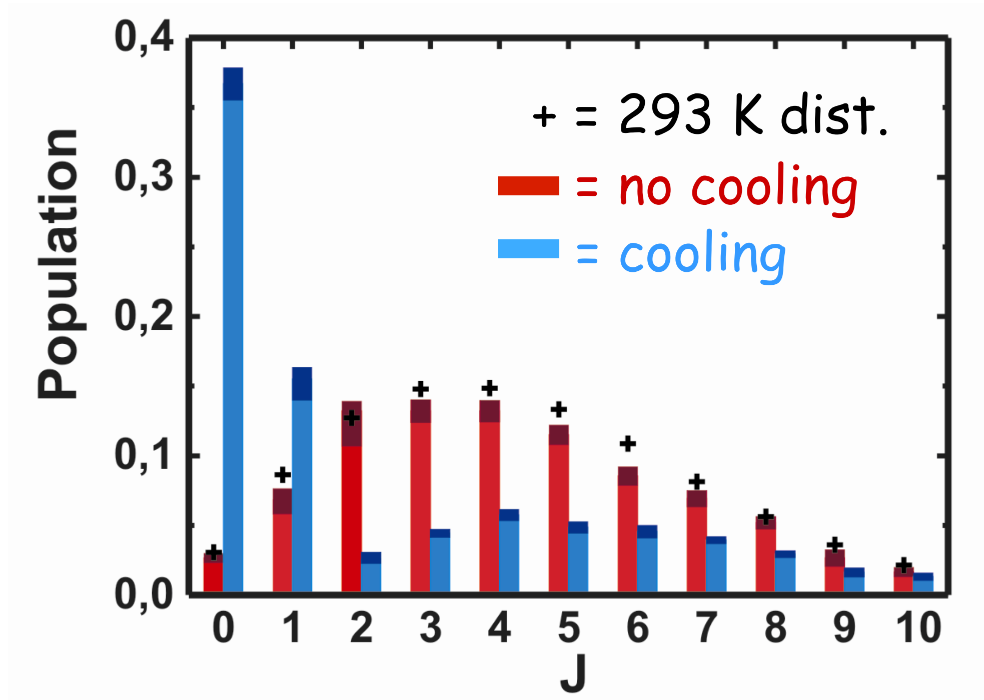
Rotationally hot !

Rotational cooling by laser-induced transitions

Steady-state rotational state distributions for $^{24}MgH^+$



Phys. Rev. Lett. **89**, 173003 (2002)
New J. Phys. **11**, 055026 (2009)



- 15 times increase in J=0 population
- J=0 state population equal to therm. dist. @ 20 K

Nat. Phys. **6**, 271 (2010)

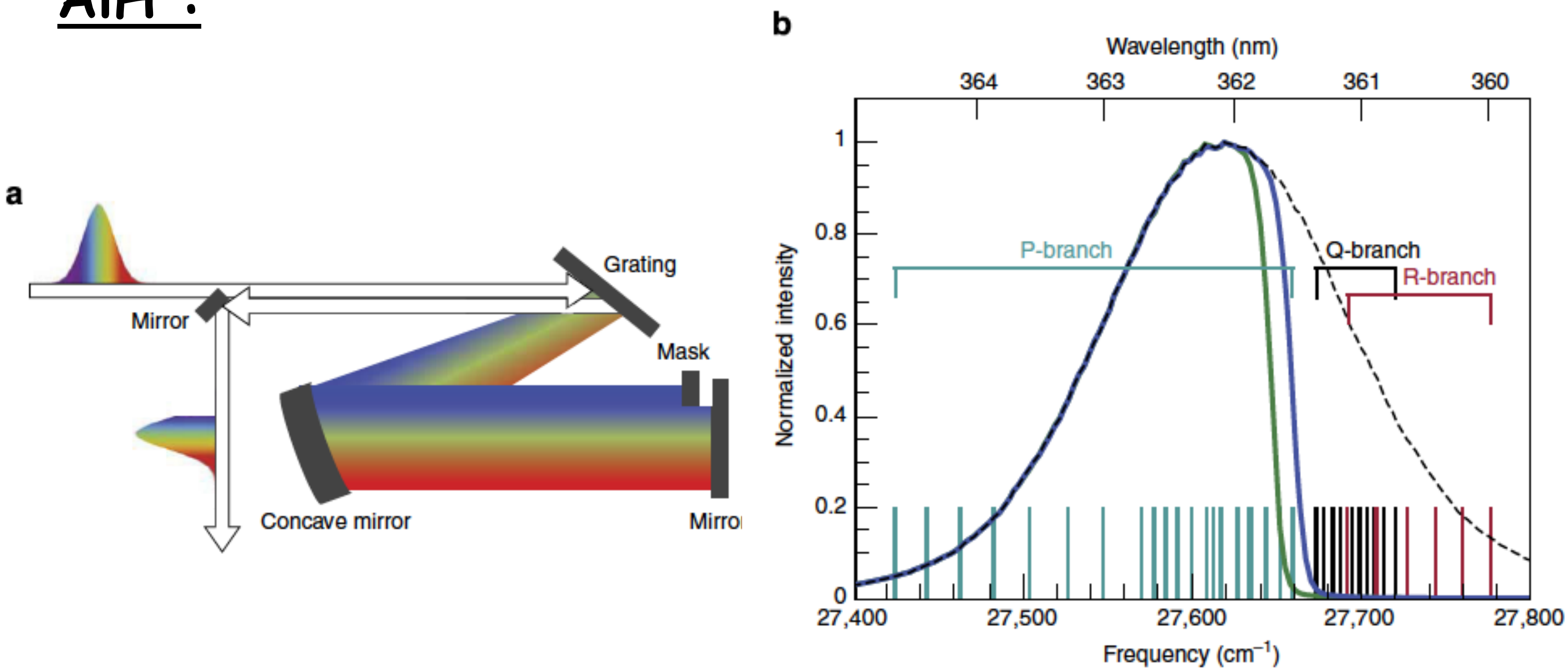
Received 29 May 2014 | Accepted 23 Jul 2014 | Published 2 Sep 2014

DOI: 10.1038/ncomms5783

Broadband optical cooling of molecular rotors from room temperature to the ground state

Chien-Yu Lien[1], Christopher M. Seck[1], Yen-Wei Lin[1], Jason H.V. Nguyen[1,†], David A. Tabor[1] & Brian C. Odom[1]

AlH^+:



