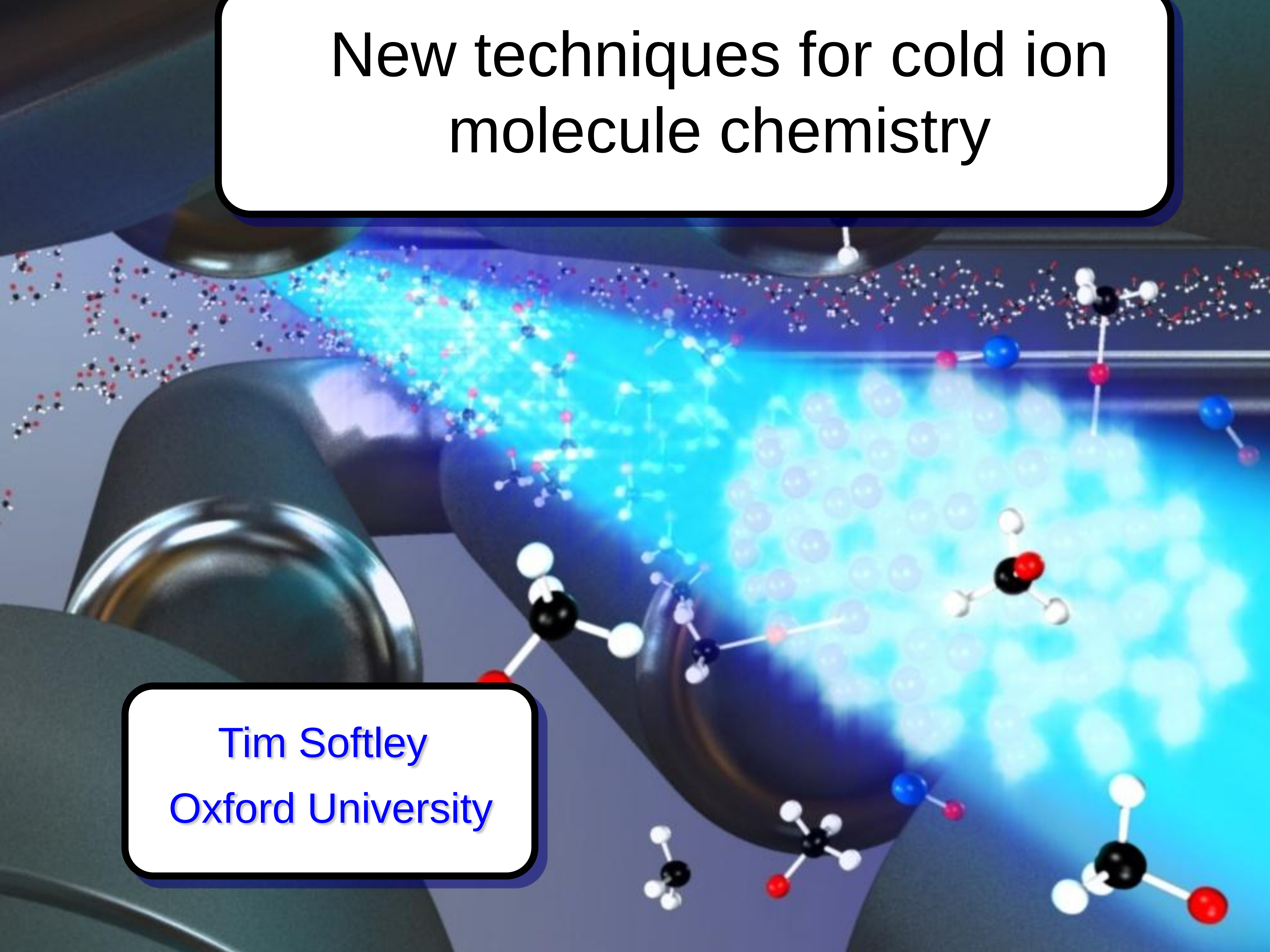
New techniques for cold ion molecule chemistry



Tim Softley
Oxford University

Why Chemistry at temperatures ≤ 1K?

- A new physical regime for chemical reactions
- Is the cold/ultracold an ultimate medium for control of chemical processes?
- Critical test for potential energy surfaces and quantum dynamics calculations – long range interactions, non-adiabatic effects

Many body effects are also very important to chemists

Target reactive collisions involving polyatomics

Multiple outcomes

e.g., $NH_3^+ + ND_3$

$\rightarrow NH_3 + ND_3^+$ (electron transfer)

$\rightarrow NH_2 + ND_3H^+$ (proton transfer)

$\rightarrow NH_3D^+ + ND_2$ (D atom transfer)

Isotopomer variations

e.g, $NH_2D^+ + ND_3$

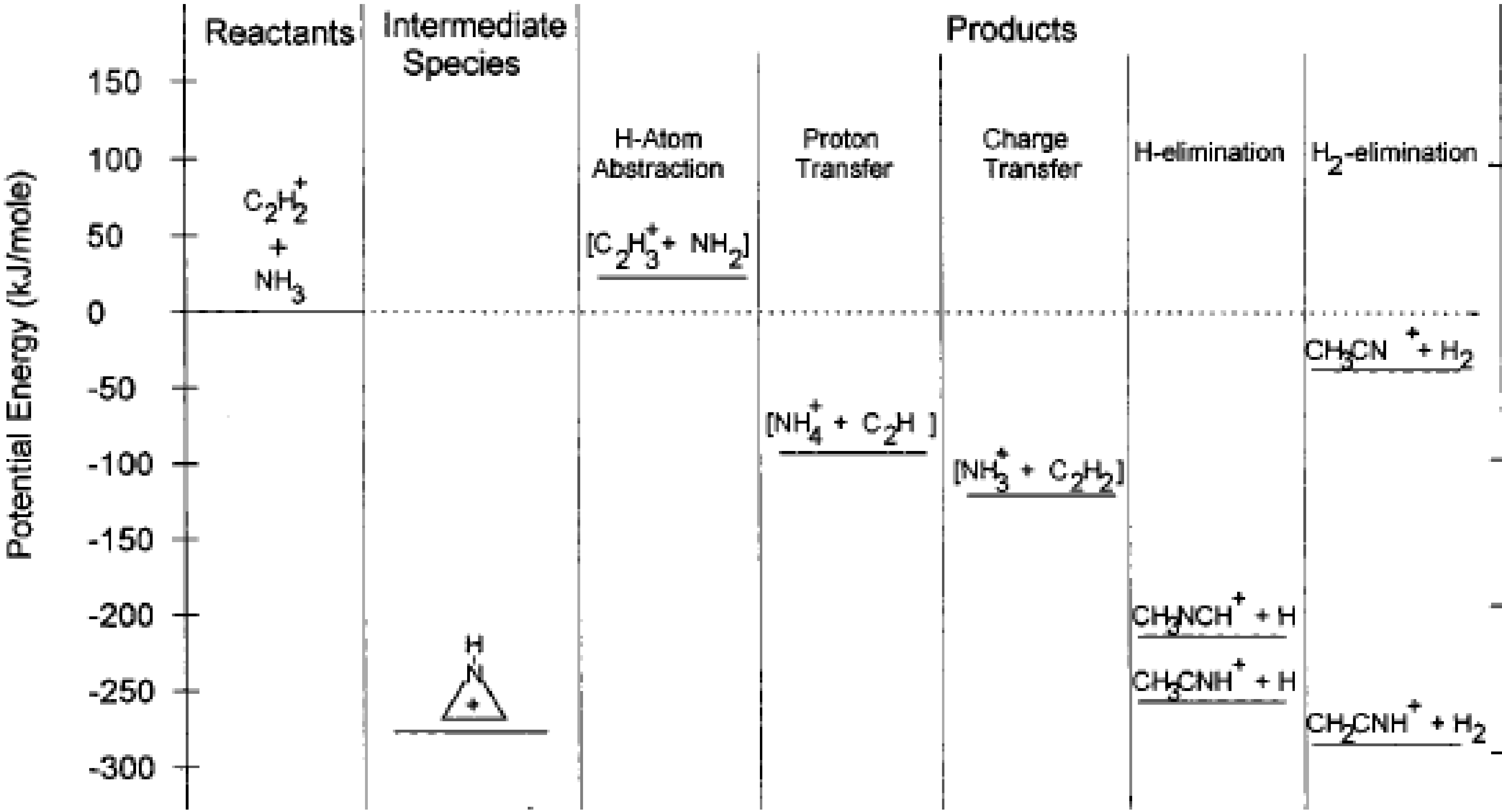
$\rightarrow NH_2 + ND_4^+$ (deuteron transfer)

$\rightarrow NHD + ND_3H^+$ (proton transfer)

More degrees of freedom – products and reactants

Vibrational (Bending, twisting, stretching....), rotational states, alignment etc.

Future directions: Reacting $C_2H_2^+$ with ND_3



Anderson et al J. Phys. Chem. A, 101, 36, 1997

Long term objectives…
dynamics not just kinetics

Measure cross-sections for fully state-selected, collision-energy selected, cold reactive collisions - chemically interesting and diverse systems

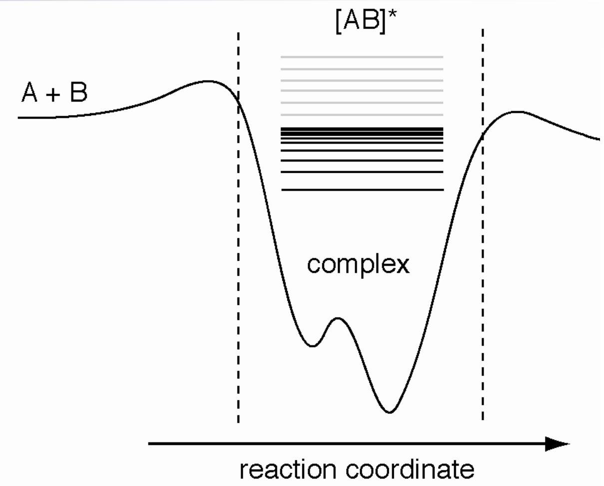
Ideally: State/product branching ratios
Differential cross sections

Comparison of experiment with high quality quantum scattering calculations + PE surfaces (non-adiabatic effects etc)

In the ‘cold’ region – wavelength typically comparable with van der Waals radius

CH_3F	Mean Velocity $(8kT/\pi m)^{1/2}$	λ (deBroglie) $p = h/\lambda$
300 K	400 m s^{-1}	0.032 nm
3 K cold	40 m s^{-1}	0.32 nm
30 mK cold	4 m s^{-1}	3.2 nm
300 μK ultracold	40 cm s^{-1}	32 nm

ion-molecule reactions



- Very high (single-particle) sensitivity for detecting occurrence of reactions

- Deep ion traps – ionic products captured

- No barrier or low barrier – enhanced rates at low T – capture process.
- $1/r^2$ or$1/r^4$ leading term in V(r))
- Photoionization techniques (e.g., REMPI) for for internal state selection
- Astrophysical interest

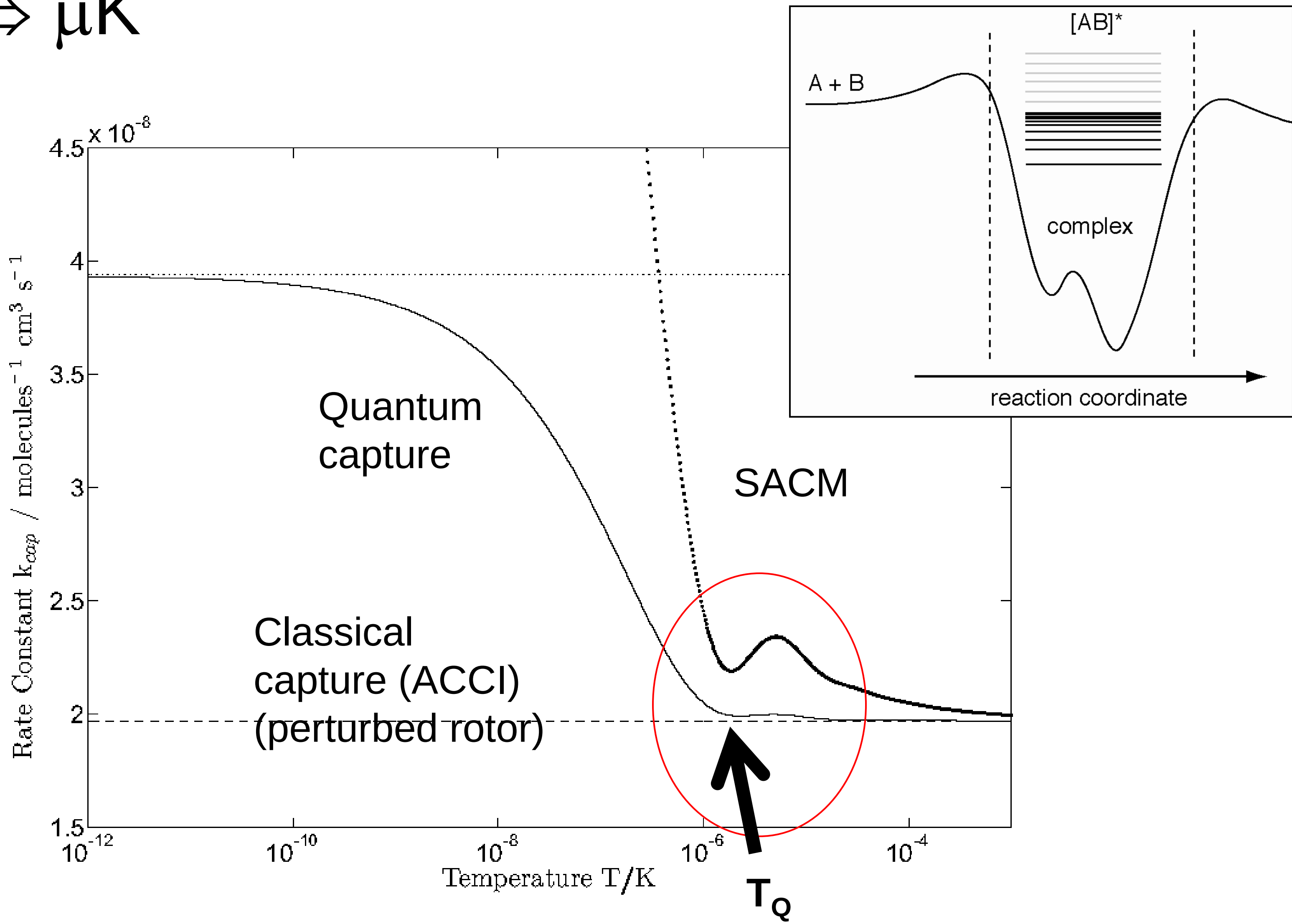
Capture theories: predicted divergence temperature of classical and quantum capture rates ⇒ μK

$H_3^+ + HCl$

L Harper, M Bell, T Softley (unpublished)

See also E. E. Nikitin, J. Troe

e.g., JCP 120, 9989 (2004).



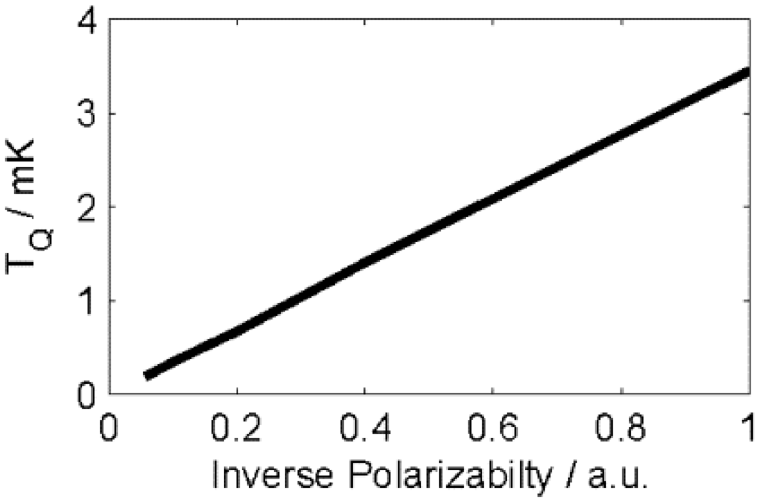
Quantum capture predictions

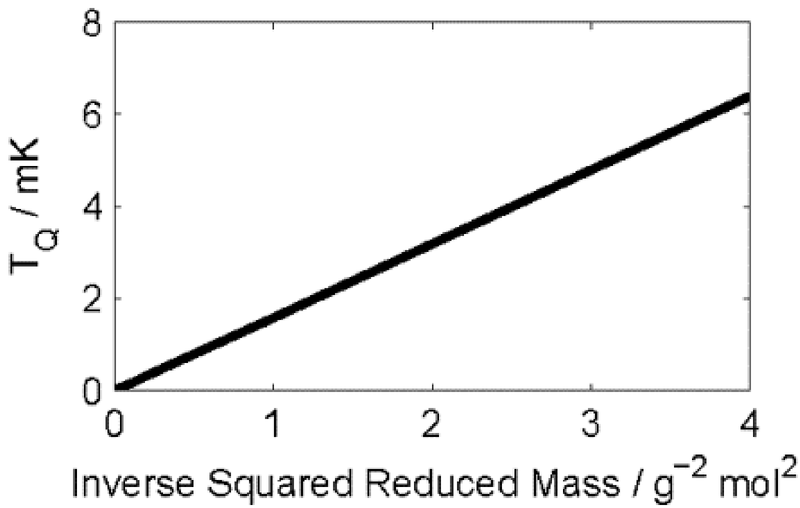
For Ion non-polar molecule collisions (Langevin)

$$T_Q \approx 0.3 \frac{\hbar^4}{(4\pi\epsilon_0)^2 q^2 \mu^2 \alpha k_B}$$

For Ion- dipolar molecule collisions

$$T_Q \approx 0.35 \frac{B}{q^2 \mu_D^2 \mu^2 k_B}$$





(L. Harper, M. Bell,, T Softley, unpublished)

Quantum Capture Calcs: Dependence on body fixed projection quantum number for H_3^+ + HCl (J=2)

(L. Harper, M. Bell,, T Softley, unpublished)