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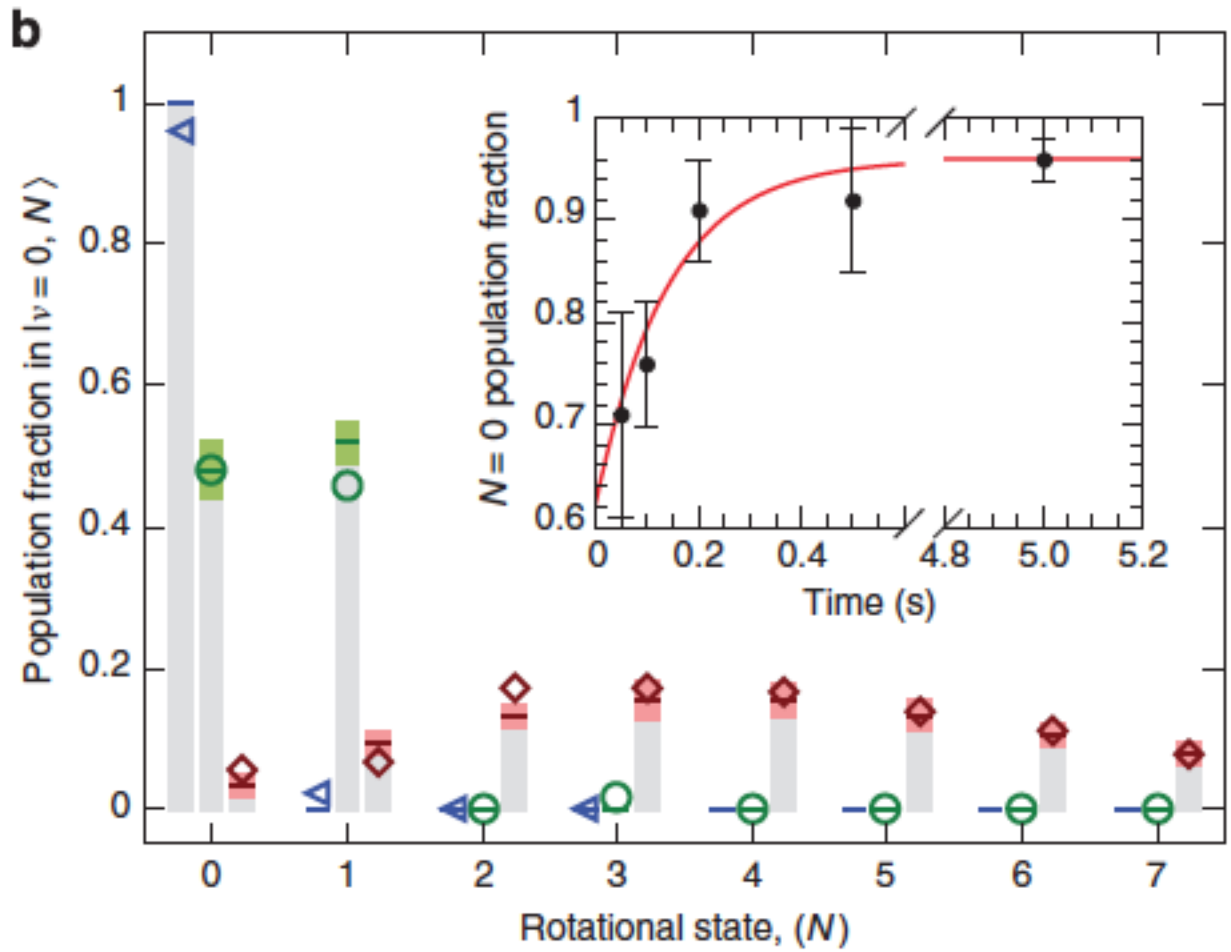
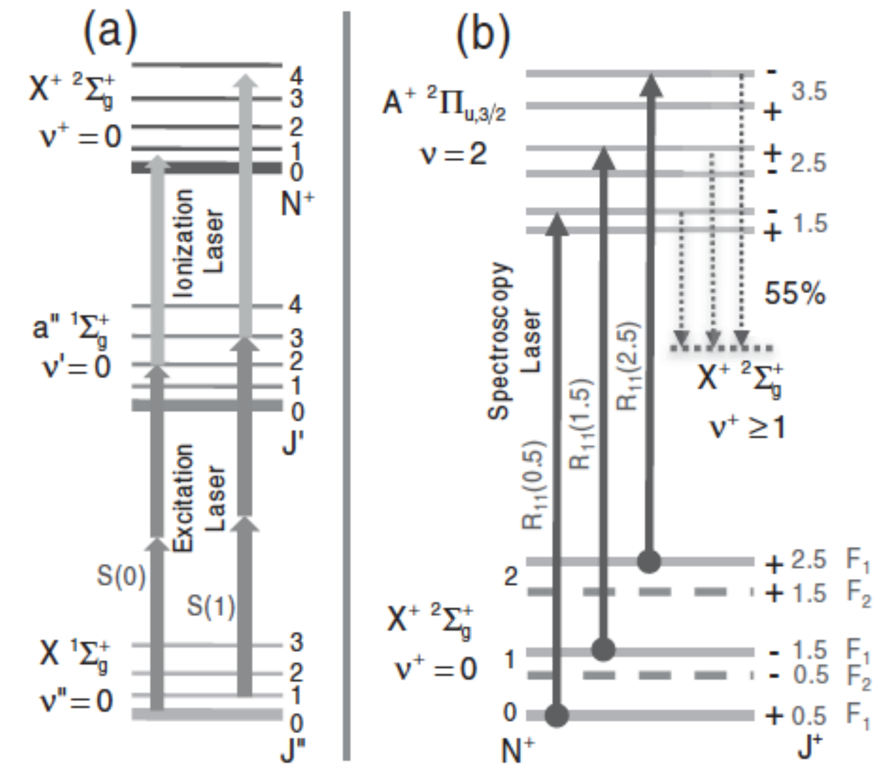


Production of state selected molecular ions from neutrals

N_2^+:

PRL 105, 143001 (2010) PHYSICAL REVIEW LETTERS week ending 1 OCTOBER 2010



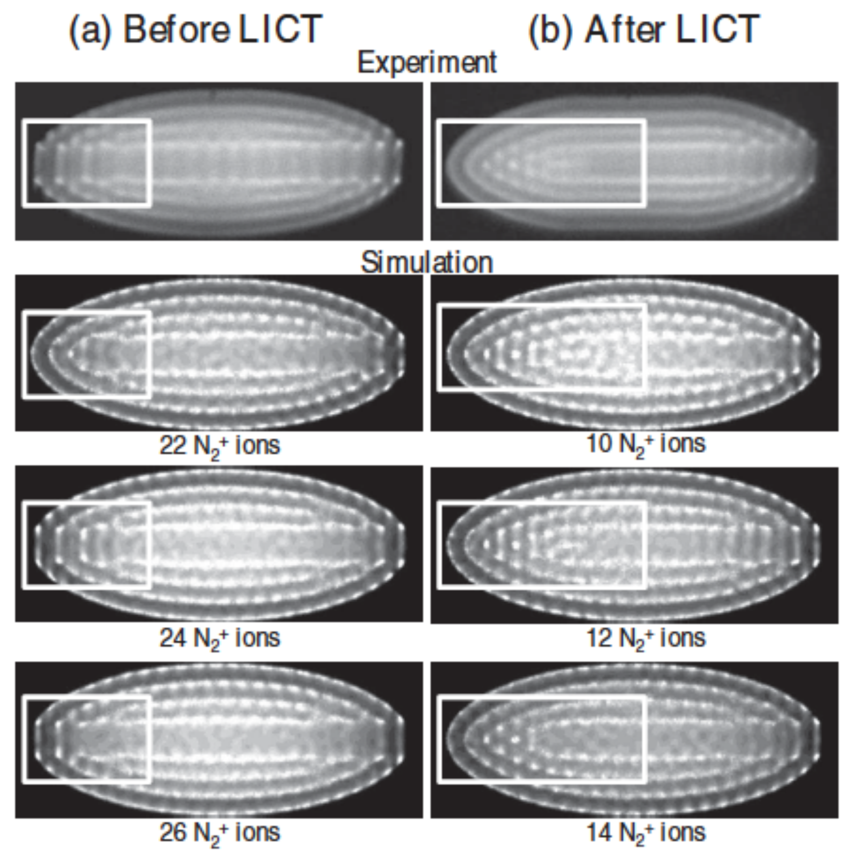
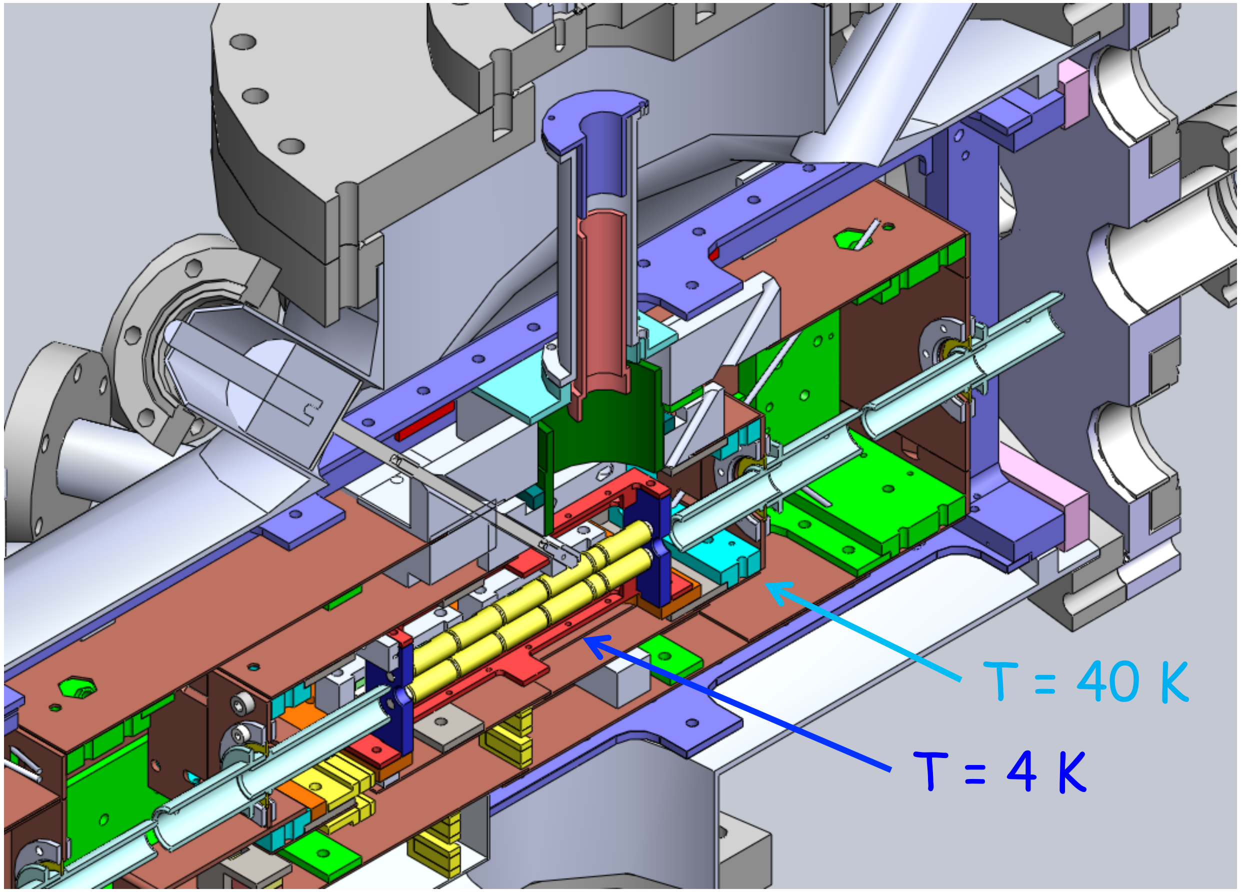