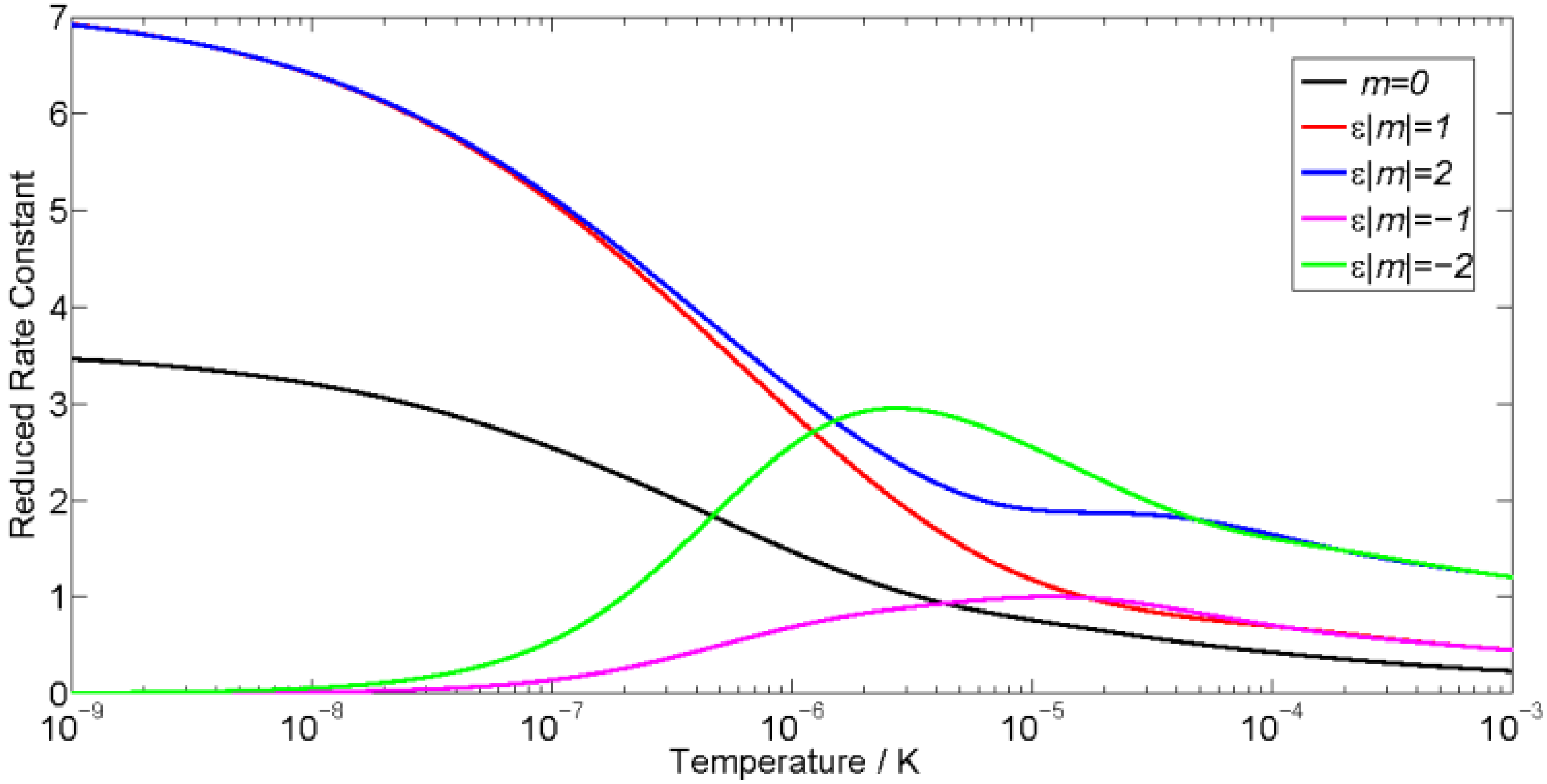
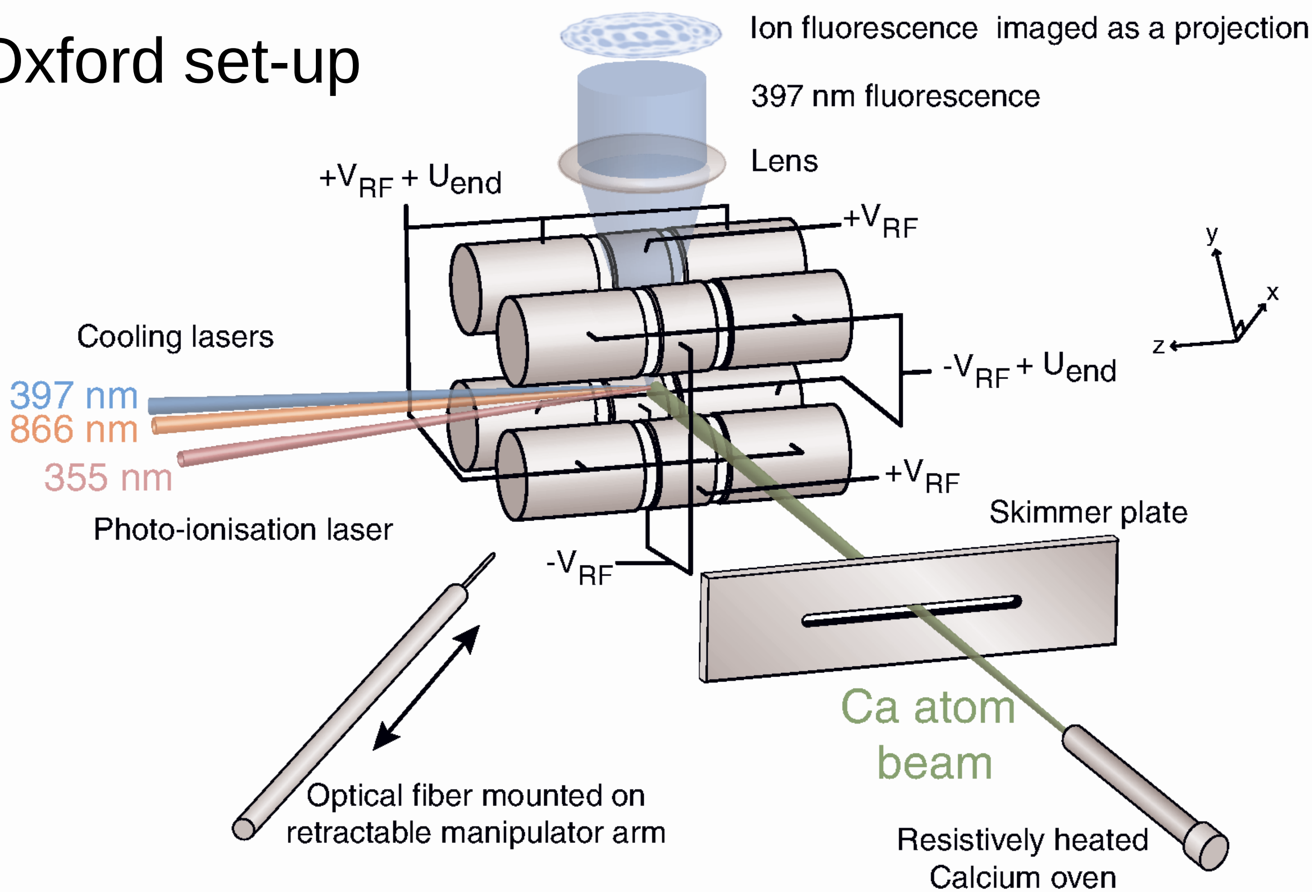
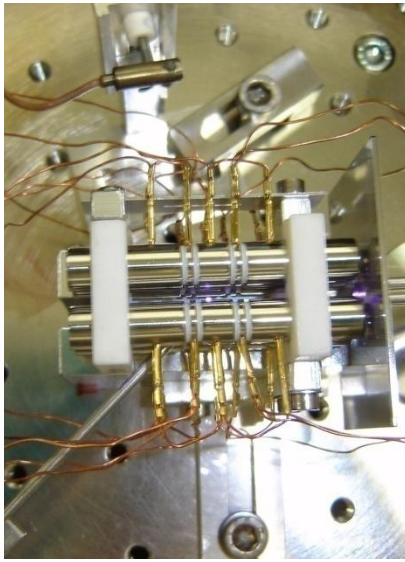


Figure 1.11: State specific reduced rate constants for the j=2 rotational manifold between 1 nK and 10 mK.

laser- cooled ions in a radiofrequency trap

Oxford set-up

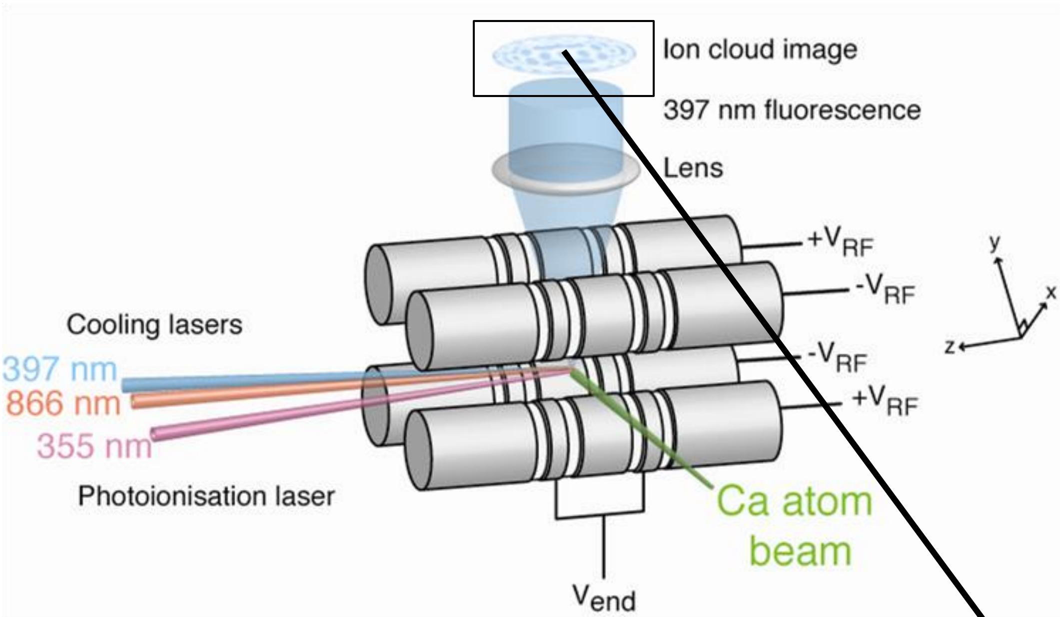


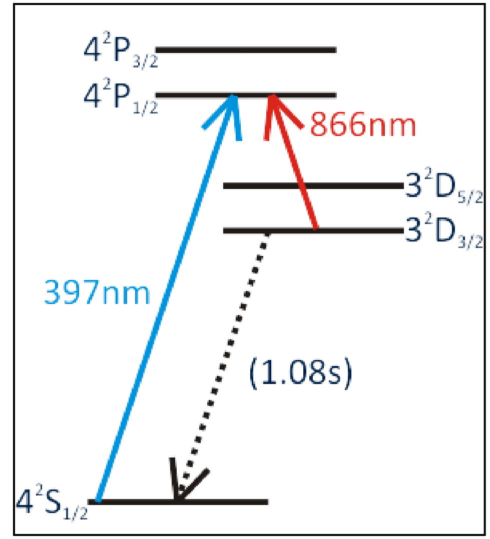


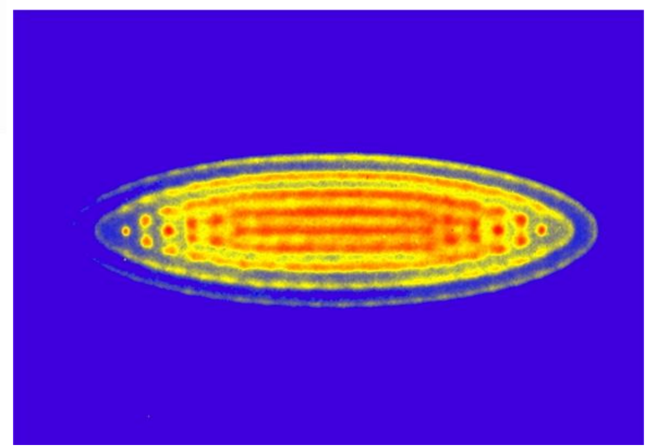
10 cm

•Ca^+ ions by multiphoton ionization of Ca at 355 nm in centre of linear Paul trap

Coulomb Crystal formed by laser cooling

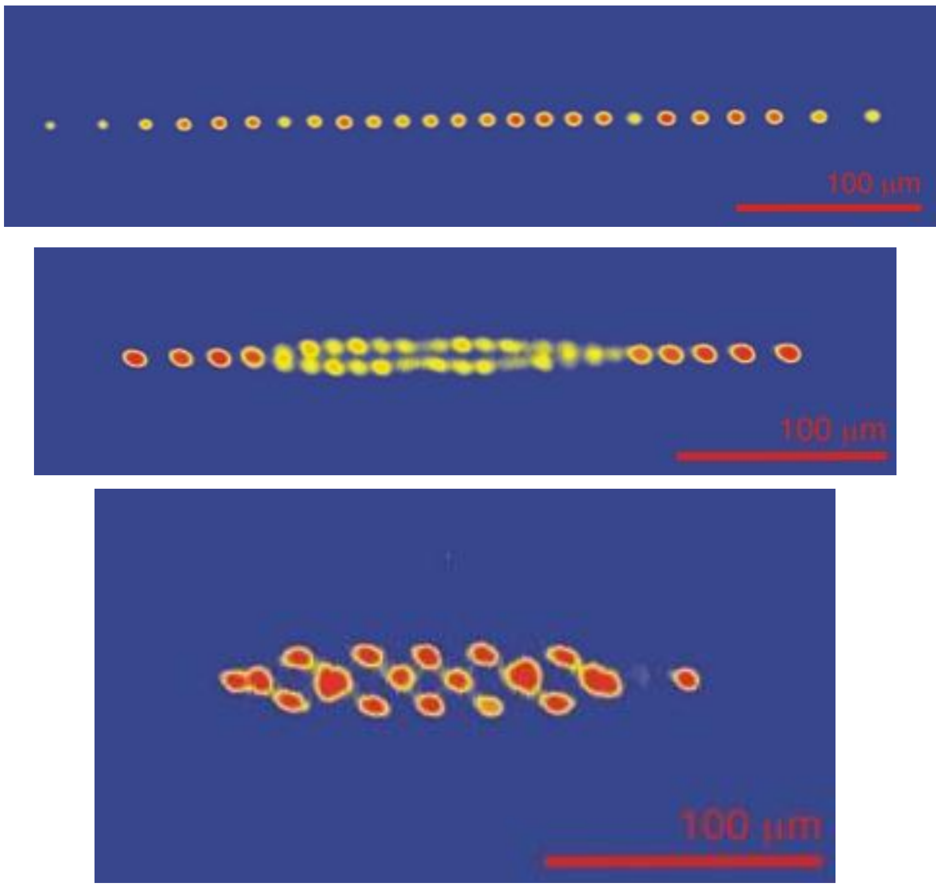




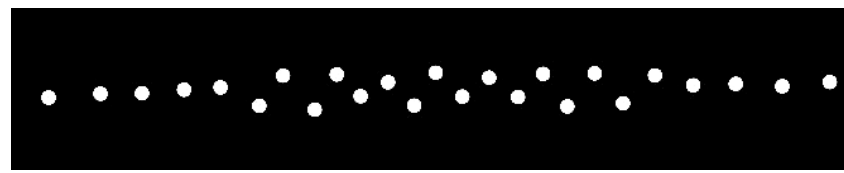


V_{RF}= 200 V;
Ω_{RF}= 2π x 3.8 MHz
Trap depth
xy: ~7.5 eV; z: ~1.2 eV

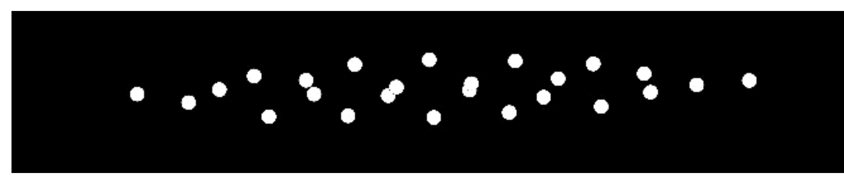
Effective temperature (primarily micromotion)



Effective T = 15 mK



Effective T = 260 mK

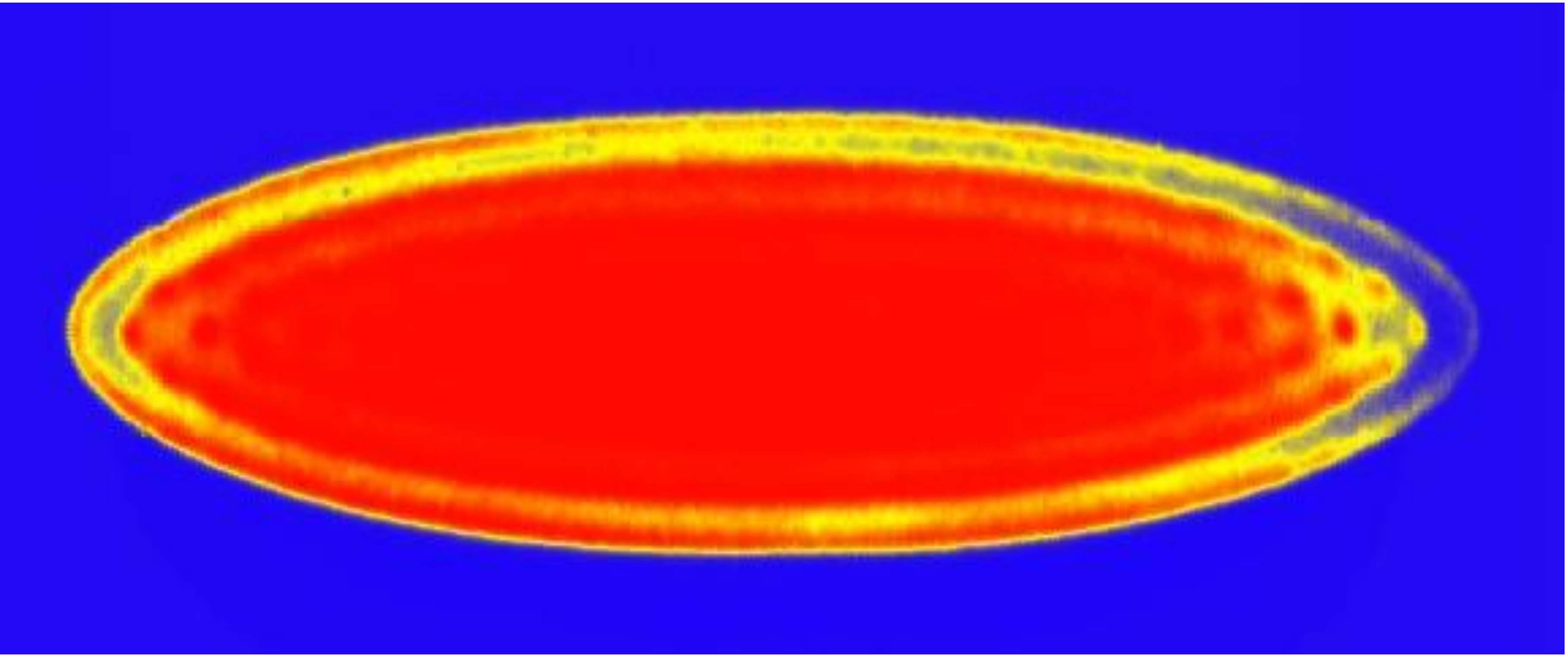


Effective T = 1.7 K

Experiment

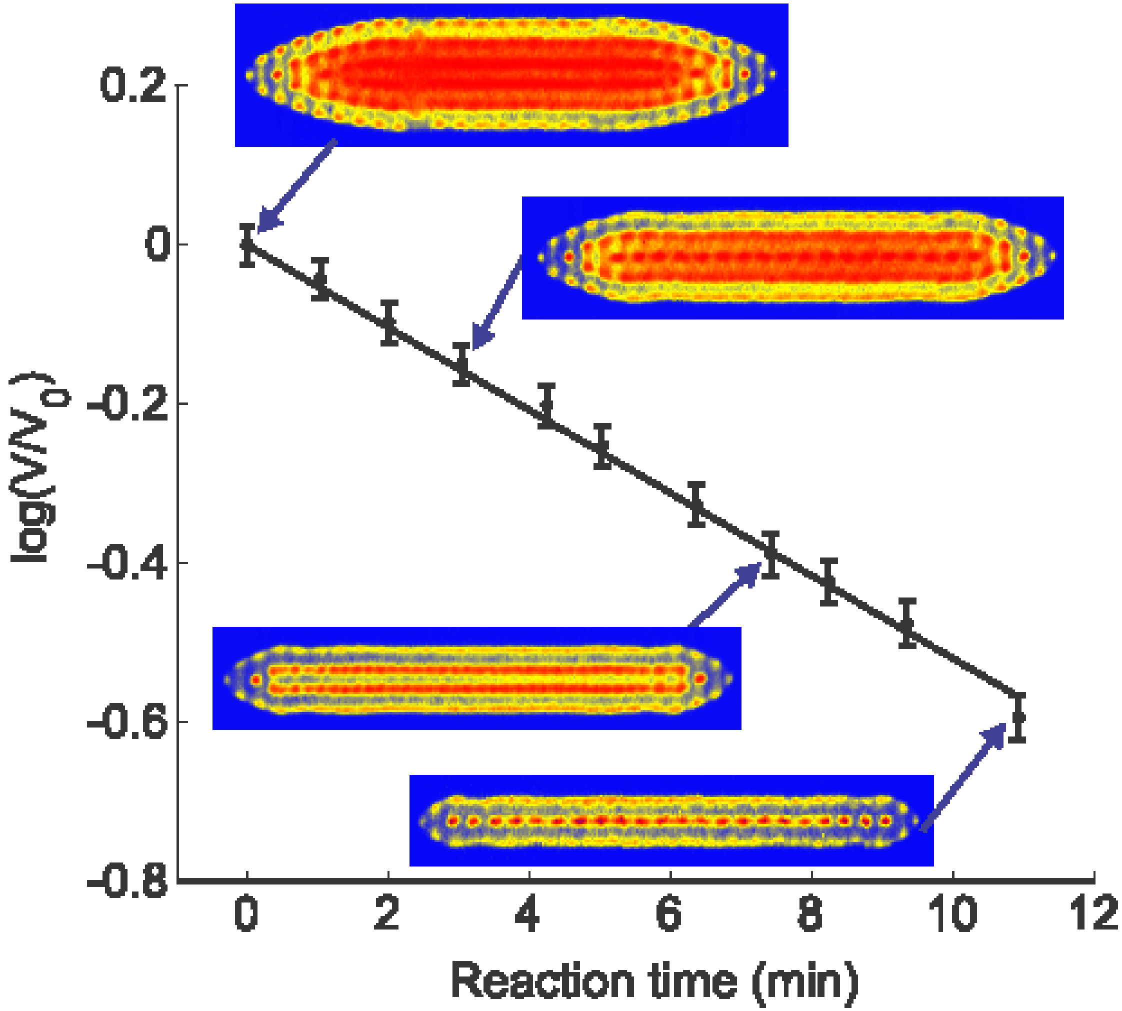
Molecular dynamics simulation

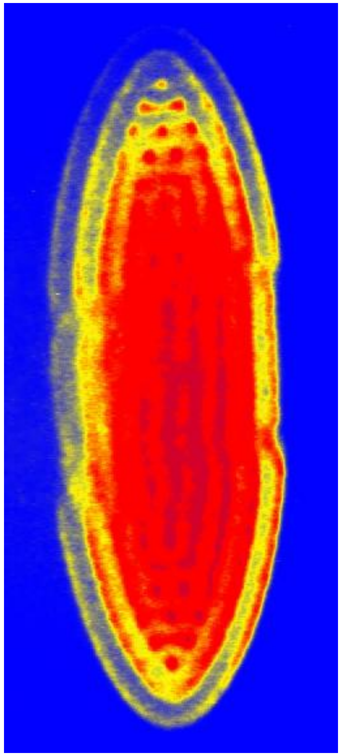
$Ca^{+} + CH_3F \rightarrow CaF^{+} + CH_3$



Require stable ion trapping to be long compared to rate of reaction

Apparent volume depletion of large Ca^+ crystal versus time through reaction with CH_3F



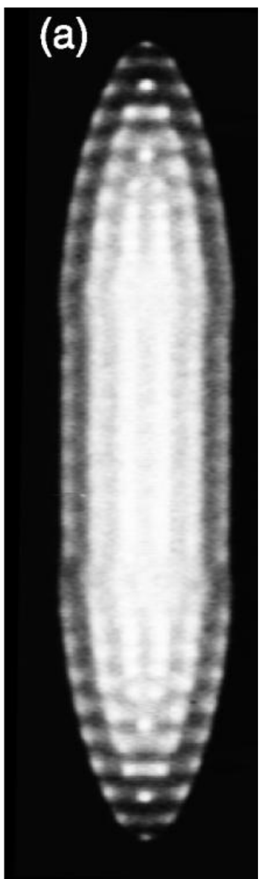


Density and size remains constant – number of fluorescing reactant ions depleted .