FIG. 1. (a) State-selective [2 + 1′] resonance-enhanced threshold-photoionization sequence for the generation of N+

Work by Willitsch's group, Basel

Rotational cooling by a helium buffer gas

Sympathetically cooled molecular ions in a cryogenic trap



In collaboration with J. Ullrich, J. José R. Crespo López Urrutia, O. Versolato, M. Schwartz,…, MPIK, Heidelberg

Rev. Sci. Instrum. **83**, 083115 (2012)

Why helium buffer gas cooling ?

- This technique have been proven very successful to cool a large variety of molecular ions in multi-pole rf traps (Gerlich, …).

- The cooling principle works independent of the molecular species (transition frequencies and rates)

- It can potentially cool translational, rotational and vibrational degrees of freedom.

<u>Important for our experiments:</u>

The translation degrees of freedom are taken care of by combination of laser and sympathetic cooling.

Why rf *quadrupole* traps ?

- Can work with localized individual ions or ion ensembles of high constant densities when Coulomb crystallized

- Enables resolved sideband cooling to the quantum mechanical ground state of the trap potential

- Very open trap geometry for the application of various laser and particle beams

<u>Issues with Coulomb-crystallized ions :</u>

1) The helium temperature is orders of magnitudes higher than the melting temperature of Coul. Cryst. !!

2) Will micromotion be a killer in rf quadrupole traps ?

Rotational He buffer gas cooling of Coulomb crystallized molecular ions?

1) The helium temperature is orders of magnitudes higher than the melting temperature of Coul. Cryst. !!

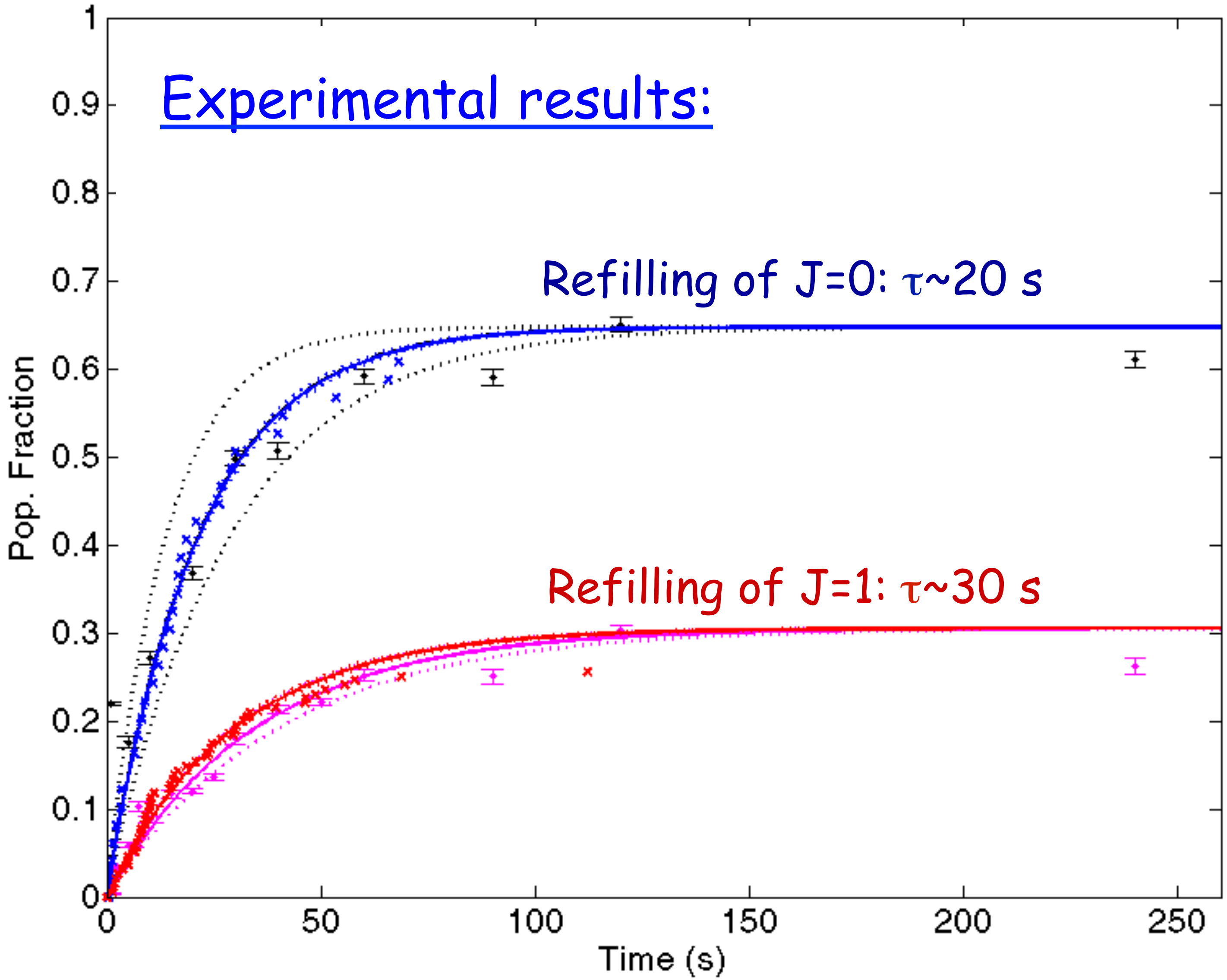
Basic requirements:

$$\Gamma_{\text{rot,heat}} < \Gamma_{\text{He coll.}} < \Gamma_{\text{symp. cool}}$$

?