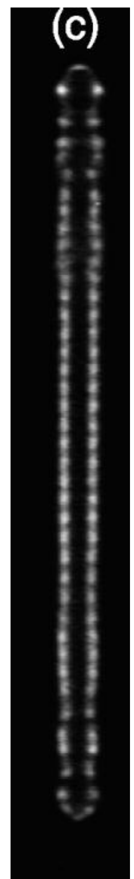
Pseudo first order – CH_3F flux is constant

Sympathetic cooling of product ions into calcium crystal – products are fully trapped.

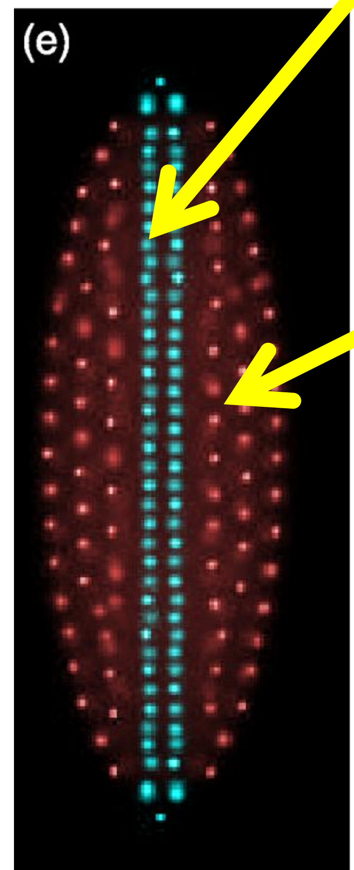
Start



End



Simulation



Ca^+

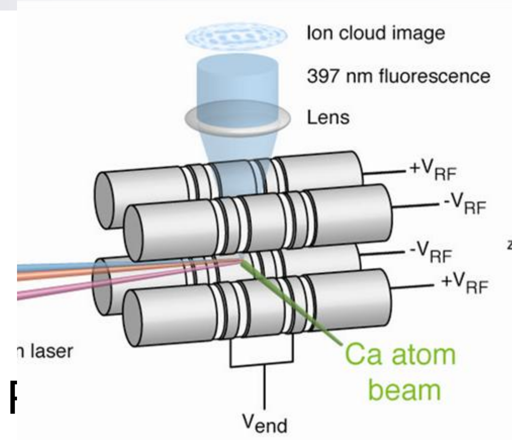
CaF^+

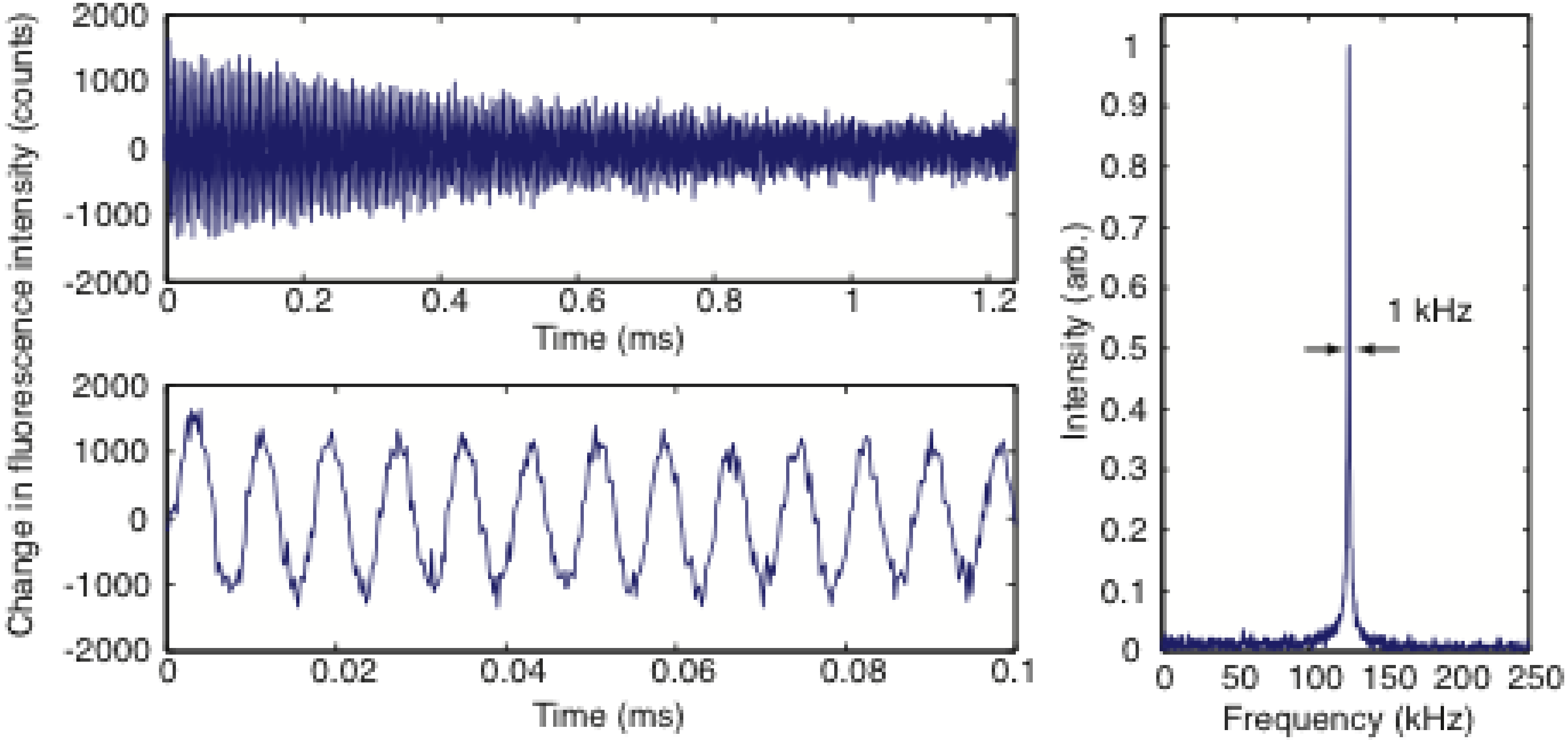
Heavier

⇒

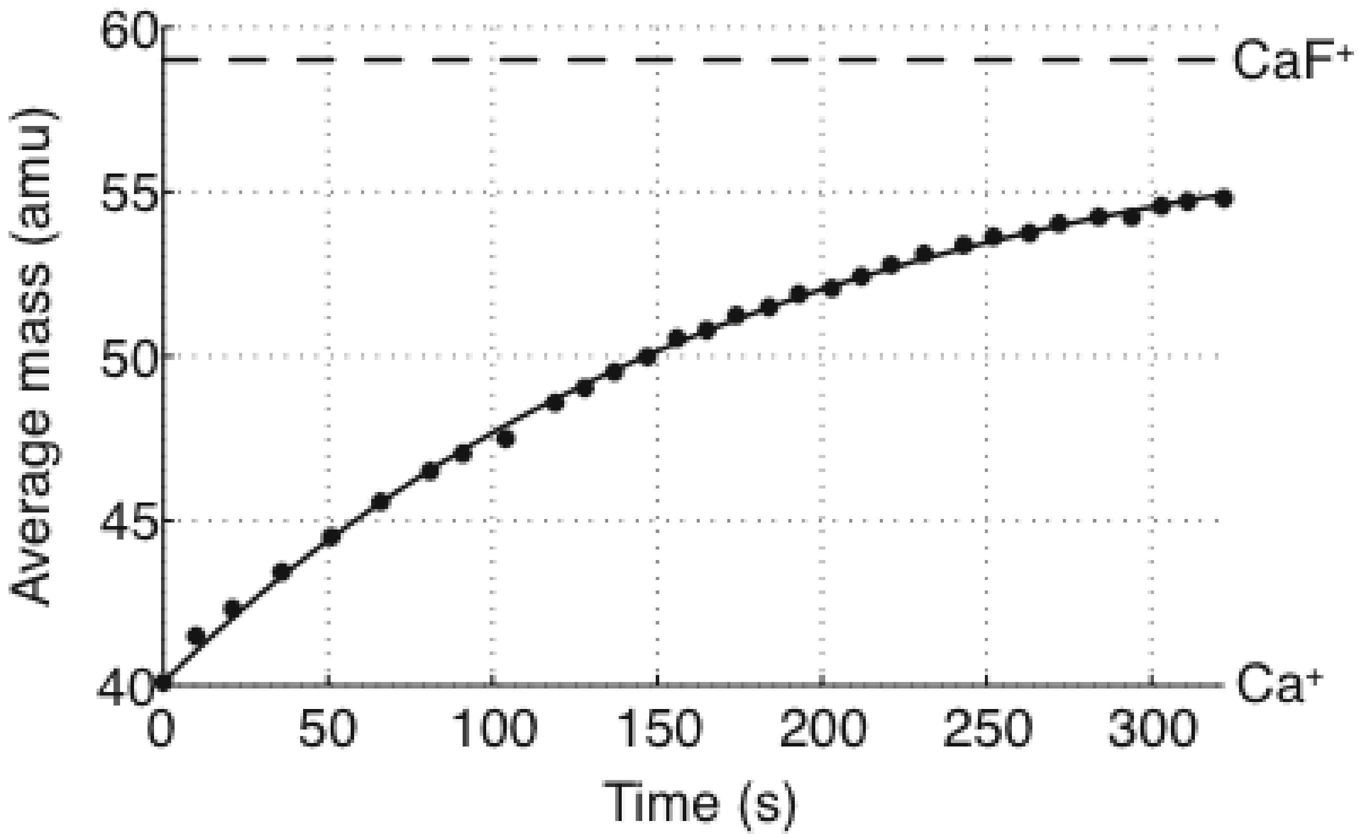
Outside

Weigh crystal by pulsed axial excitation of motion of whole crystal
30 mV amplitude, duration 1μs,
rep rate 500Hz



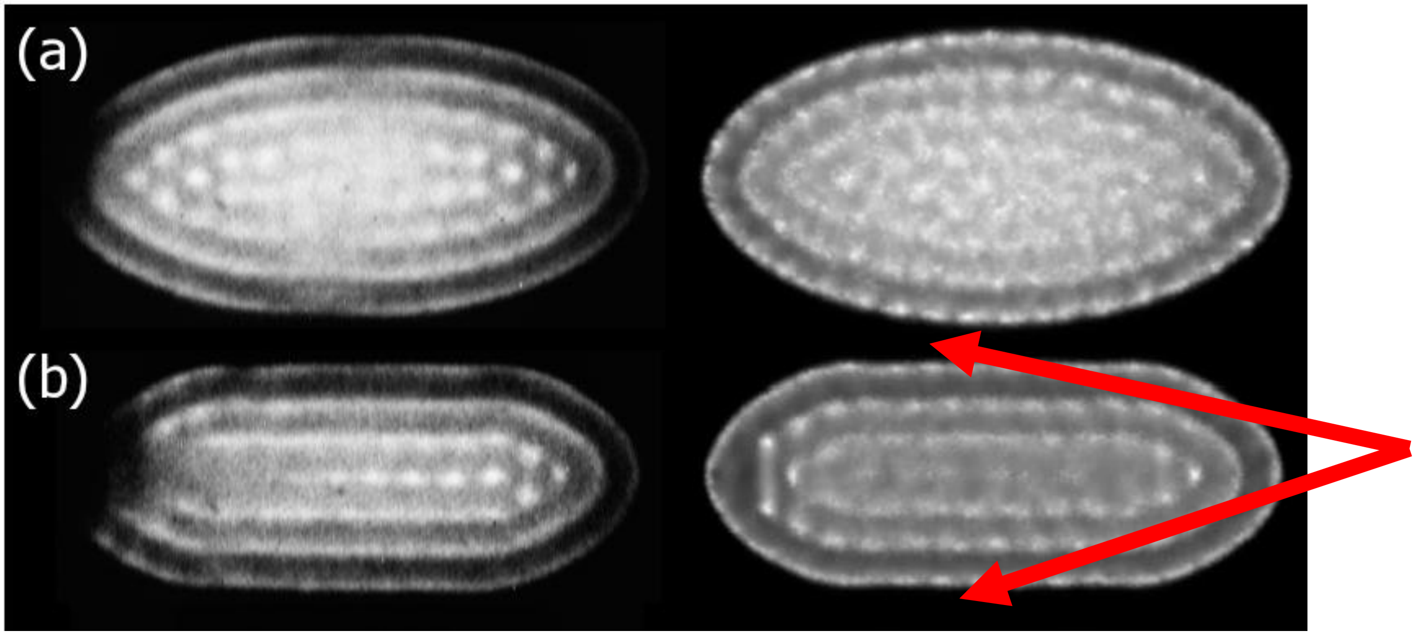


Example reaction: $Ca^{+} + CH_3F$



$$\omega_{COM}(t) = \omega_0 \sqrt{\frac{m_0}{m_{av}(t)}}$$

Sympathetically cooled molecular ions



Ca^+ only

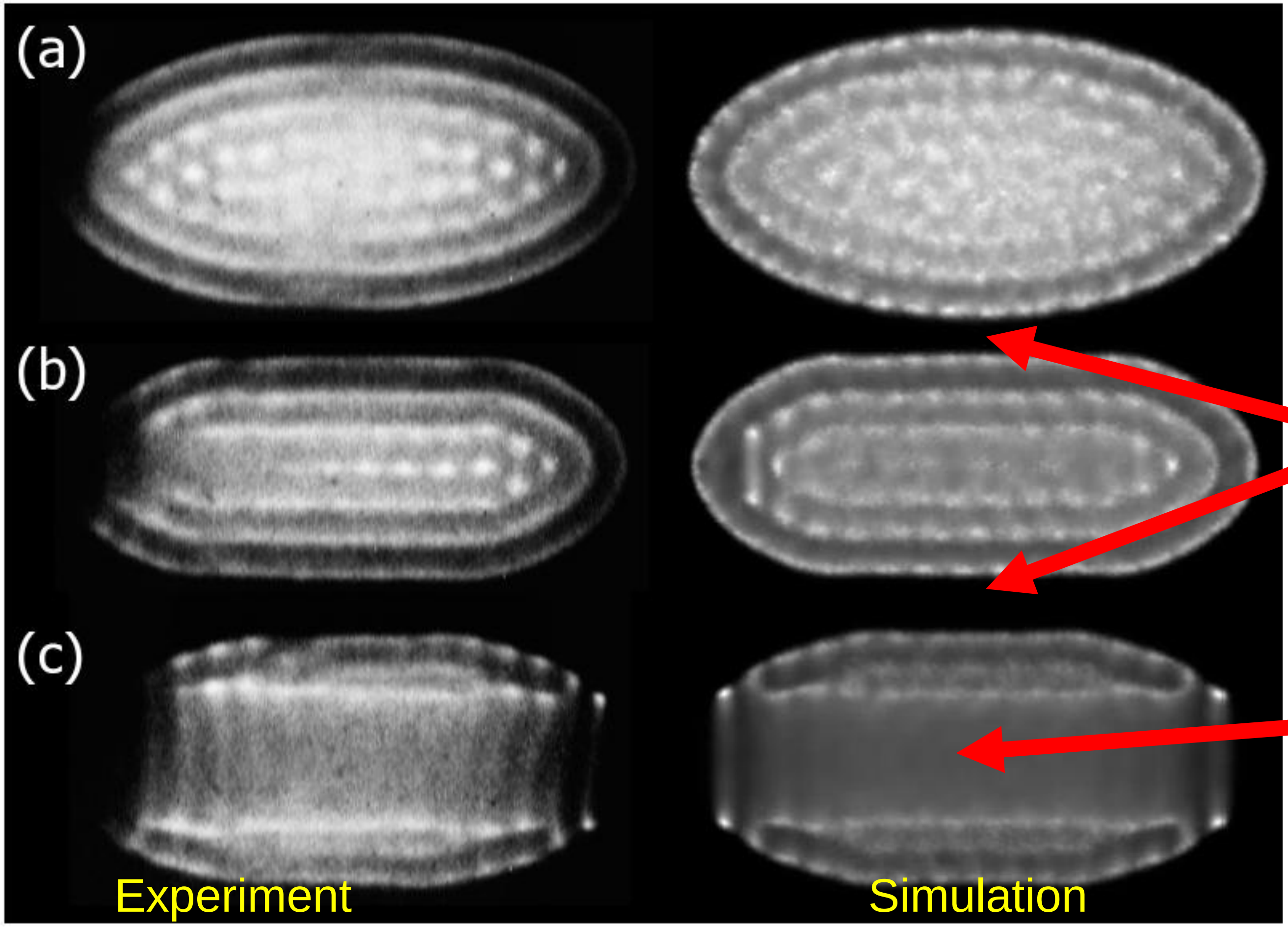
Ca^+ and OCS^+

Experiment

Simulation

OCS^+ formed by 2+1 REMPI in ion trap

Sympathetically cooled molecular ions



Ca^+ only

Ca^+ and OCS^+

ND_3^+

OCS^+ reacts with ND_3 to form ND_3^+

Candidate ions for sympathetic cooling 'easily formed' by REMPI include

- Kr^+/Xe^+
- NH_3^+/ND_3^+ etc
- $C_2H_2^+/C_2D_2^+$
- HCl^+/DCl^+
- N_2^+, H_2^+, Cl_2^+

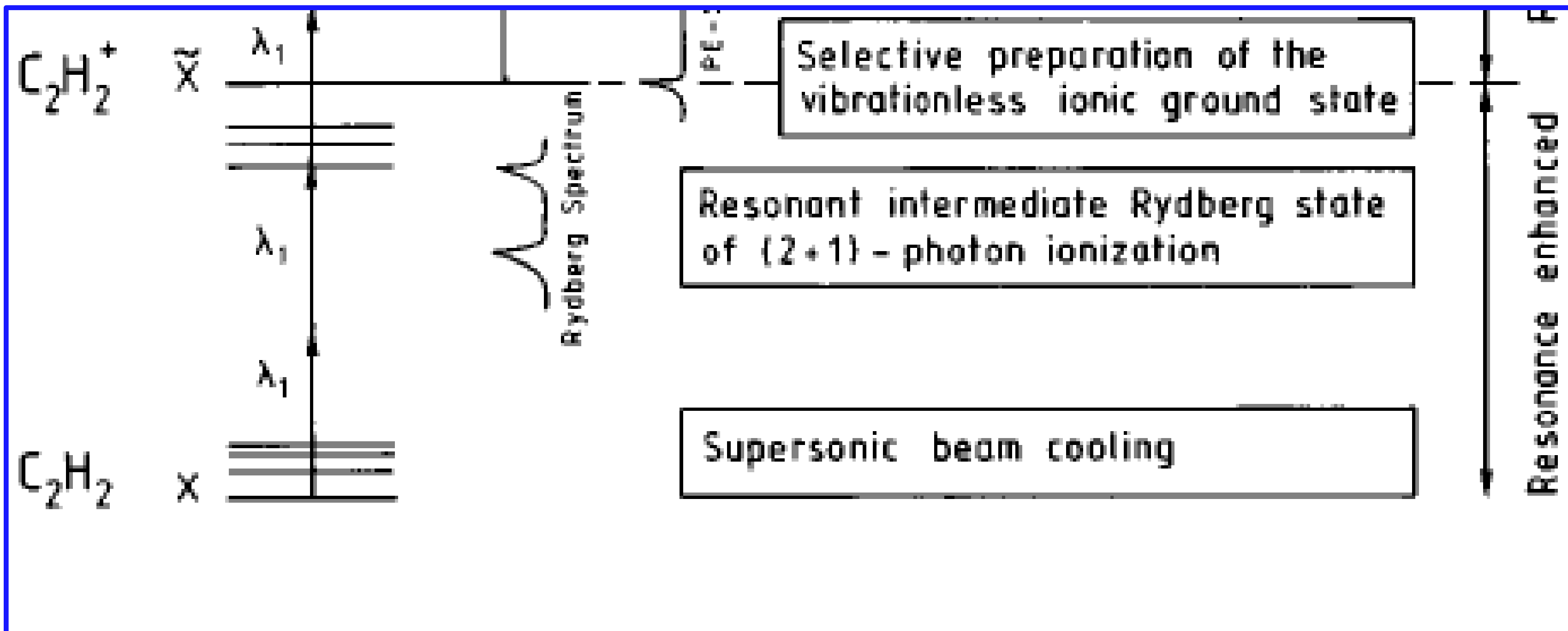
- H_20^+/ D_20^+
- OCS^+/CO_2^+
- $C_6H_6^+$

Molecular ion needs to be close in mass to laser cooled ion; hence use Be+, Mg+, Ca+, Ba+ as appropriate

Also molecular ions can be formed by reaction: NH_4^+, H_3O^+, H_3^+, MgH^+, MgO^+,CaF^+

State selection of ions by REMPI

- Threshold ionization/REMPI leads to state selection.