~100-1000 Hz

Rotational state refilling times without a helium buffer gas



Rotational He buffer gas cooling of Coulomb crystallized molecular ions?

1) The helium temperature is orders of magnitudes higher than the melting temperature of Coul. Cryst. !!

Basic requirements:

$$\Gamma_{\text{rot,heat}} < \Gamma_{\text{He coll.}} < \Gamma_{\text{symp. cool}}$$

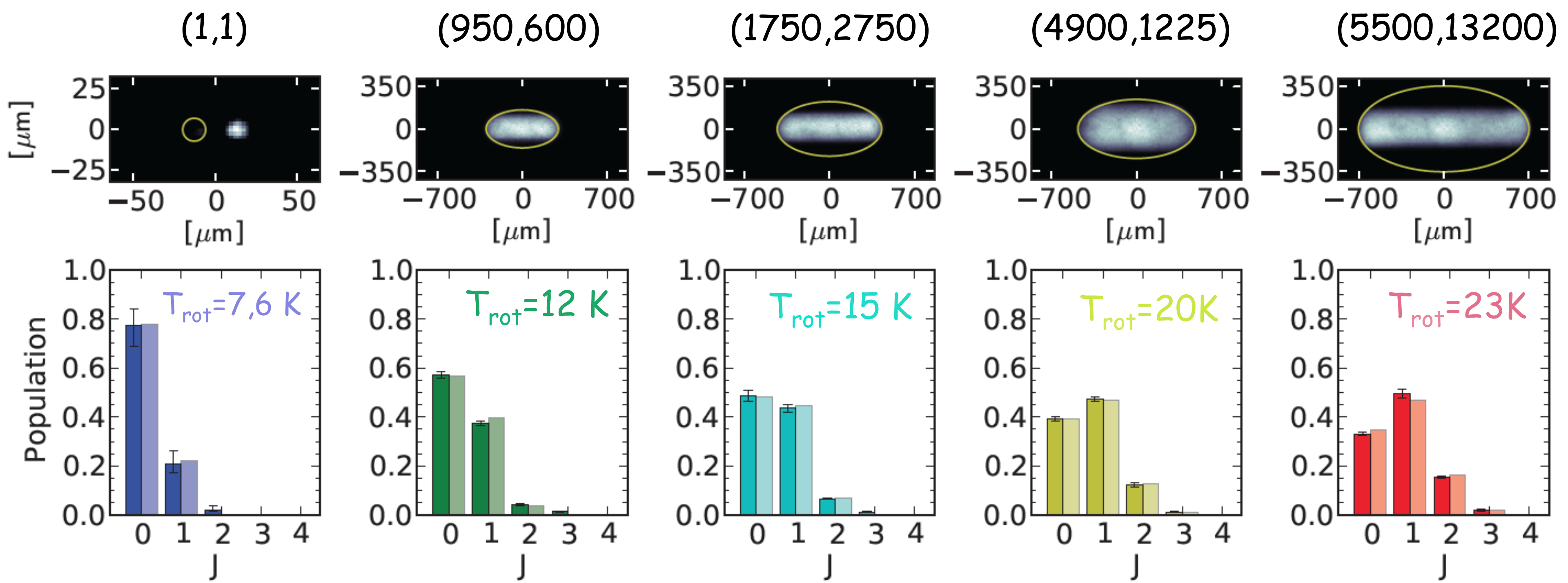
~0.01-0.1 Hz   Quite some room!   ~100-1000 Hz

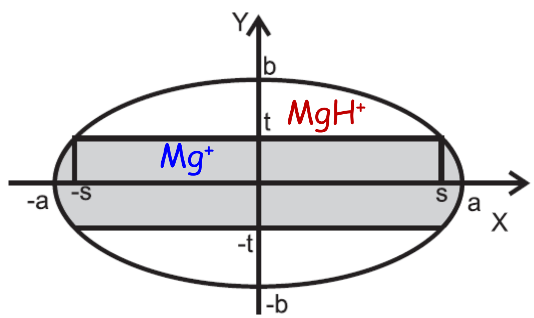
2) Will micromotion be a killer in rf quadrupole traps ?

Let's see !

No !

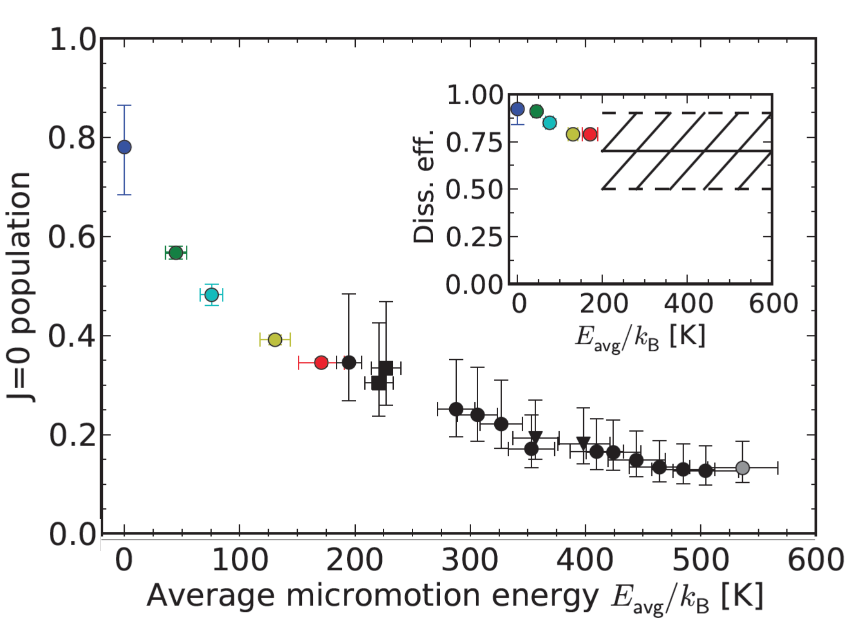
(N_{Mg},N_{MgH}):

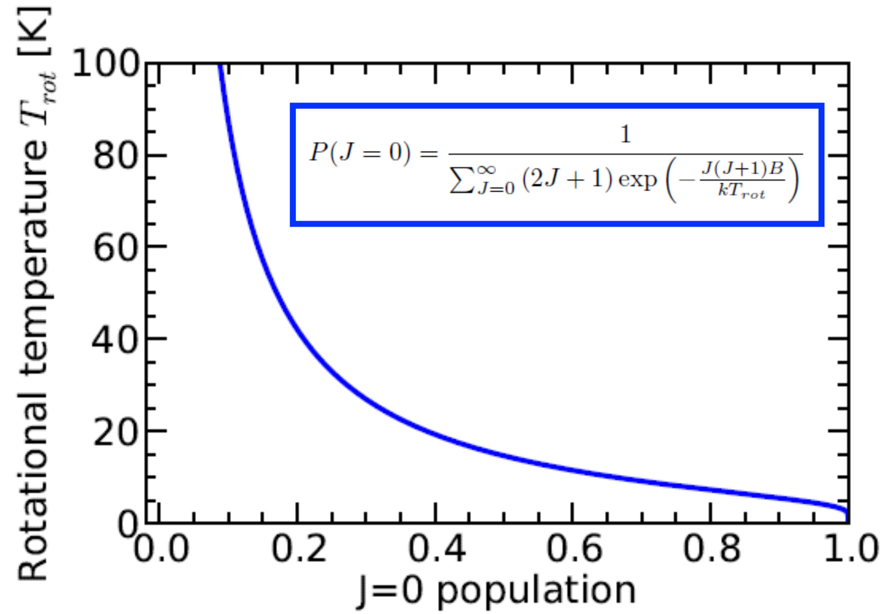


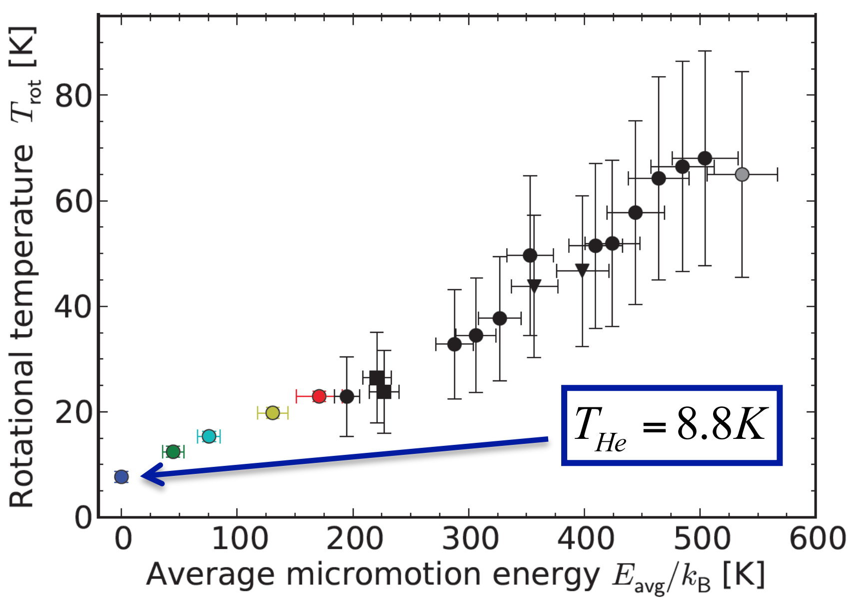


$$\boxed{E_{avg} = \frac{C}{5}(2b^2 + 3t^2), \quad C = \frac{1}{4}\frac{e^2U_{rf}^2}{M_{ion}\omega_{rf}^2 r_0^4}}$$

Rotational temp. vs. averaged micromotion energy





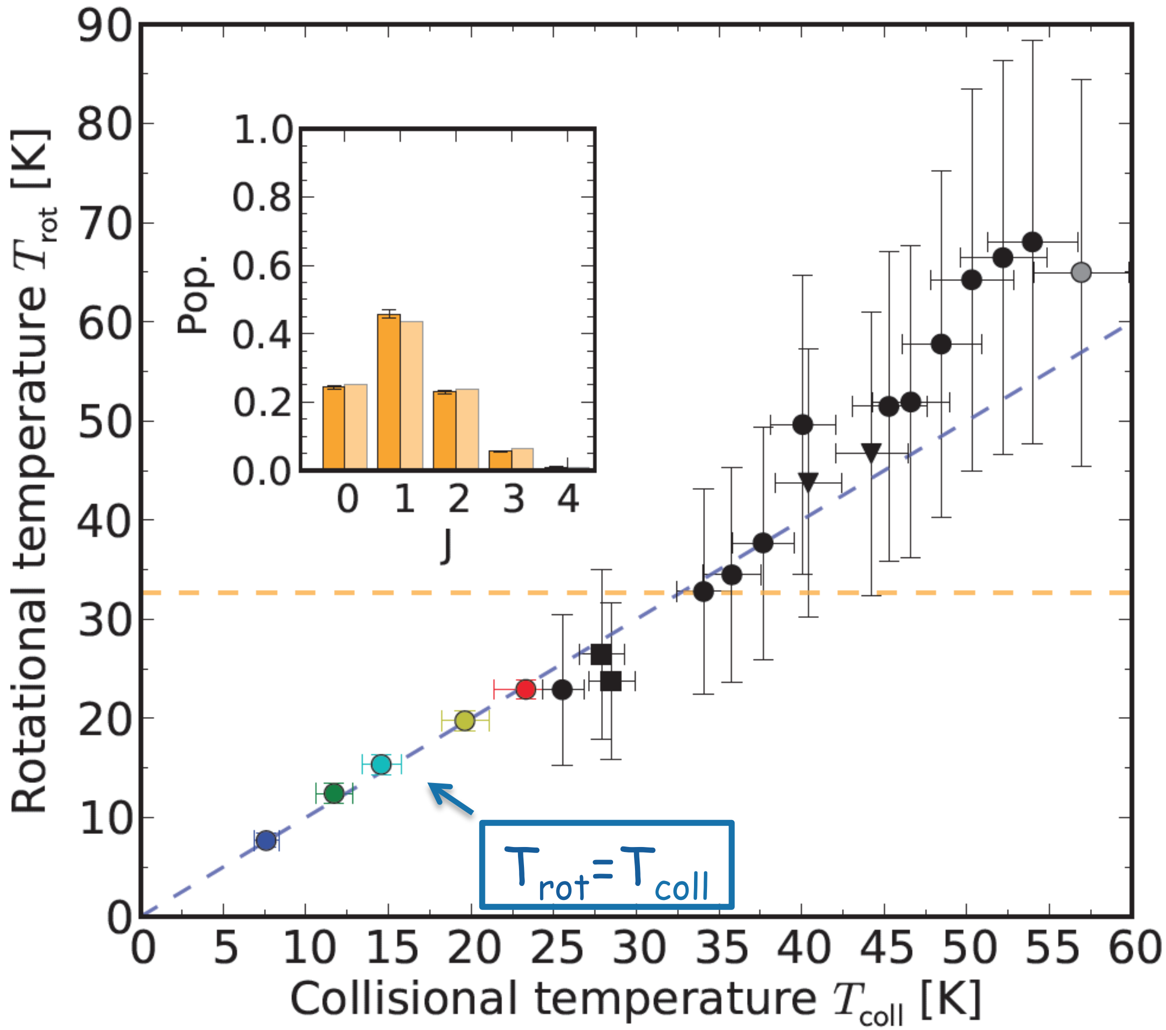


Expected collisional temperature

$$T_{coll} = \frac{25}{29} \boxed{T_{He}} + \frac{8}{87} E_{avg}$$

if the collisions are thermal !