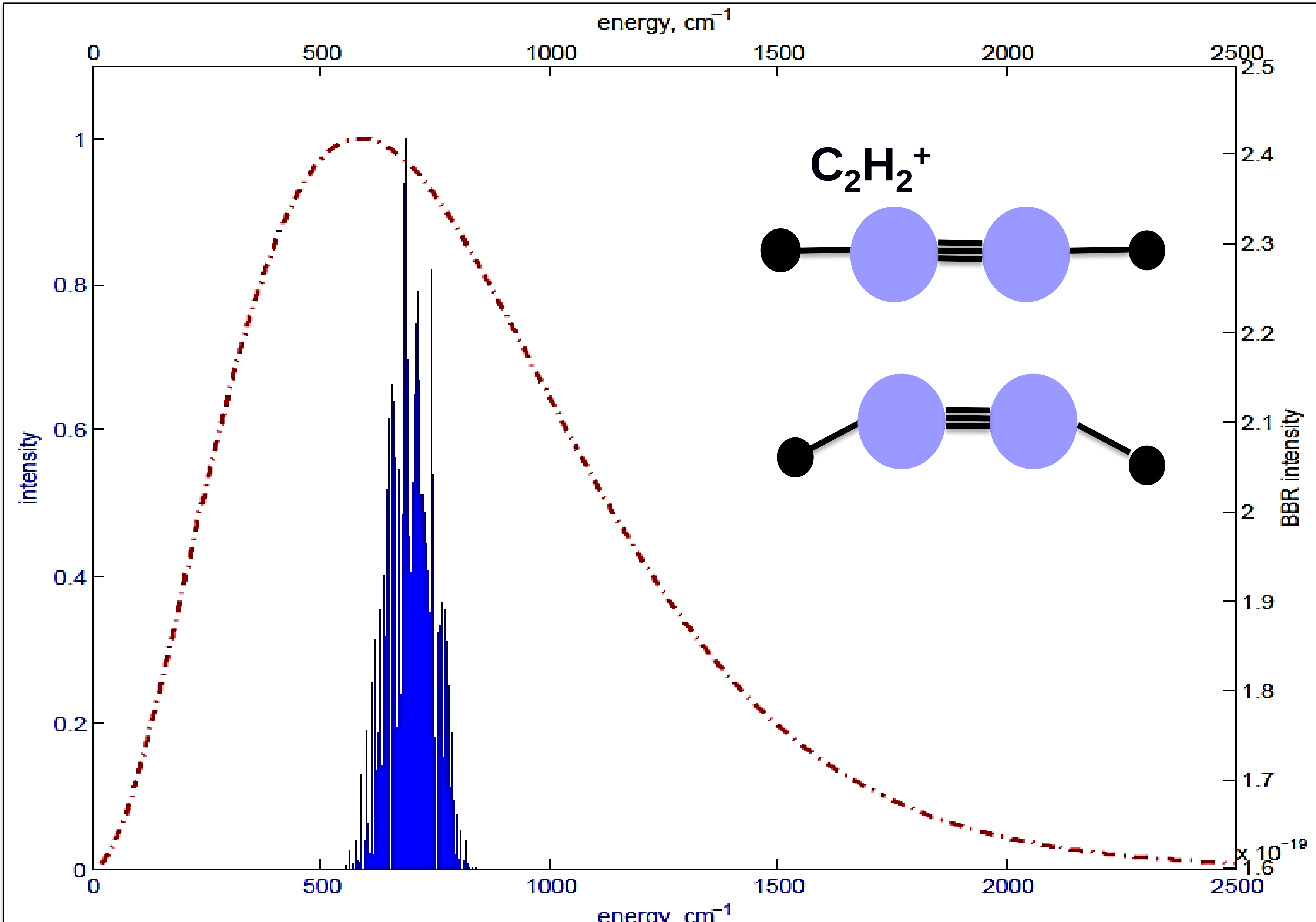


State selection of ions by REMPI

- Threshold ionization/REMPI leads to state selection.
  - But black body radiation $\Rightarrow$ thermalization on timescale of experiment (minutes)
  - $\Rightarrow$ Use non-polar ions N_2^+, Cl_2^+, $C_2H_2^+$, NH_3^+ $BrCl^+$

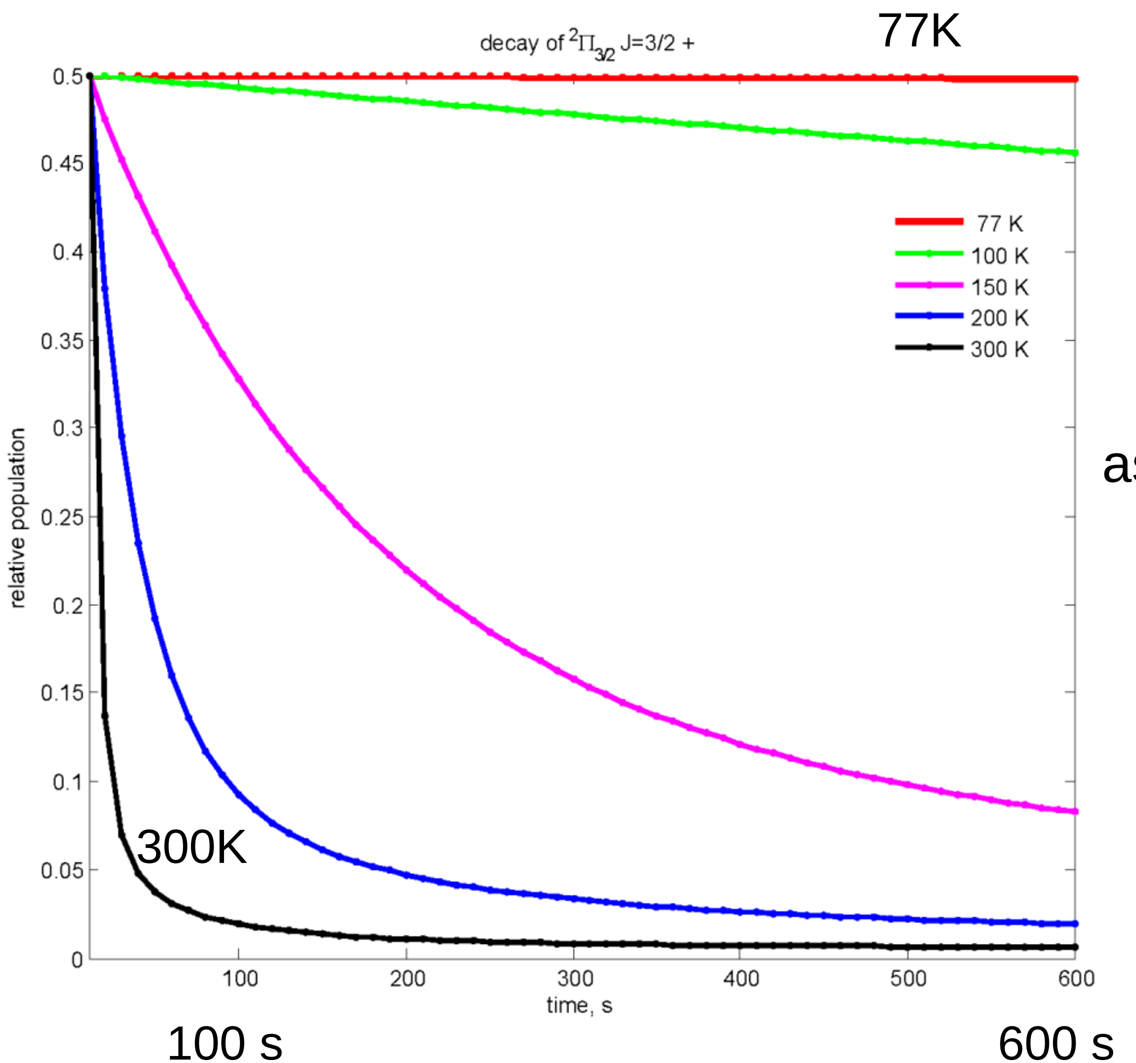
See Stefan Willitsch talk

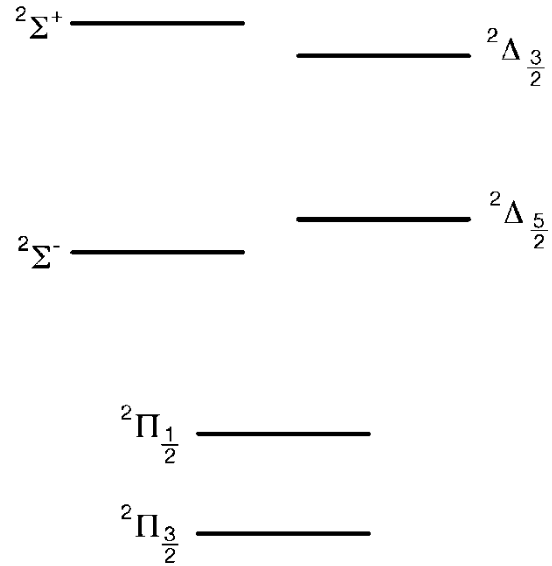
Spectrum at 300K



Rotational lifetimes in $C_2H_2^+$

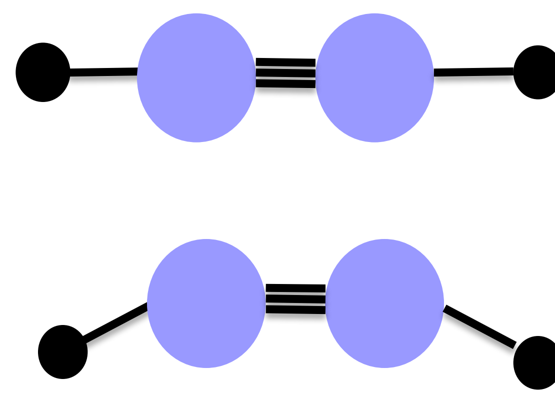
Nabanita Deb



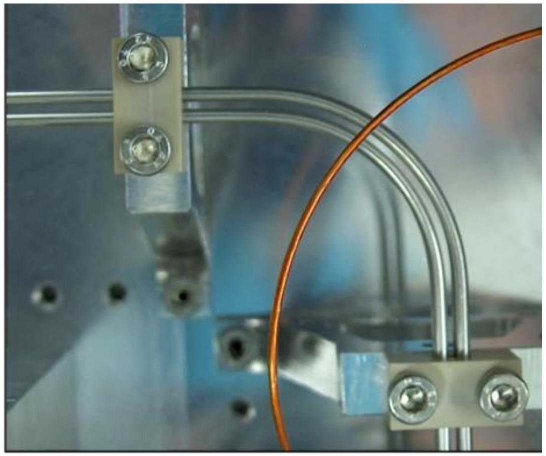


Effect of black body radiation pumping of asymmetric bend vibration at ca 700 cm^{-1}

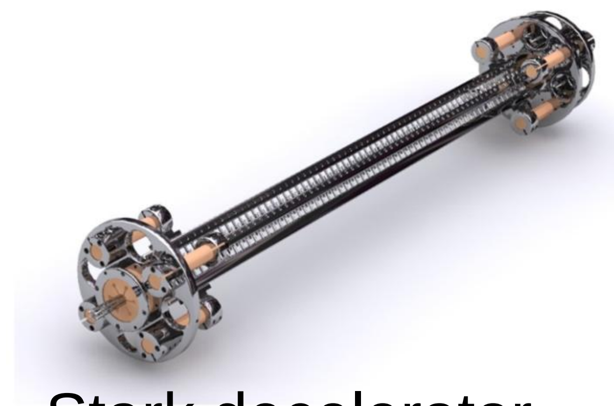
$C_2H_2^+$



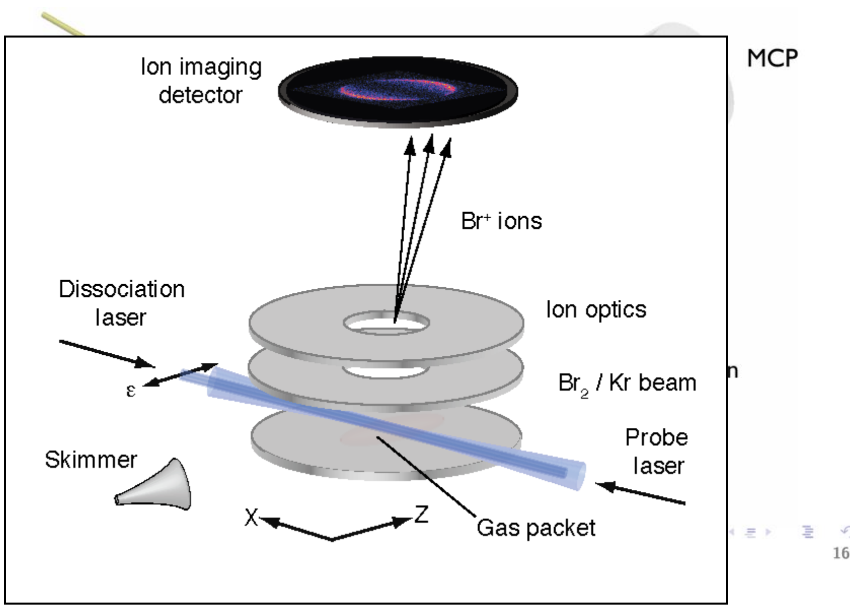
We explore 4 ways to make cold neutrals



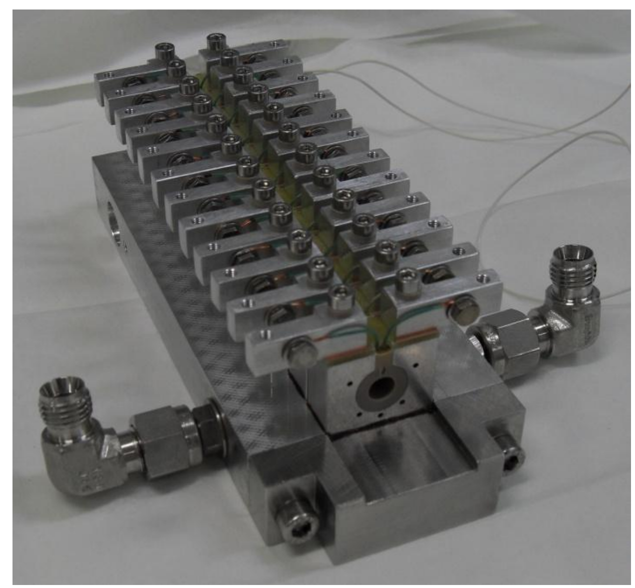
Velocity selector with buffer gas cooling