Rotational temp. vs. averaged micromotion energy

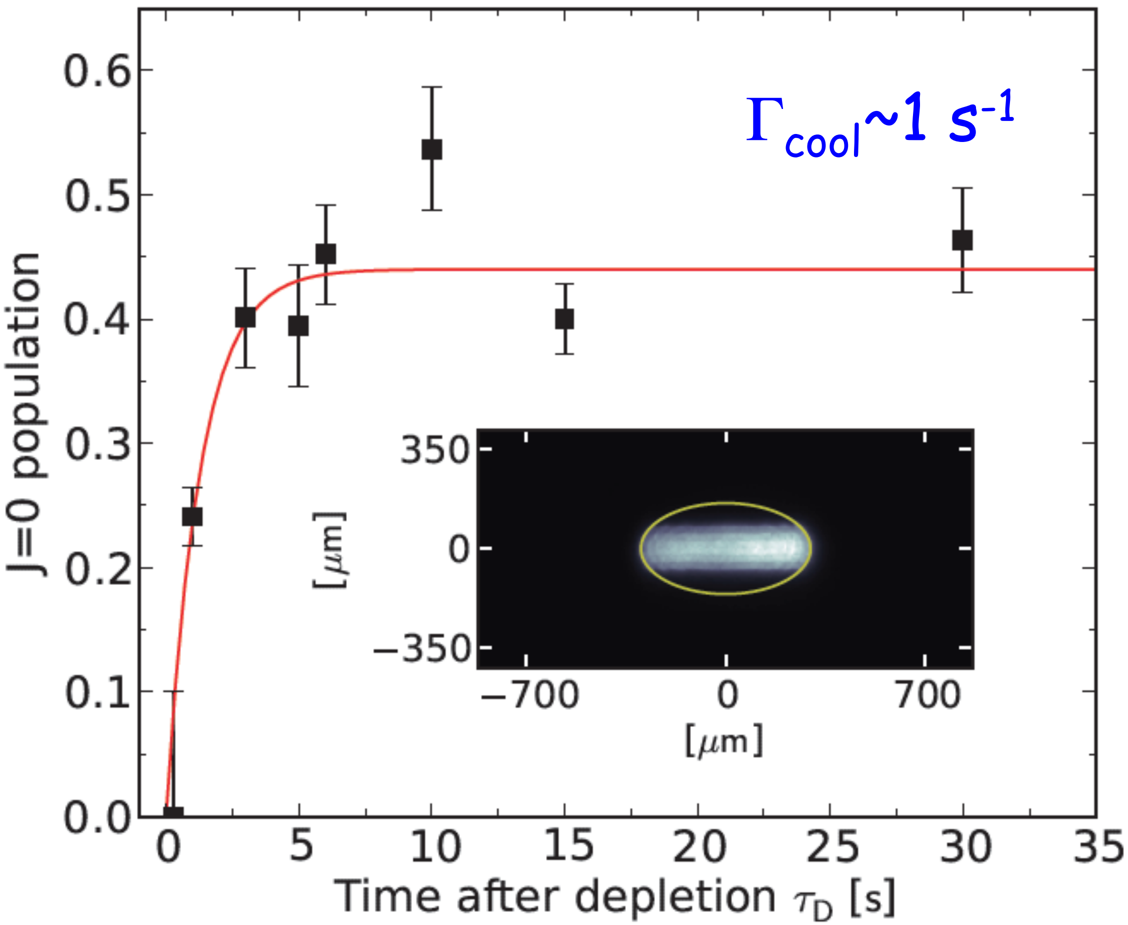


Message: Micromotion can be ***exploited*** to tune the rotational temperture !

Nature **508**, 76 (2014)

What about the cooling dynamics?

Refilling experiment at a He pressure/density 10x lower than in the main experiments



=> Γ_{cool}~10 s^{-1}

in experiments @ He density of ~10^{10}cm^{-3}

i.e.

4-5 orders of magnitude lower density than in usual buffer gas cooling settings !

Nature **508**, 76 (2014)

Rotational He buffer gas cooling of Coulomb crystallized molecular ions?

1) The helium temperature is orders of magnitudes higher than the melting temperature of Coul. Cryst. !!

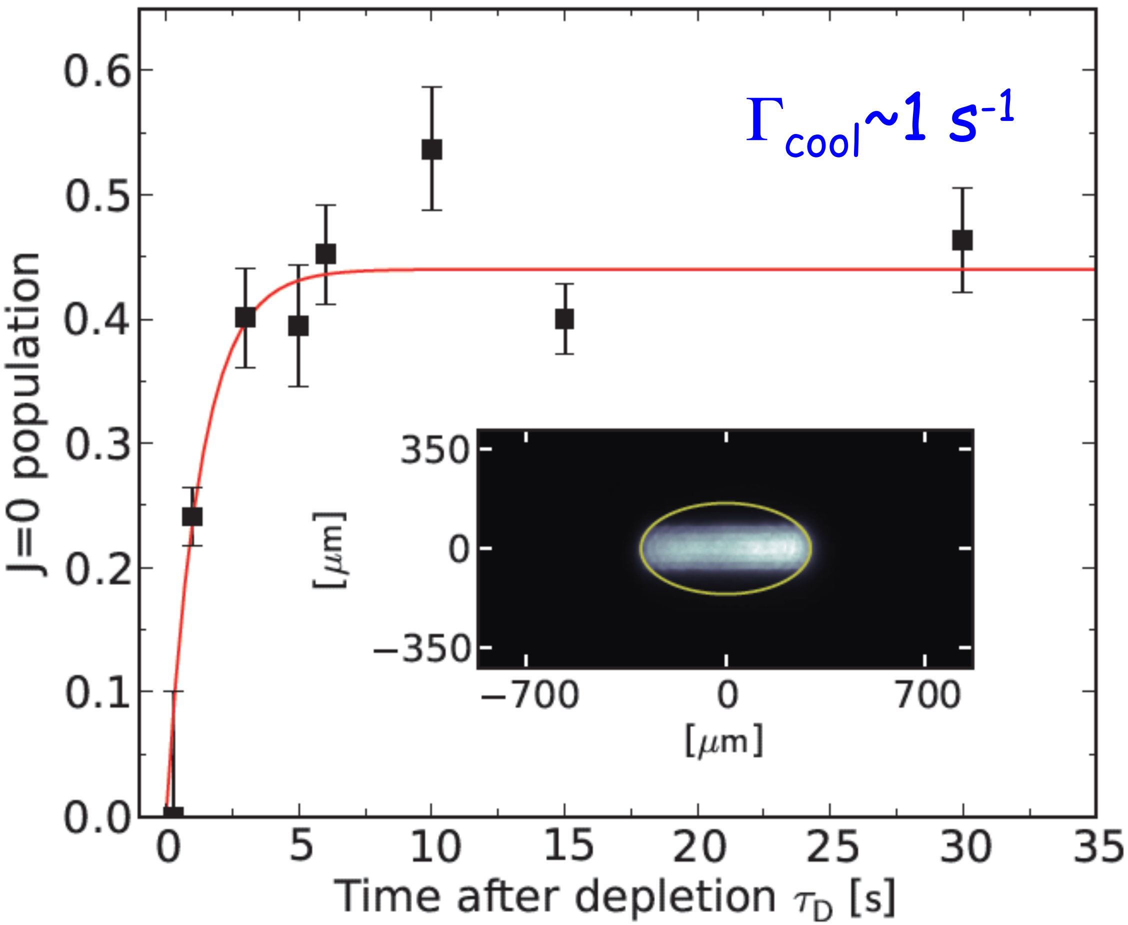
Basic requirements:

$$\Gamma_{\text{rot,heat}} < \Gamma_{\text{He coll.}} < \Gamma_{\text{symp. cool}}$$

~0.01-0.1 Hz   ~1-10 Hz   ~100-1000 Hz

What about the cooling dynamics?

Refilling experiment at a He pressure/density 10x lower than in the main experiments



=> Γ_{cool}~10 s^{-1}

in experiments
@ He density of
~10^{10}cm^{-3}

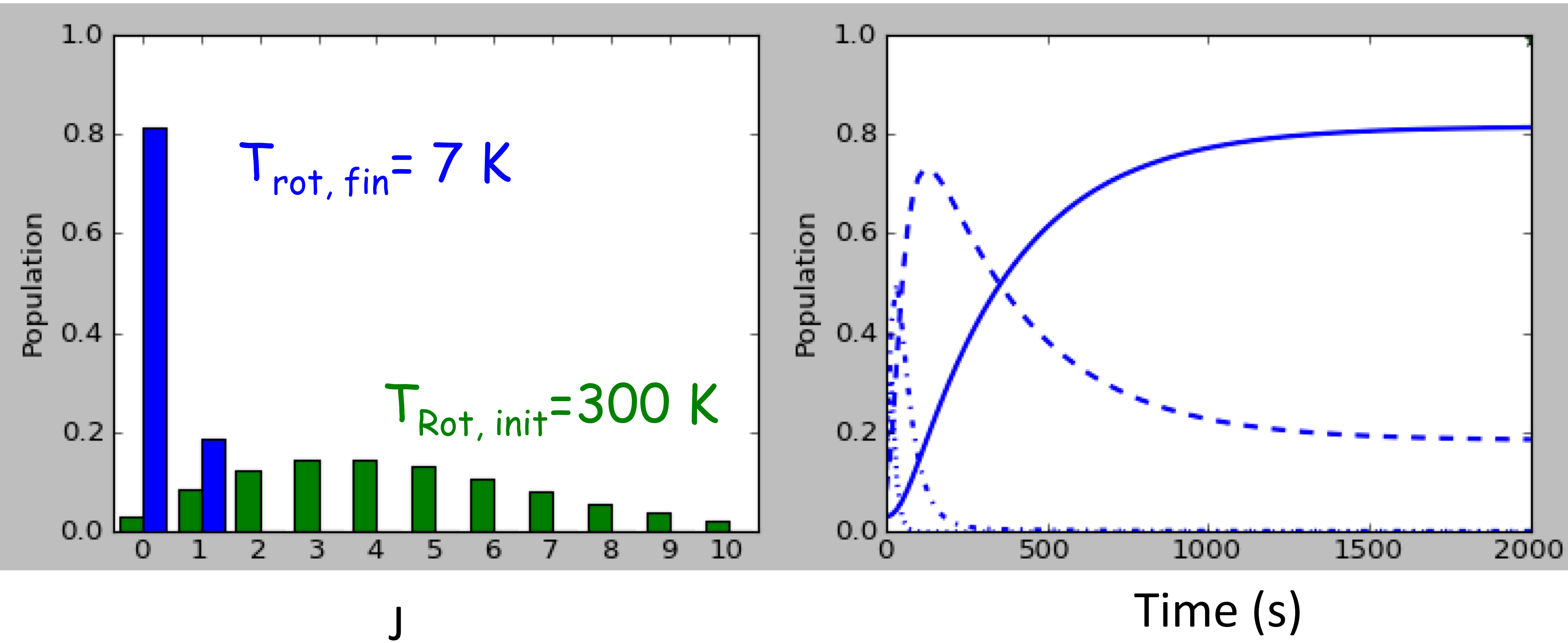
⇓

Plenty of time for coherent state manipulation, incl. resolved sideband cooling?!

Why not just rely on BBR equlibration?

Ex: T_{BBR}= 7 K

It could work!



But:

Cooling time needed: ~1800 s = ½ hour !

Will only work for polar molecules !

Colder internal temperatures by buffer gases?

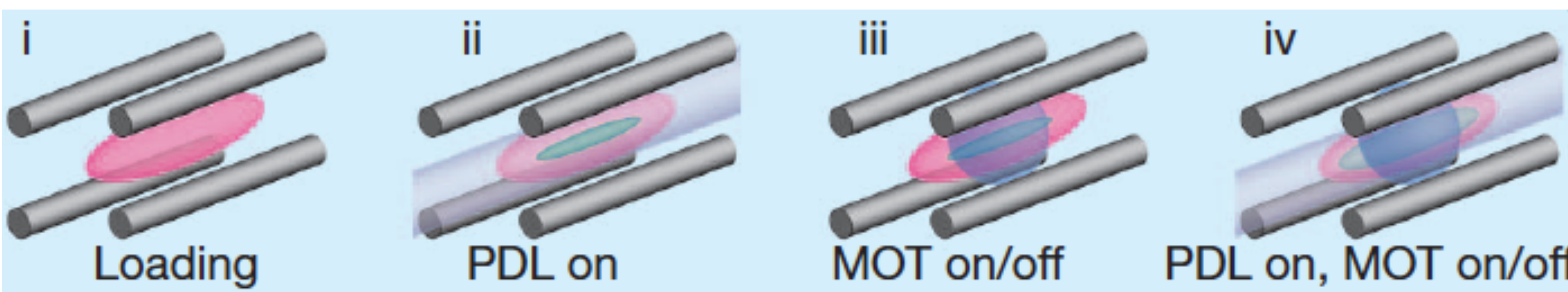
Use a buffer gas of laser cooled atoms !

490 | NATURE | VOL 495 | 28 MARCH 2013

Evidence for sympathetic vibrational cooling of translationally cold molecules

Wade G. Rellergert[1], Scott T. Sullivan[1], Steven J. Schowalter[1], Svetlana Kotochigova[2], Kuang Chen[1] & Eric R. Hudson[1]

$BaCl^+$ ions overlayed by a few mK cold Ca atoms in a Magneto Optic Trap (MOT)



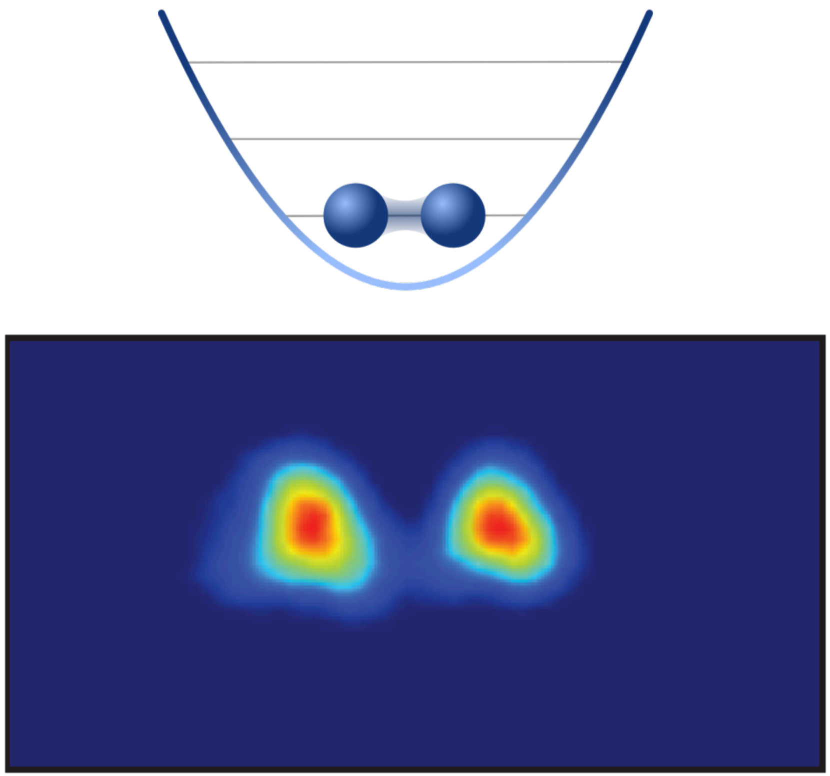
First results on vibrational cooling:

$P_{v=0}$= 80% (T_{vib}~300 K) -> $P_{v=0}$= 90% (T_{vib}~200 K)

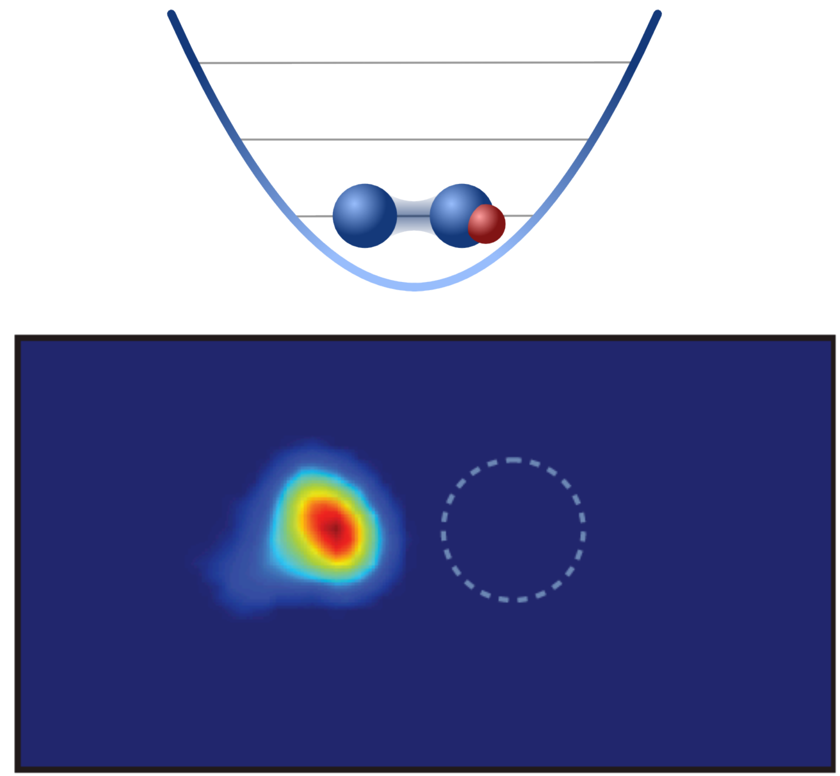
Potential problems with reactive scattering

Sideband cooling of a molecular ion in a buffer gas cooling setting?