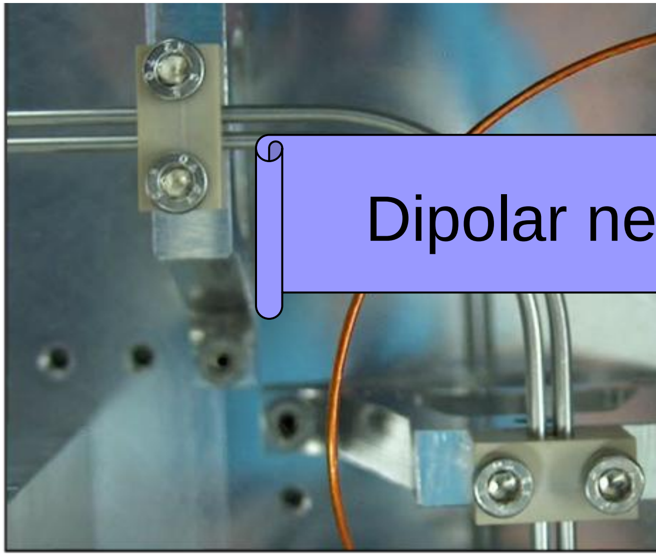
Stark decelerator



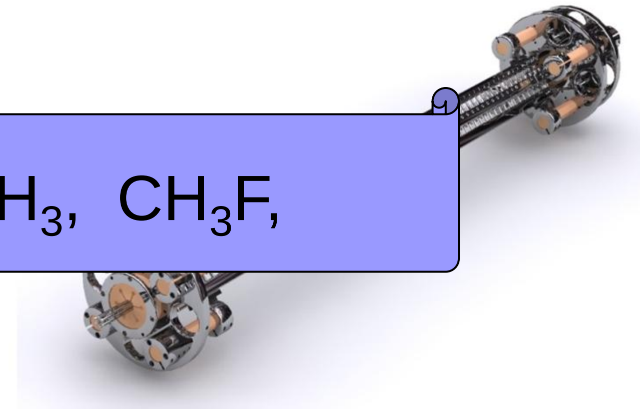
Threshold Photodissociation



Zeeman decelerator

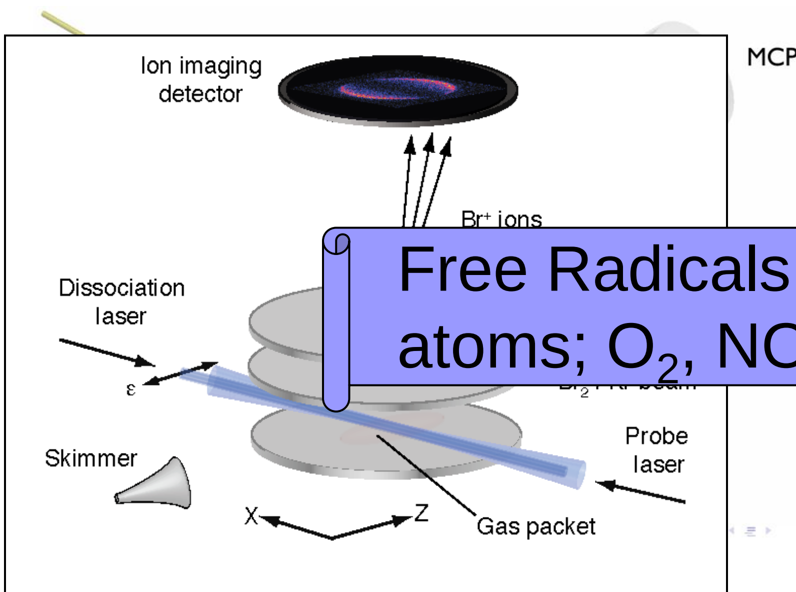


Velocity selector with buffer gas cooling

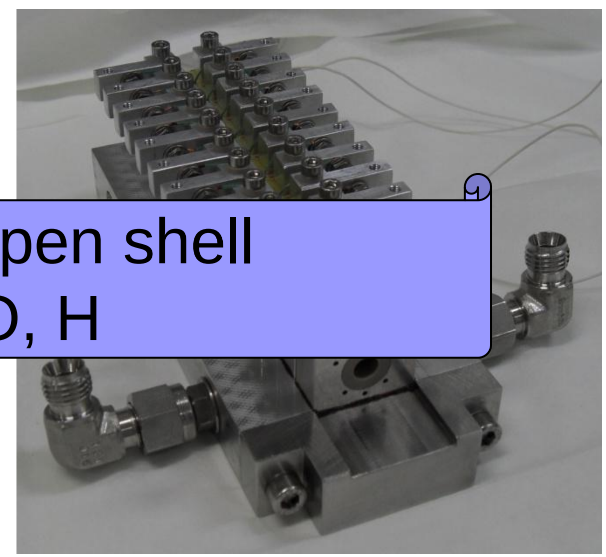


Stark decelerator

Dipolar neutrals; NH_3, CH_3F,



Threshold Photodissociation



Zeeman decelerator

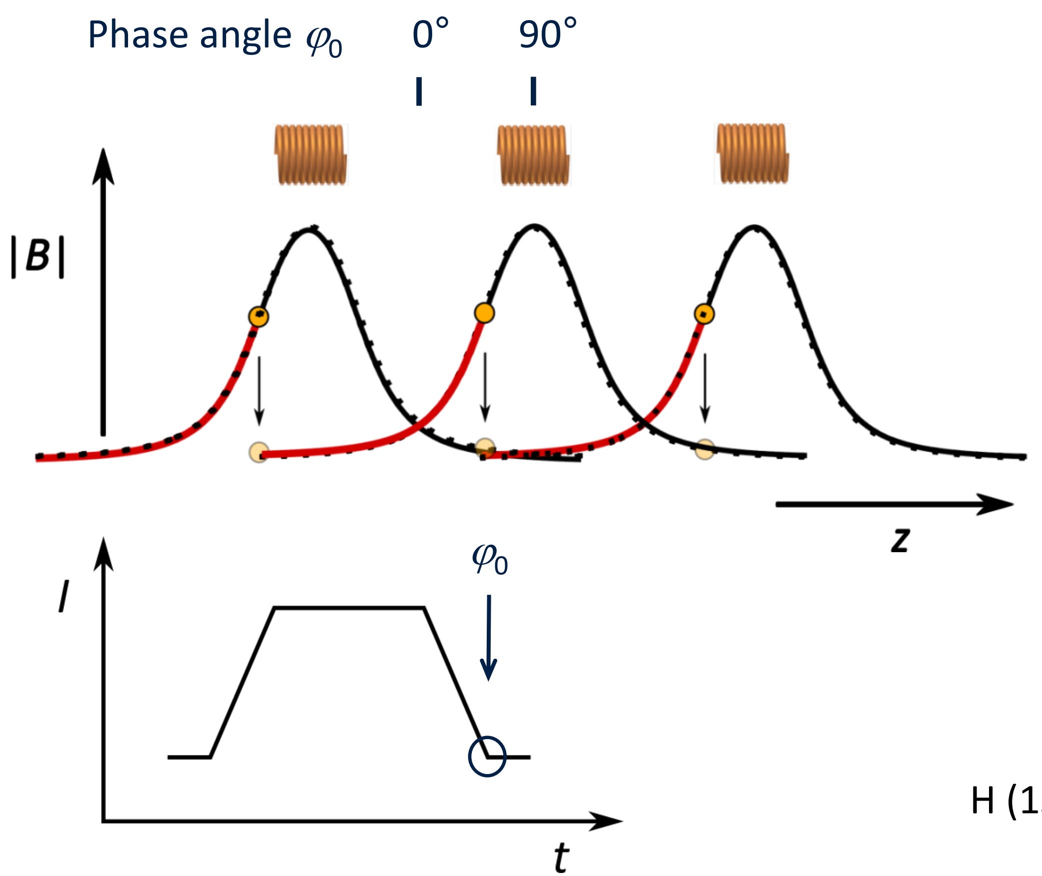
Free Radicals and open shell atoms; O_2, NO, Br, O, H

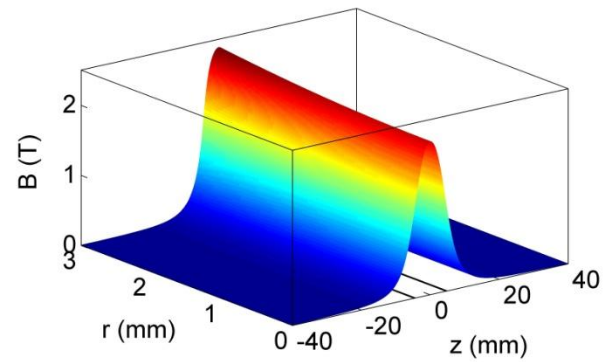
Towards reactions of free-radical (magnetic dipolar) species

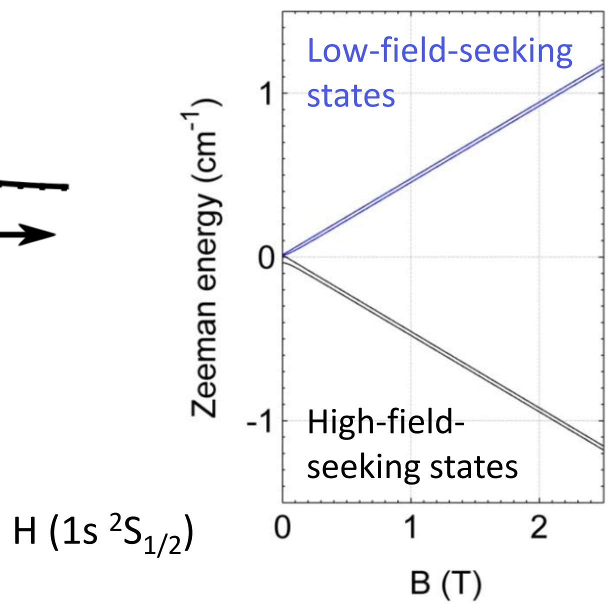
(1) Zeeman declerator

(2) Photodissociation recoil ('Photostop')

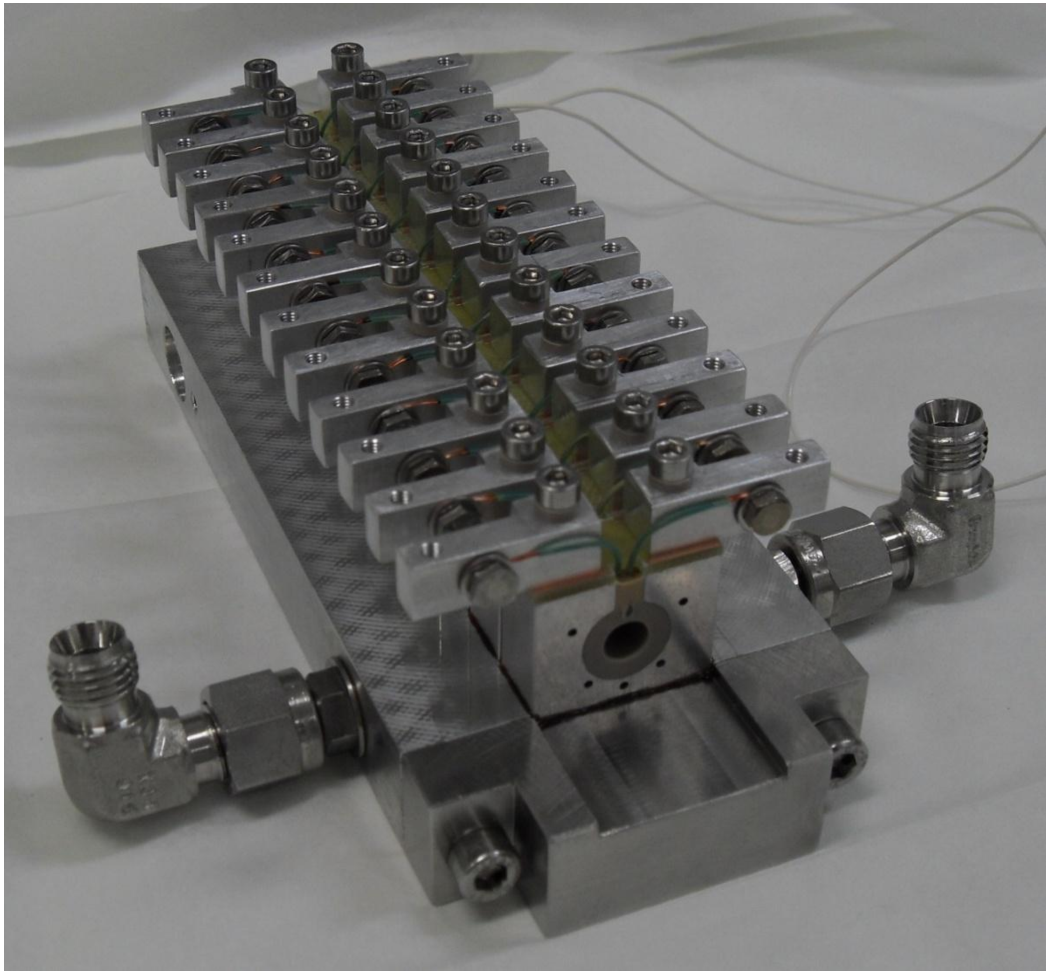
Basics of Zeeman Deceleration







12 stage Zeeman decelerator for H atoms

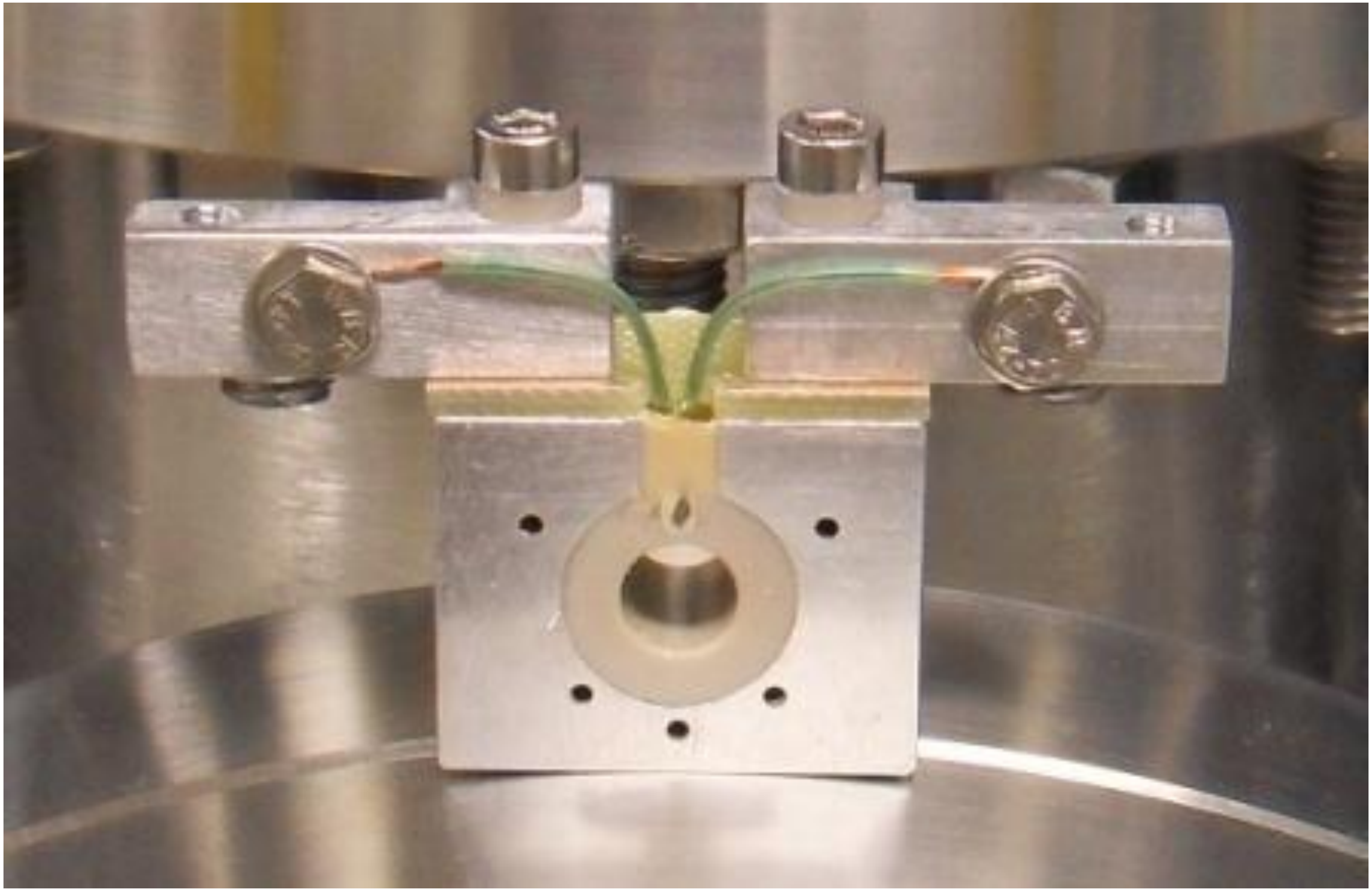


Coils and cooling inside vacuum.

Modular design

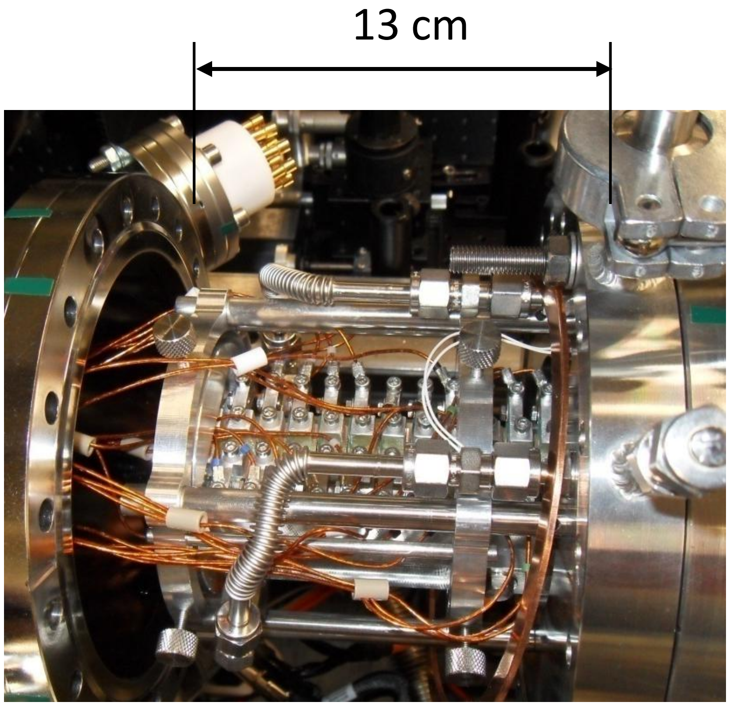
(Katrin Dulitz, collaboration ETH Zurich)

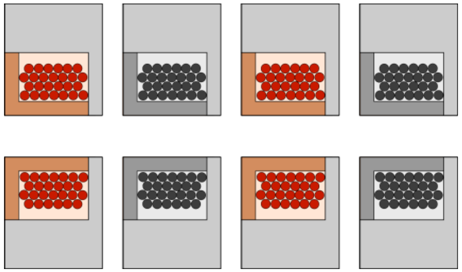
Magnetic coil holder



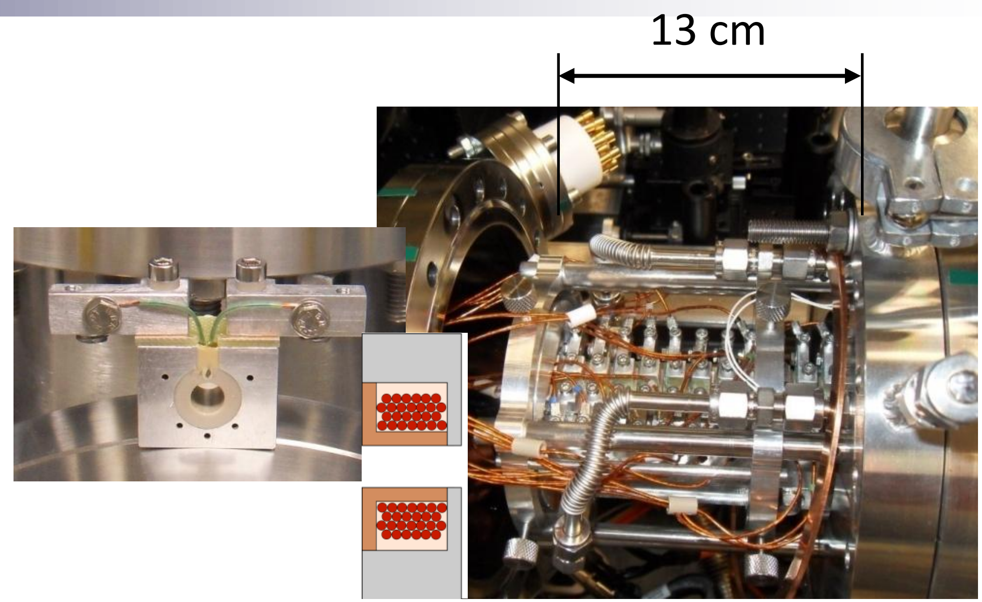
Experimental Setup: Zeeman Decelerator

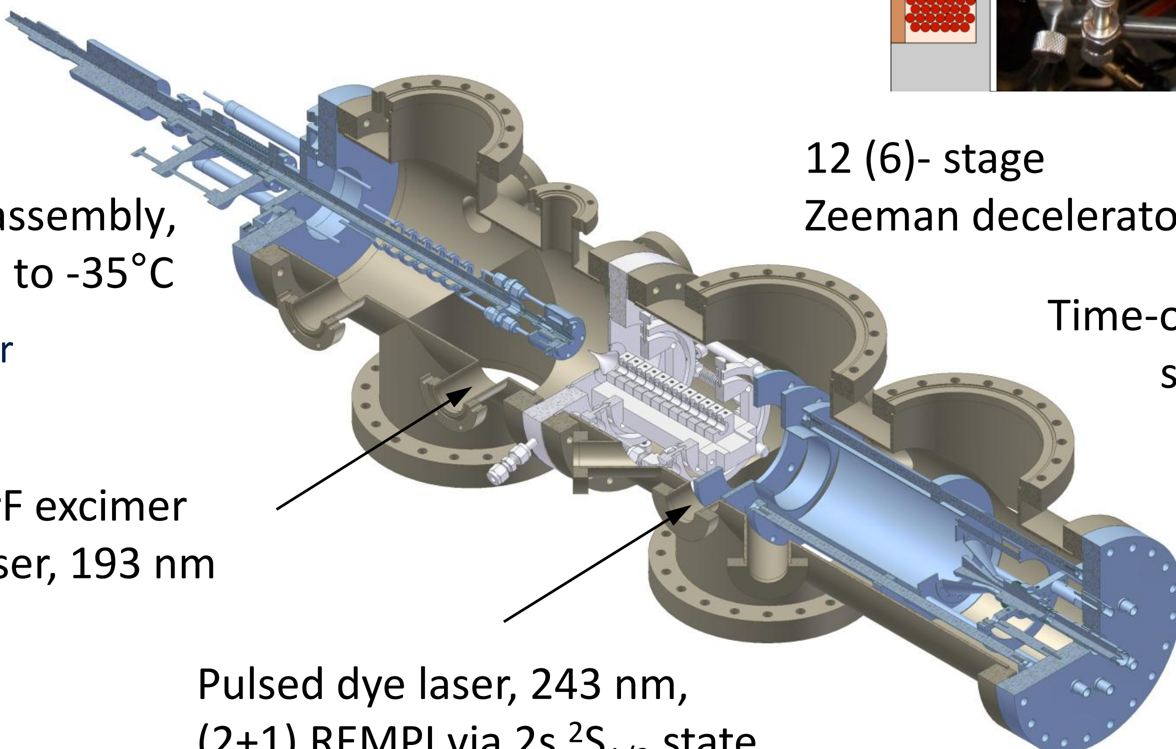
- 12 solenoid coils
  (at present: every second coil pulsed)
- 300 A/10 μs
  $\Rightarrow$ *B* = 2.2 T on axis
  (at present: 250 A/ 8.6 μs)
- Water cooling in vacuum chamber
  (*T* < 25°C at 10 Hz)
- Deceleration stages are exchangeable
- Extensions possible





Magnetic Decelerator for H Atoms





Deceleration of H atoms
6 coils pulsed T_{valve} = -35C v_0 = 420 ms^{-1}

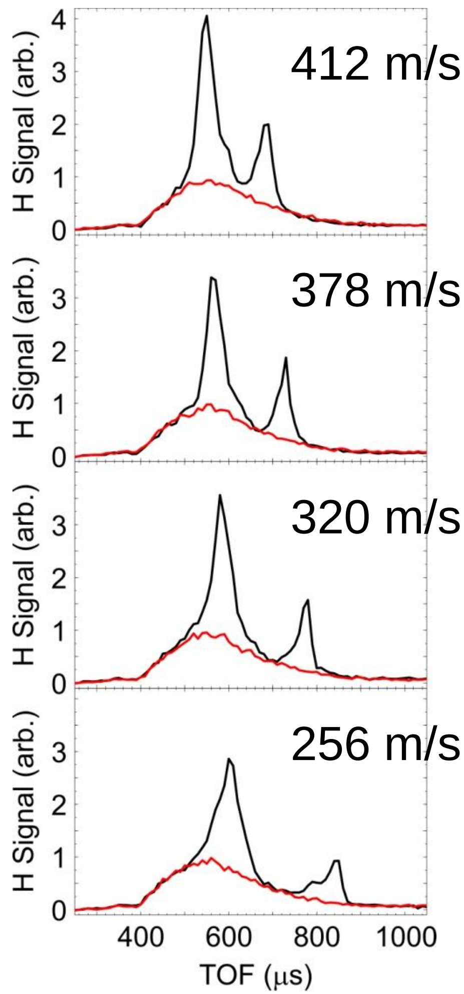
Experiment

ϕ_0 = -90°

ϕ_0 = 0°

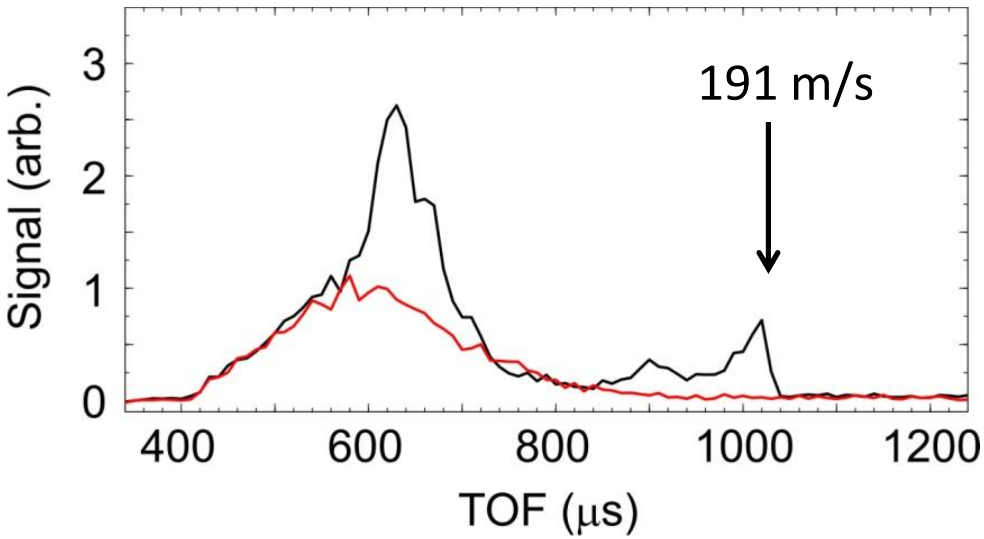
ϕ_0 = 45°

ϕ_0 = 90°



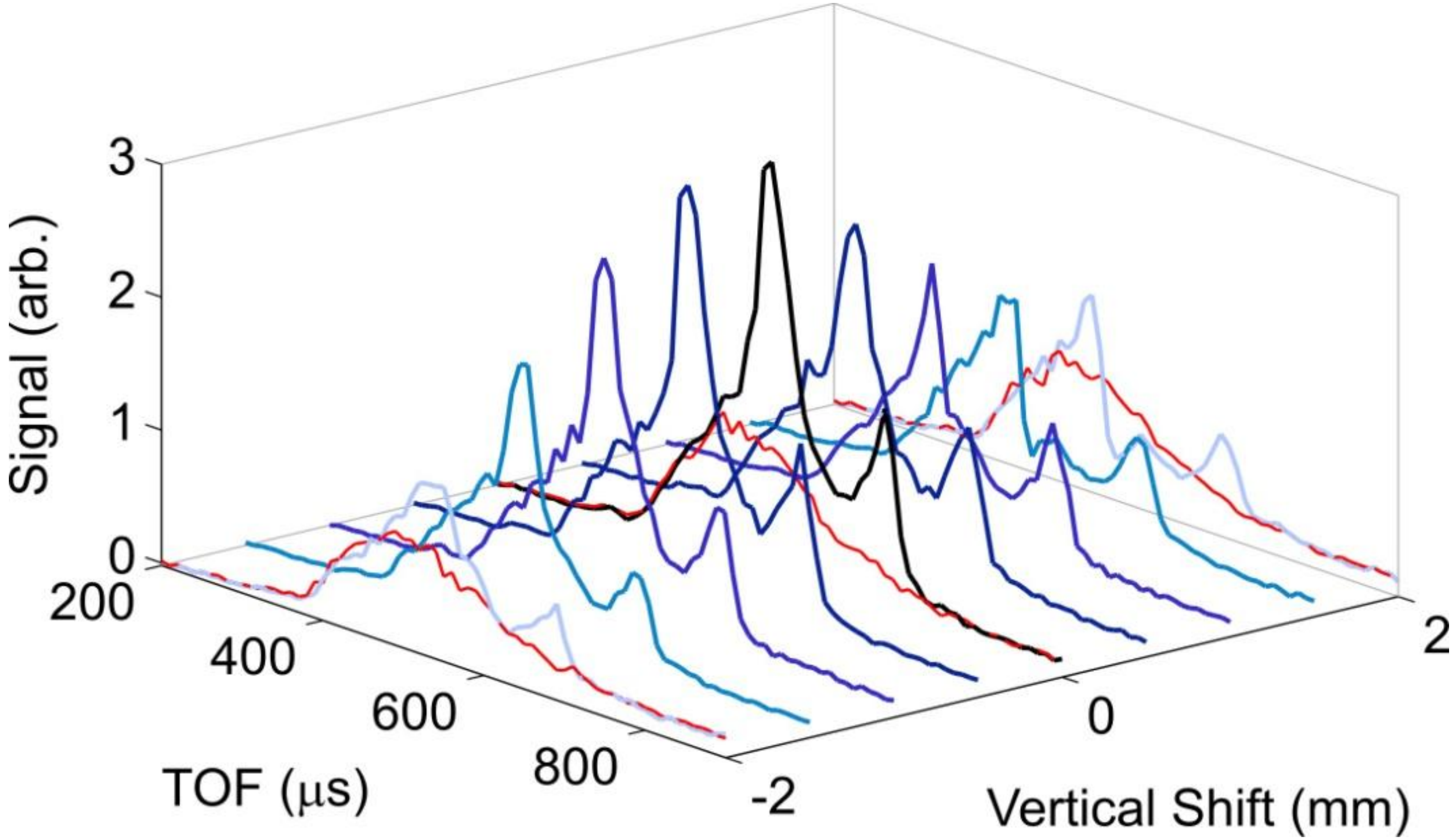
Results: 6 coil deceleration: v_0 = 385 m/s (T_{valve} = -35°C)

$\varphi_0 = 90°$



Transverse Effects

- v_0 = 480 m/s, ϕ_0 = 90°



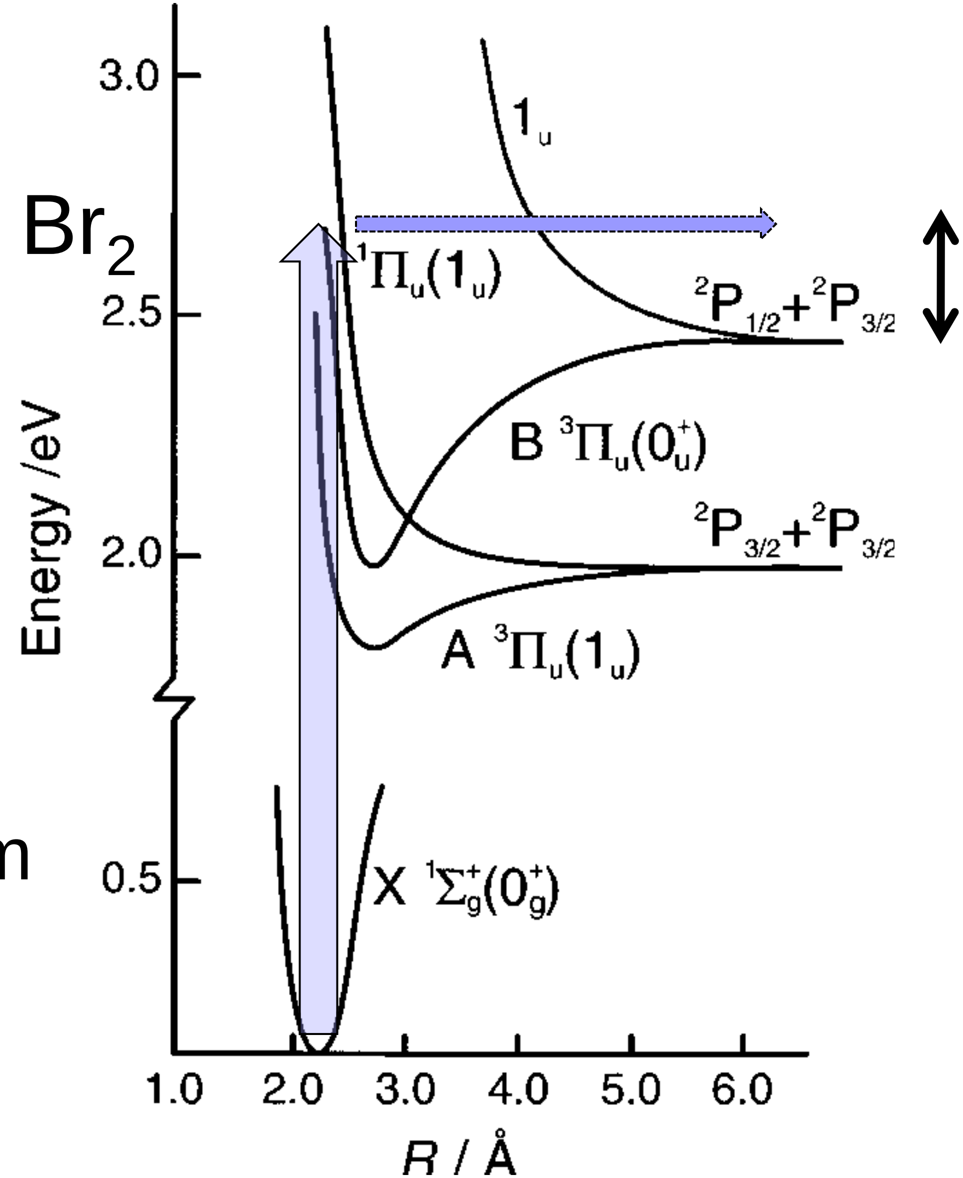
Scan REMPI detection laser across decelerated beam spatially

Zeemen decelerator applications

- H, D or O atom reactions with trapped ions (e.g., H + CO_2^+)
- Explore co-trapping of H atoms and e.g. OH or ND_3 (cf J. Hutson calcs).
- Metastable penning ionization collisions

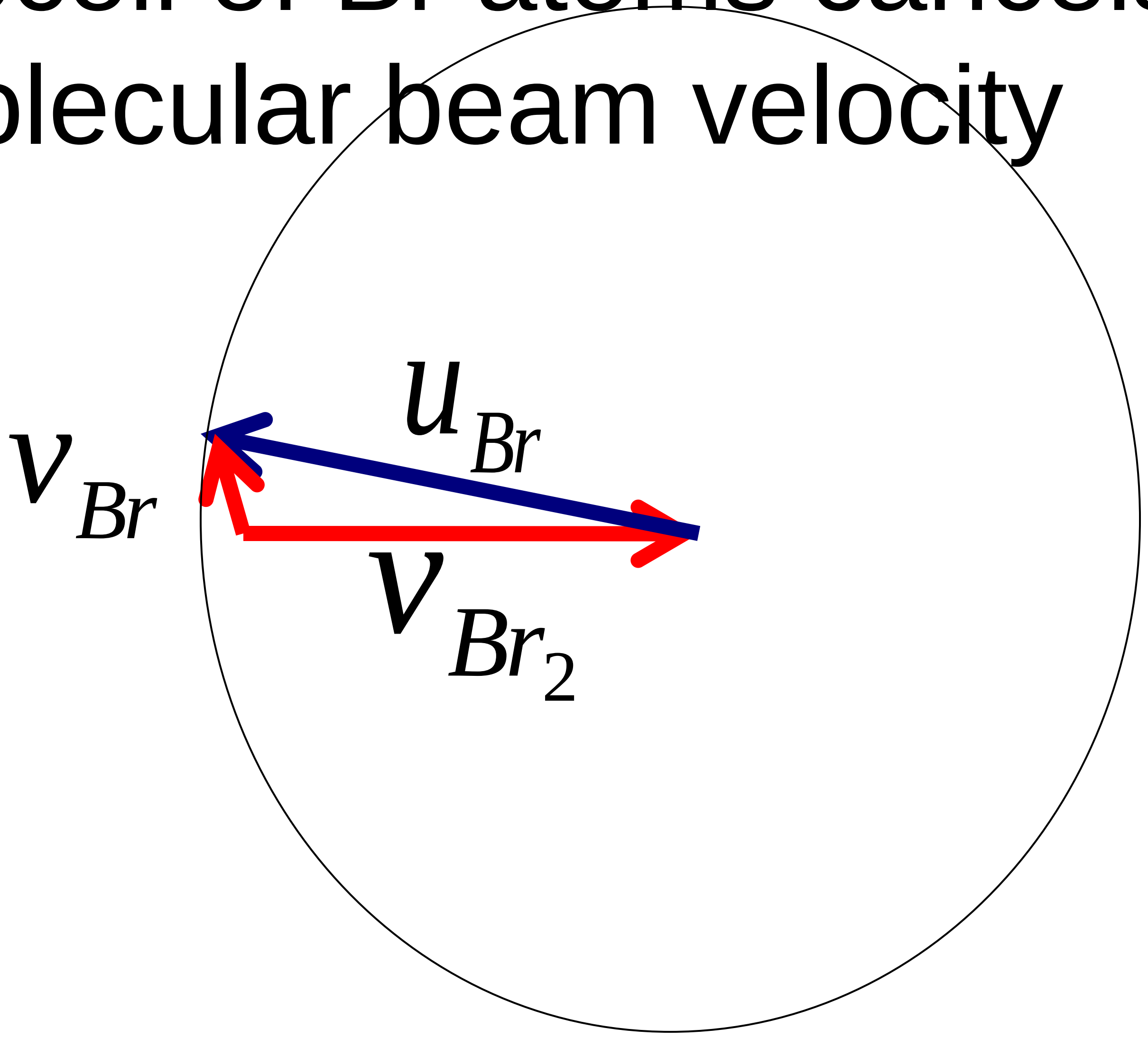
Production of Cold Br atoms by photolysis of Br_2

- Photolysis at 486 nm
- Mainly Br + Br* formed
- Probe Br by 2+1 REMPI at 264.211 nm

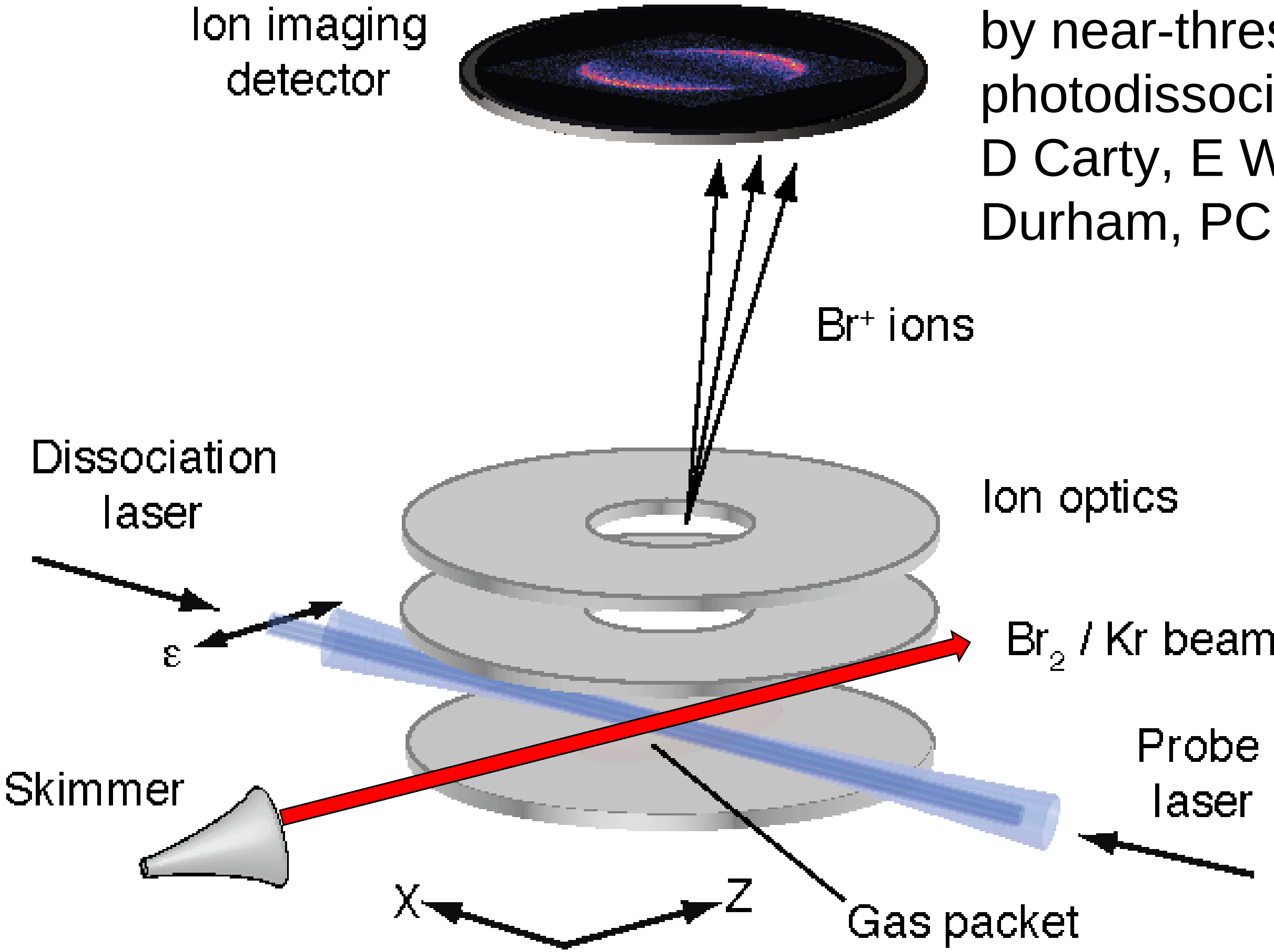


J. Chem. Soc., Faraday Trans., 1998, **94**, 2901-2907, Cooper *et al*.

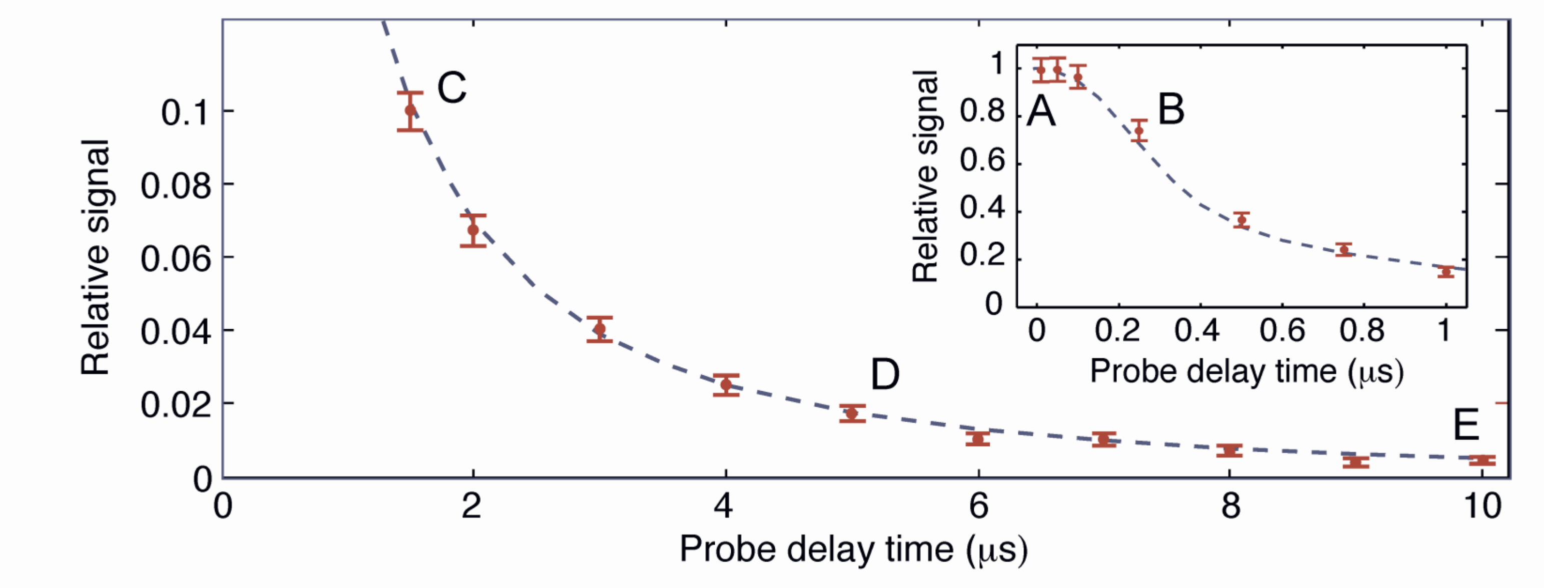
Recoil of Br atoms cancels Br_2 molecular beam velocity