So far (without He!):



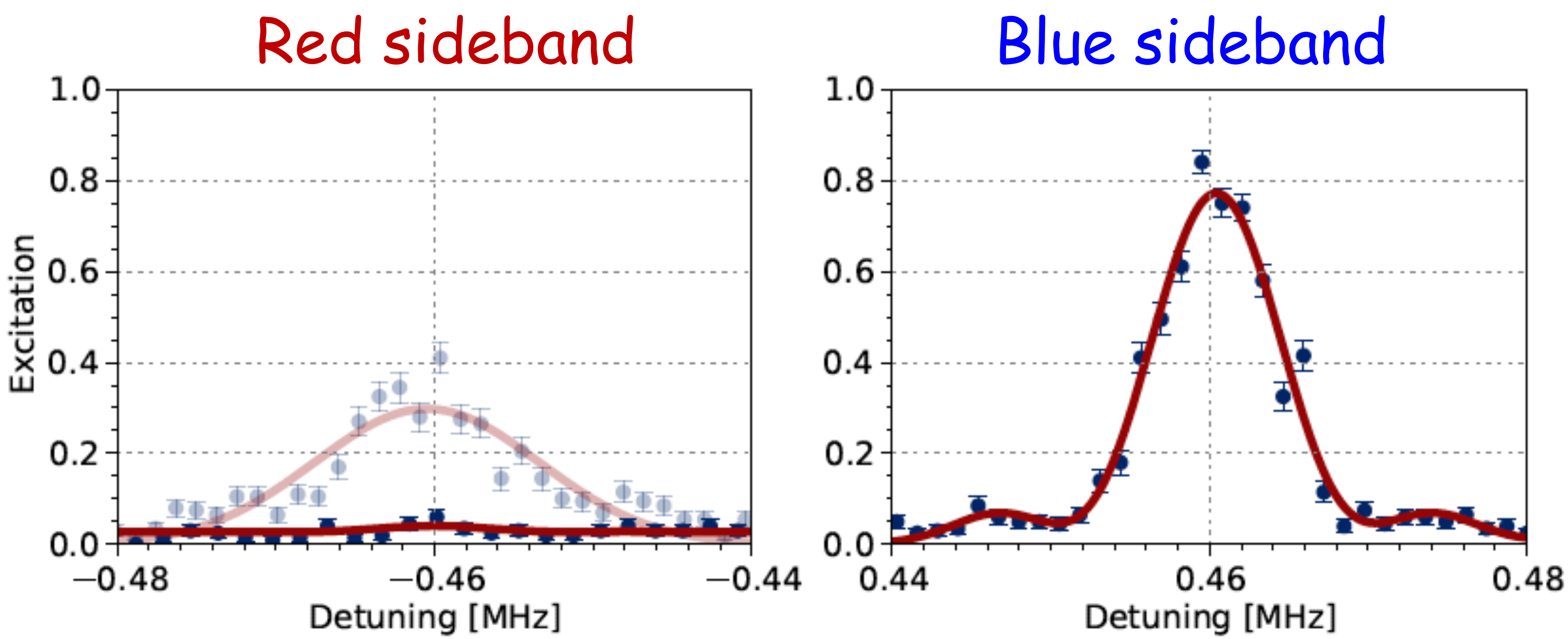
$^{40}Ca^{+} + {}^{40}Ca^{+}$



$^{40}Ca^{+} + {}^{40}CaO^{+}$

Ph.D. Thesis, Gregers Poulsen, 2011, Aarhus University

Continuoues sideband cooling of out-of-phase mode of the $^{40}Ca^{+}$ - $^{40}CaO^{+}$ systems



Ground state population: P_0=99±1%

in τ_{SB}~10 ms

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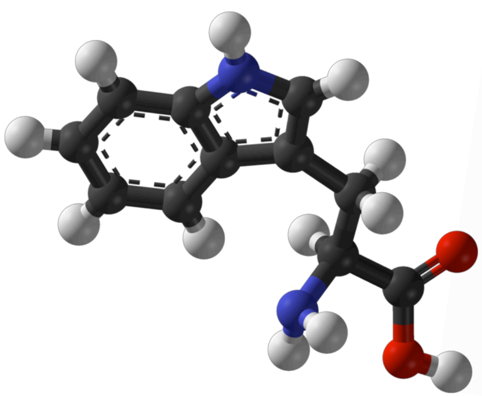
Quantum logic spec. of buffer gas cooled mol. ions !?

P. Schmidt *et al.*: $^{9}Be^{+}$ - $^{27}Al^{+}$ [Science **309**, 749 (2005)]

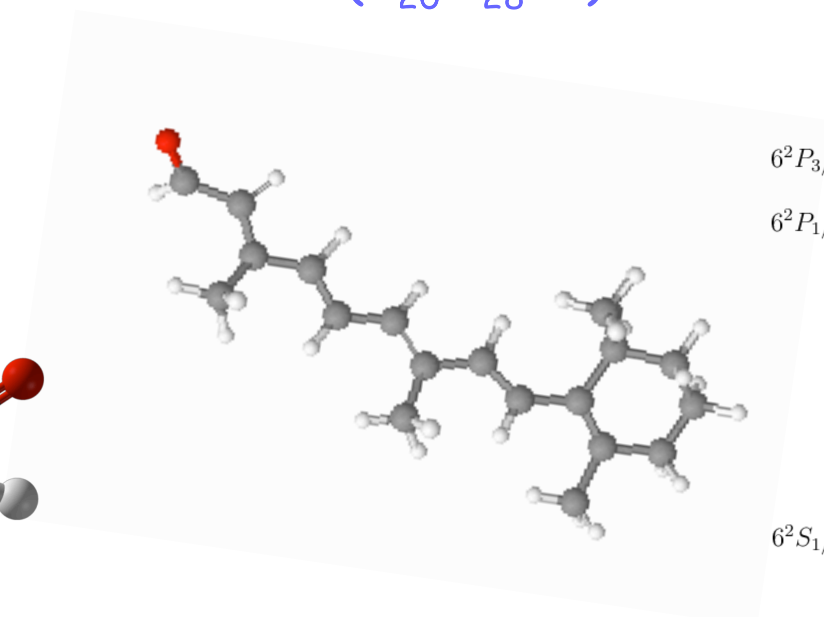
Experiments with biological relevant molecular ions

Tryptophan$^+$
($C_{11}H_{12}N_2O_2^+$)



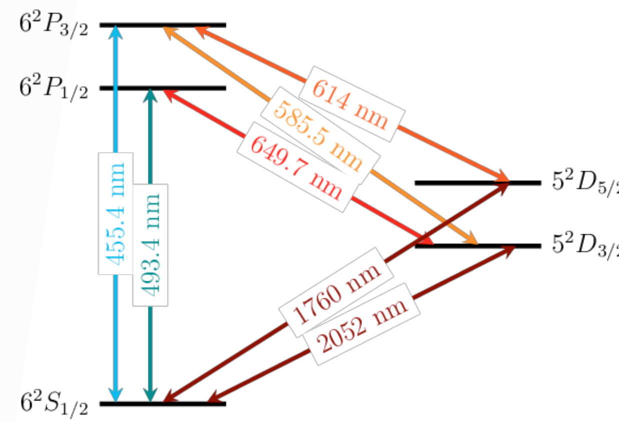
Mass: 204 a.m.u

Retinal$^+$
($C_{20}H_{28}O^+$)



Mass: 284 a.m.u

Ba$^+$



Mass: 138 a.m.u

Buffer gas cooling:

$$\boxed{T_{\text{coll}} = \frac{m}{(m_{\text{He}}+m)}T_{\text{He}} + \frac{2m_{\text{He}}}{3(m_{\text{He}}+m)}\frac{E_{\text{avg}}}{k_{\text{B}}}}$$