Cold Bromine atoms by near-threshold photodissociation (with D Carty, E Wrede, Durham, PCCP 2011)



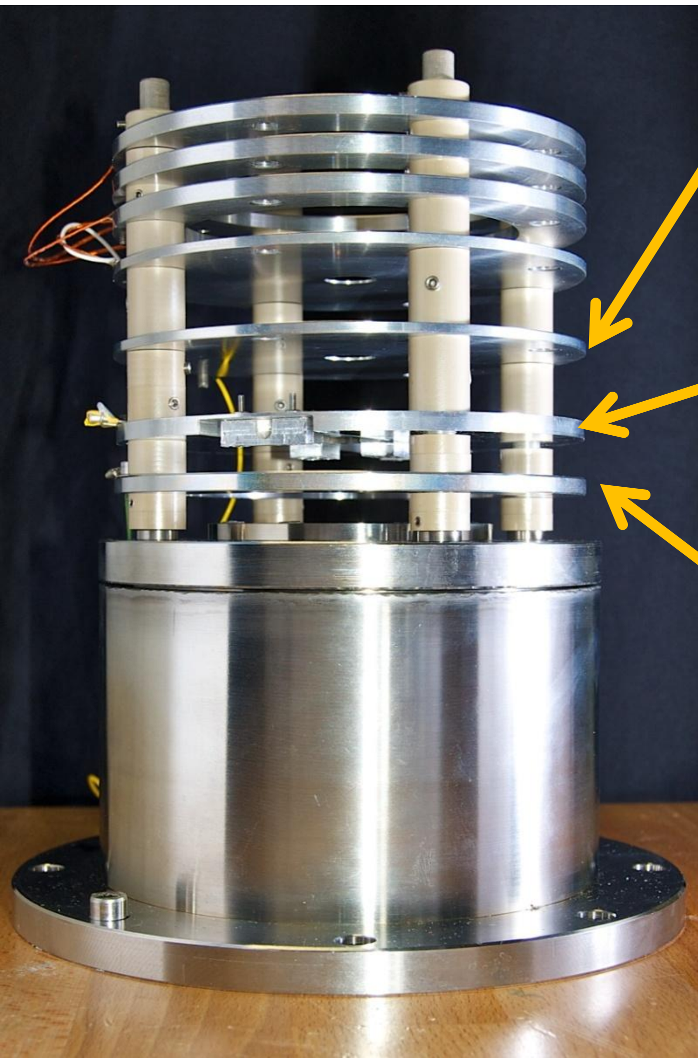
Br atoms detected by 2+1 REMPI in dissociation volume



‘Photostopped atoms observed to 100 μs, 100 mK

(with D Carty, E Wrede, Durham, PCCP 2011)

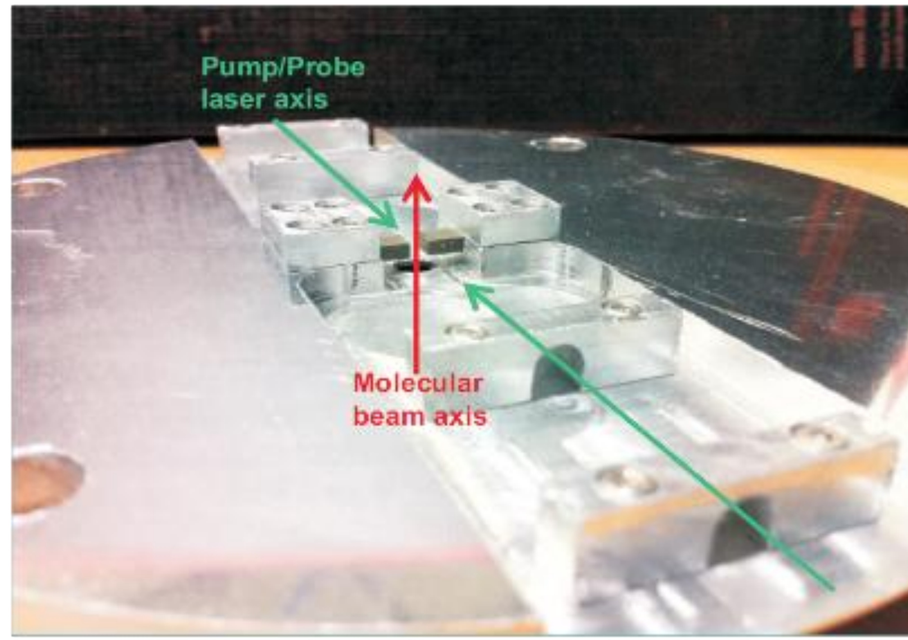
Add in a Magnetic Trap



Extractor plate

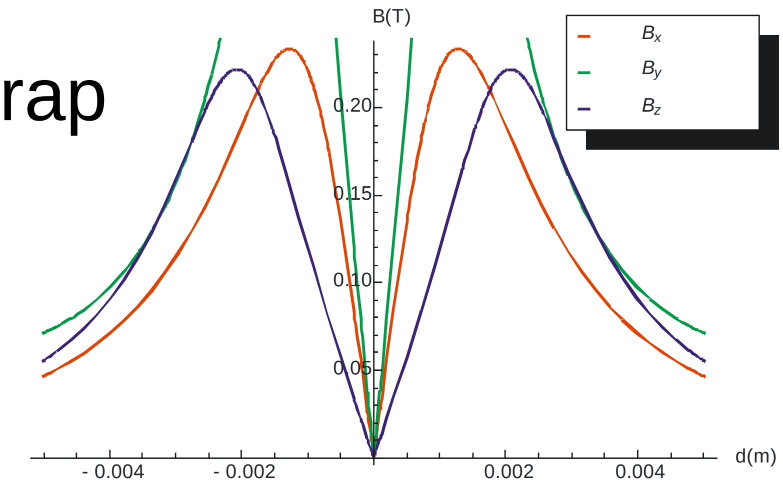
Magnet plate

Repeller plate

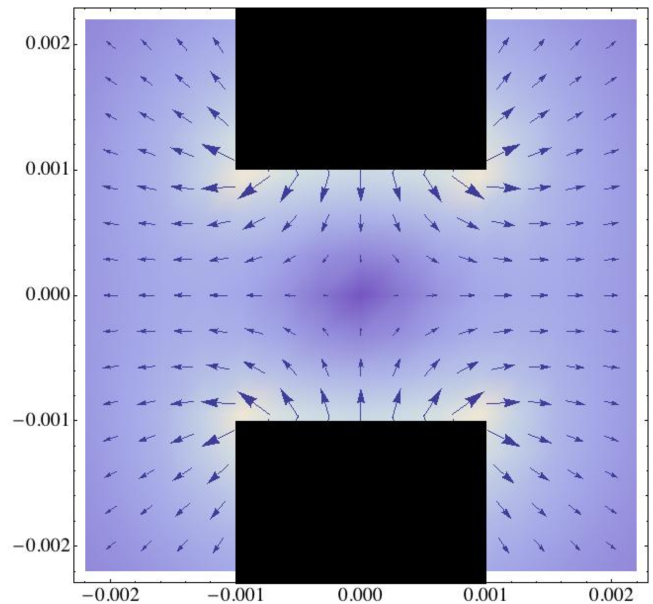


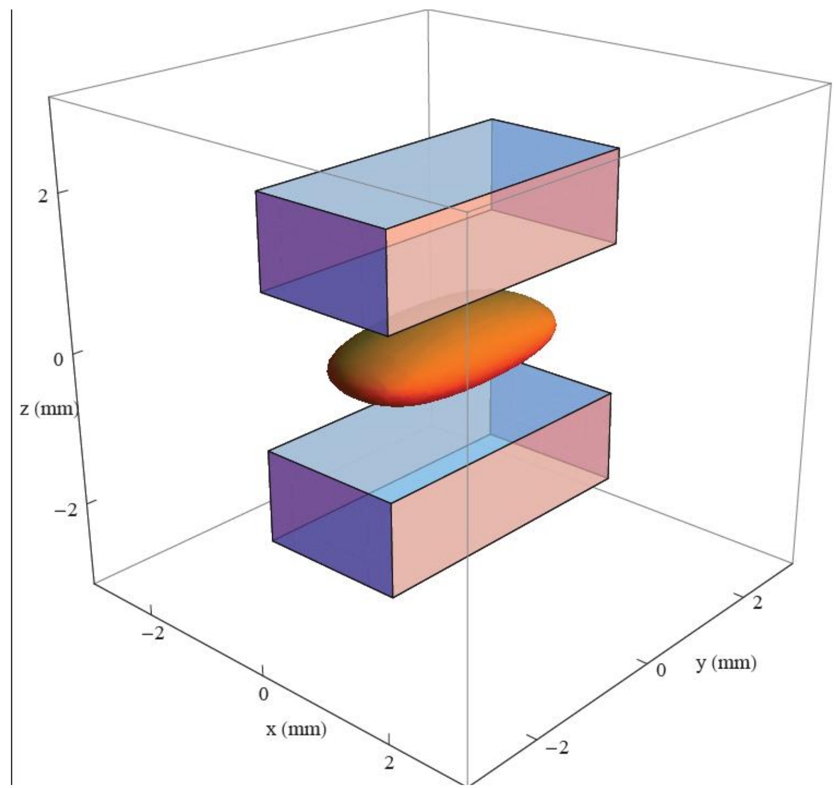
UNIVERSITY OF OXFORD

NdFeB magnets –quadrupole trap
Depth for Br = 0.2 T (8 ms^{-1})

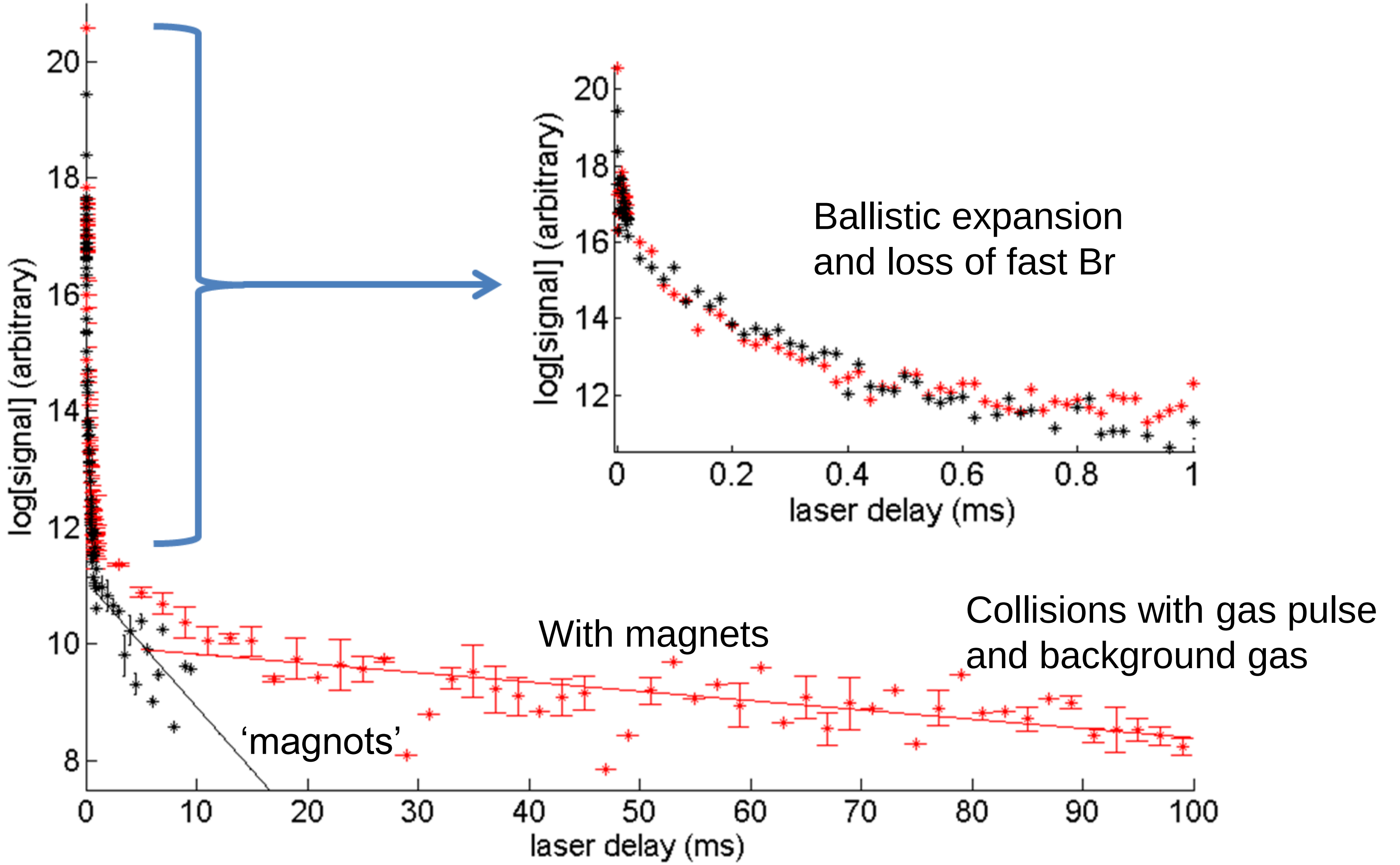


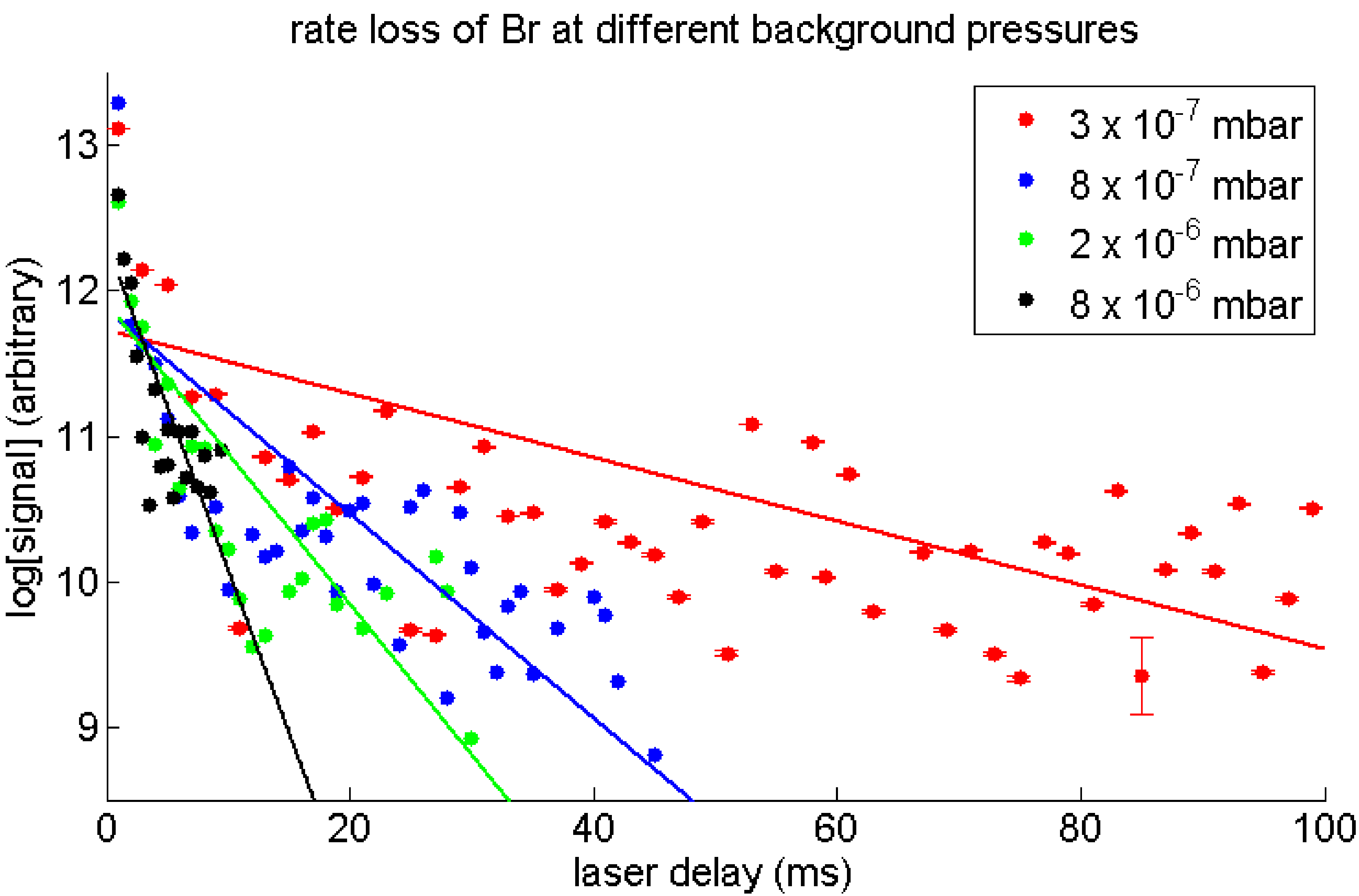
Chris Rennick,
Will Doherty
Jessica Lam





Decay of Br atom signal





rate loss of Br at different background pressures
3 x 10-7 mbar
8 x 10-7 mbar
2 x 10-6 mbar
8 x 10-6 mbar
log[signal] (arbitrary)
13
12
11
10
9
0
20
40
60
80
100
laser delay (ms)

Cold Br atom trapping

- Densities around 10^8 cm^{-3} currently (but accumulation possible).
- Limitation – collisions with carrier gas: trapped to >100 ms
- mK temperature range
- Applicable to e.g., $Br + BrCl^+ \rightarrow Br_2^+ + Cl$

with magnetic guide/decelerator or by superimposing traps

- Neutral – neutral? e.g., $F + H_2$
- Extendable to molecular fragment systems

e.g., $NO_2 \rightarrow NO + O$ (Carty and Wrede – SH)

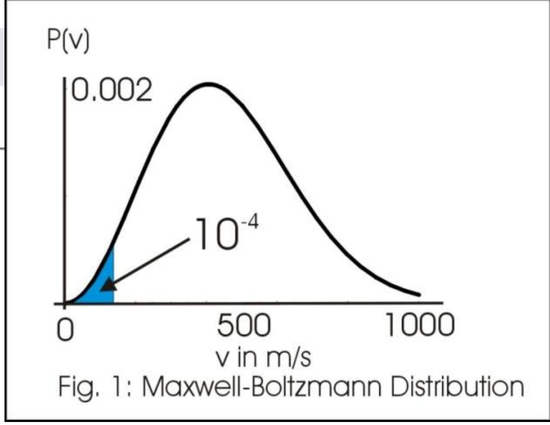
Cold ion molecule reactions with dipolar molecules

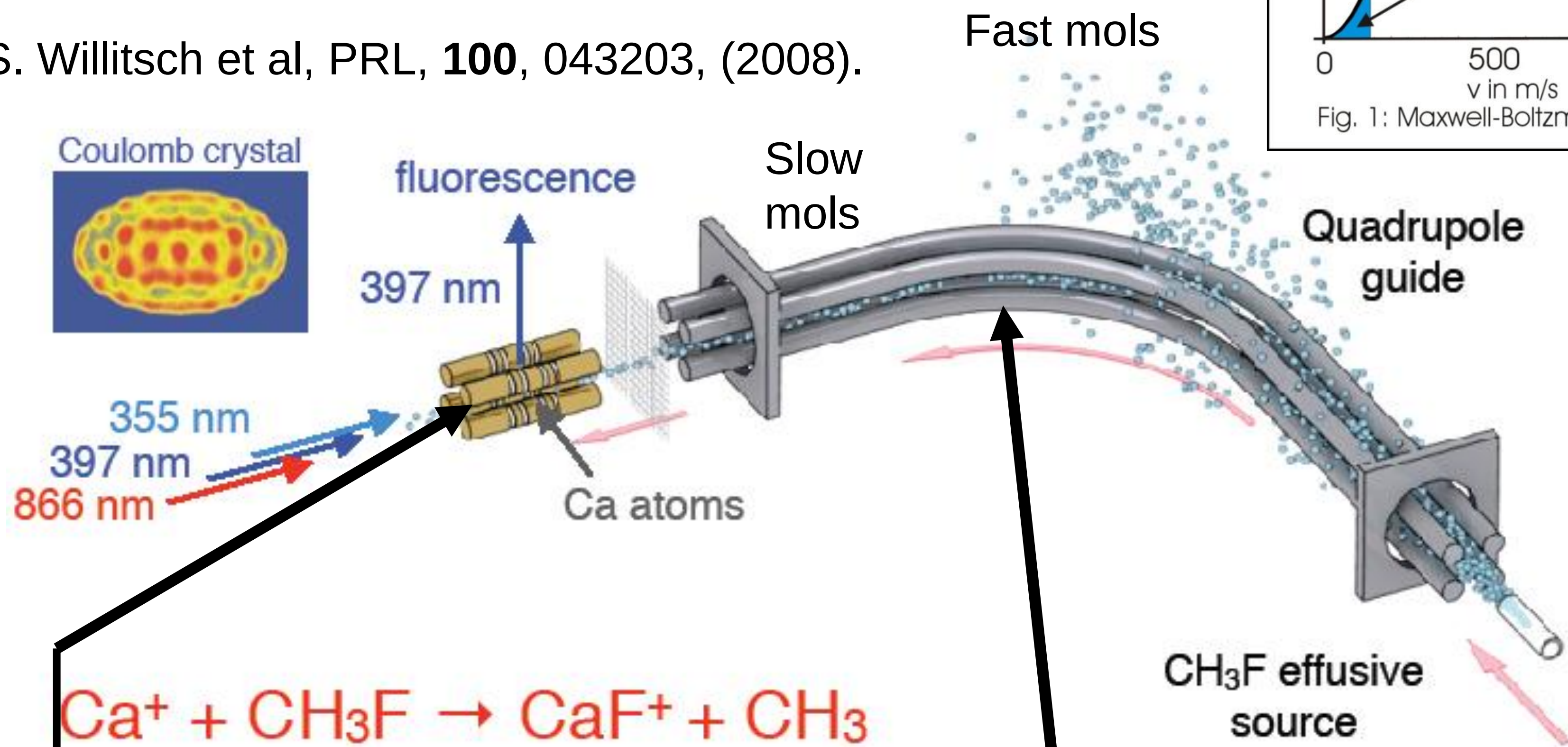
(1) Quadrupole guide

(2) Stark decelerator

Cold ion-molecule reactions

S. Willitsch et al, PRL, **100**, 043203, (2008).





Laser cooled Ca^+ ions in a *rf* Paul trap ~ 10 mK

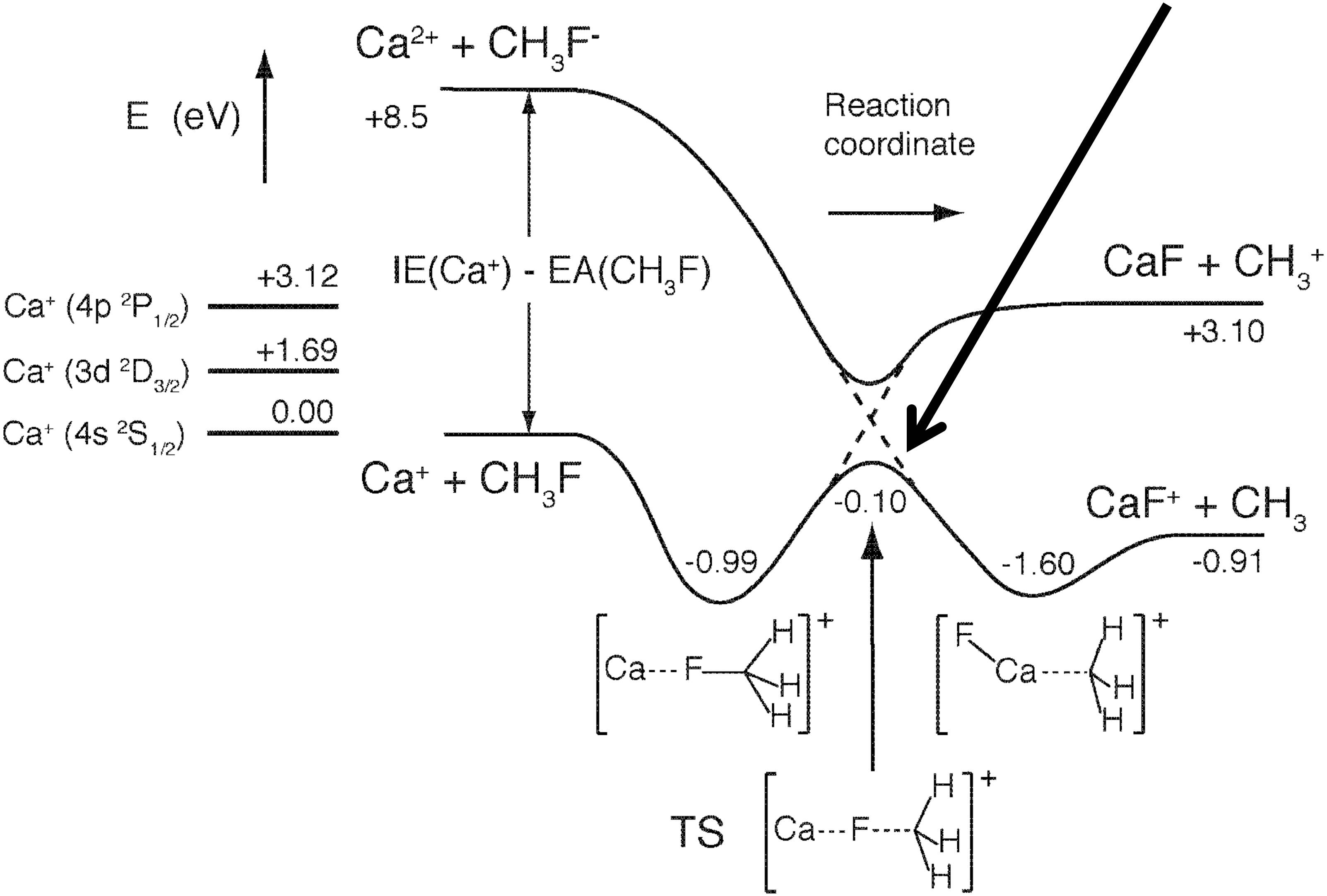
Cold neutrals CH_3F (CH_3Cl, CH_2F_2, ND_3) using quadrupole velocity selector ~ 1K (Rempe et al)

3K rates for 3 different reactions (k x 10^9 /cm^3s^{-1})

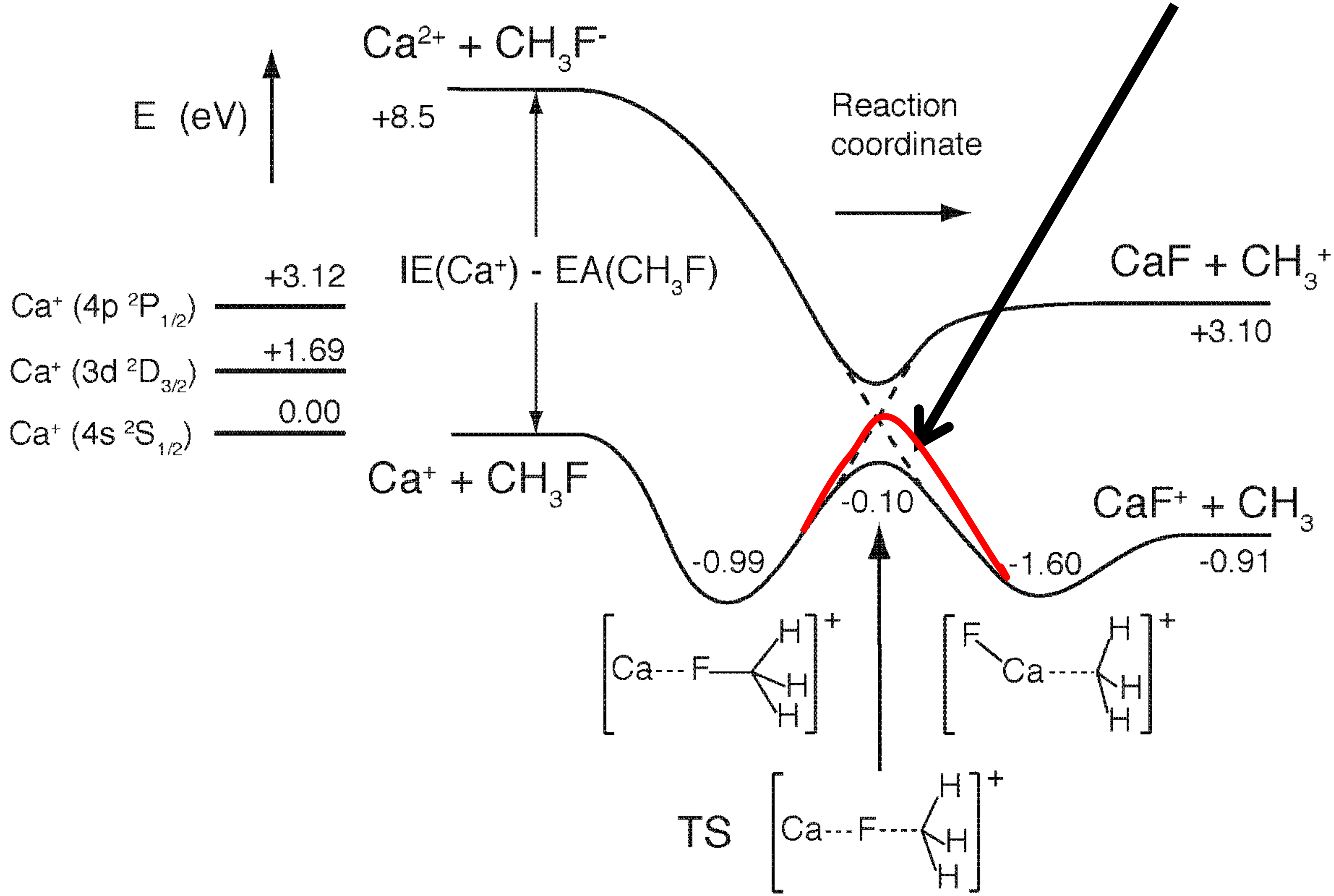
	$CH_3F + Ca^+$	$CH_3Cl + Ca^+$	$CH_2F_2 + Ca^+$
Ca^+ Ground state ($^2S_{1/2}$)	0.66	0.18	< 0.04
Excited states ($^2P_{1/2}$ + $^2D_{3/2}$)	1.29	1.41	0.41
Capture Theory	1.85	1.73	1.83

A Gingell et al, JCP **133** 194302 (2010)

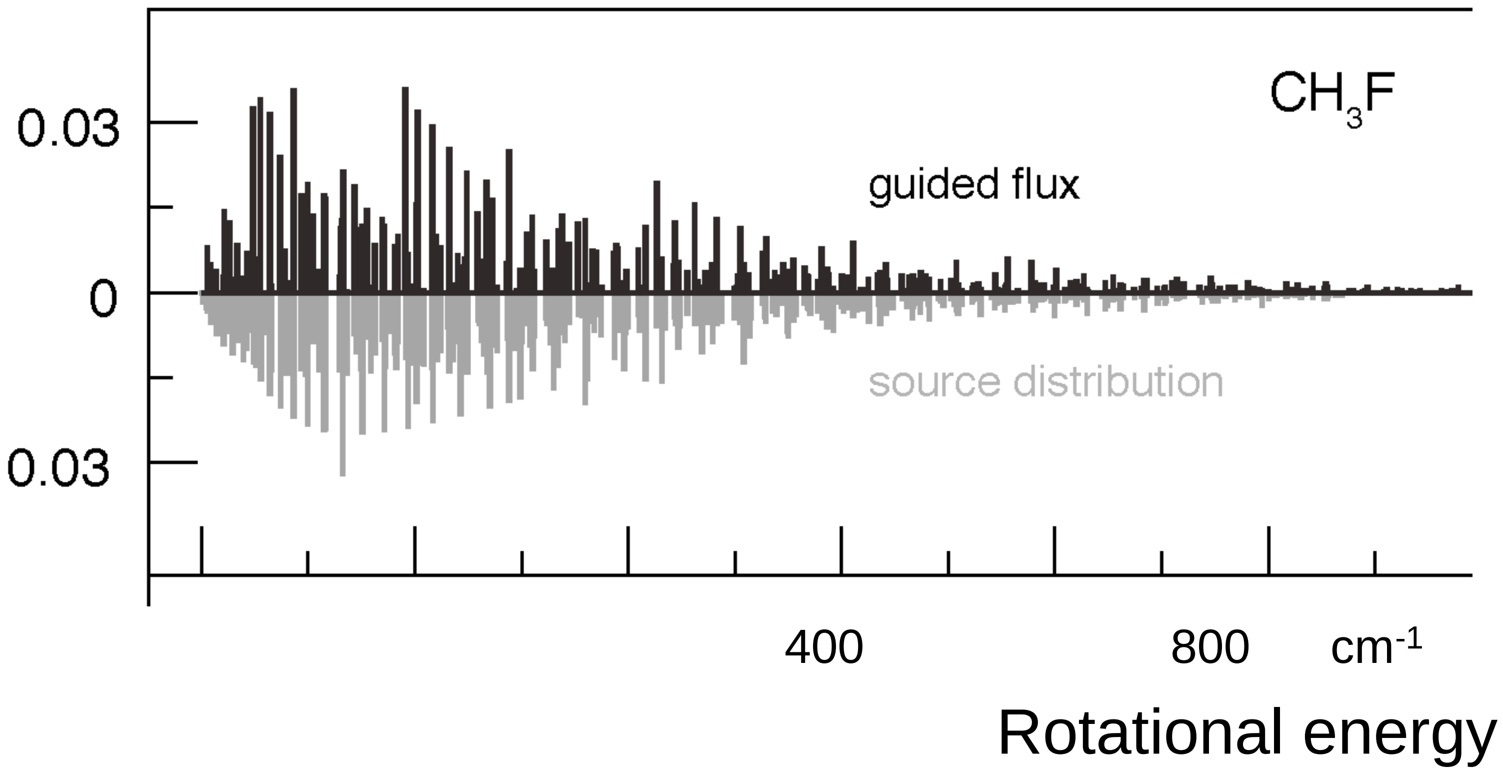
Reaction with a submerged barrier



Reaction with a submerged barrier



Rotational populations from quad guide

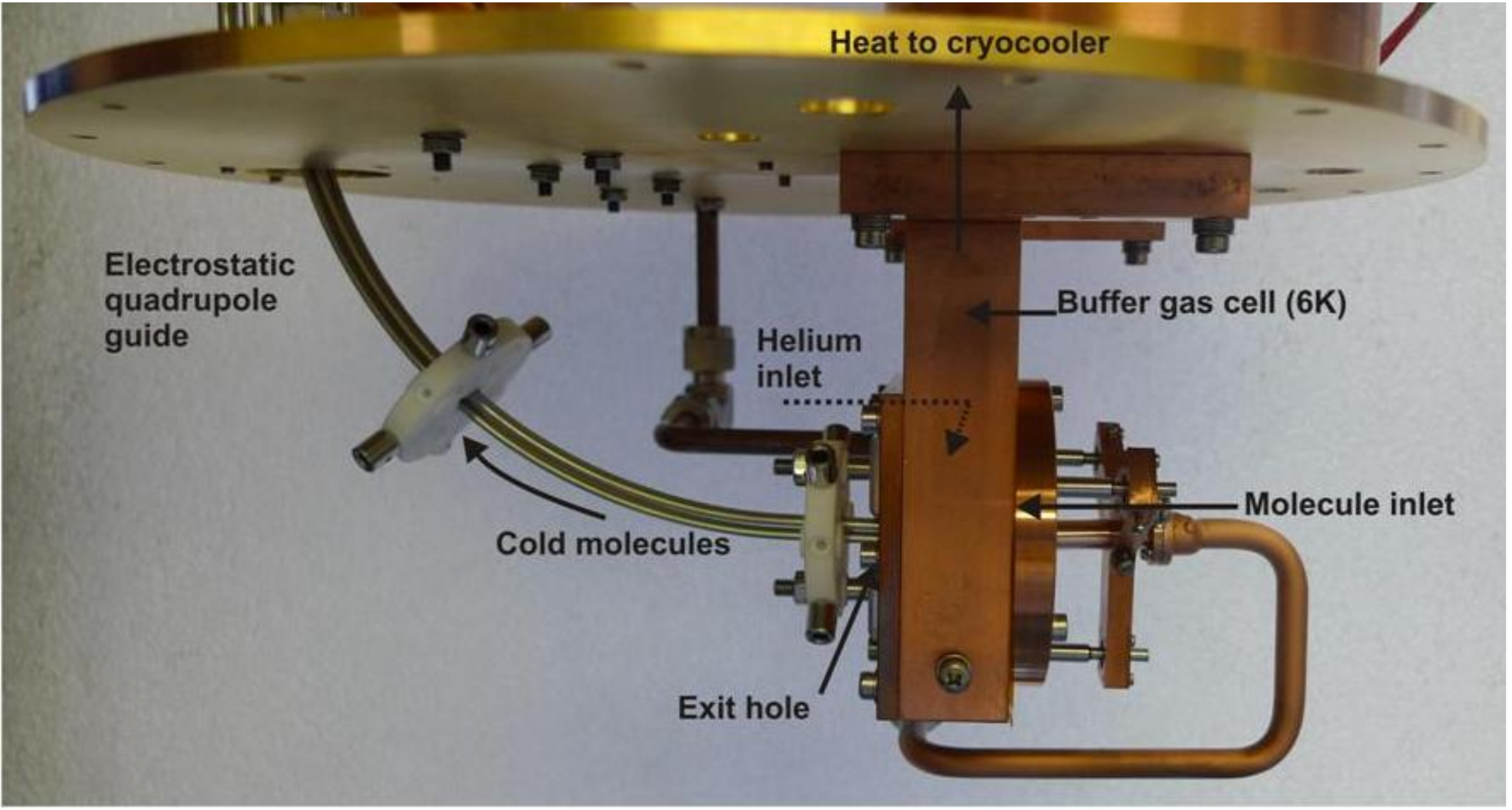


But......neutrals are rotationally warm (300K) translationally cold

Controlling rotational state populations

(1) Use 5 - 20 K buffer-gas cooled source for quadrupole guide: vary source temperature to control rotational populations
(2) Replace quadrupole guide with Stark decelerator (single rotational quantum state): also improves velocity resolution

Combining the quad guide with a He/Ne buffer gas cell



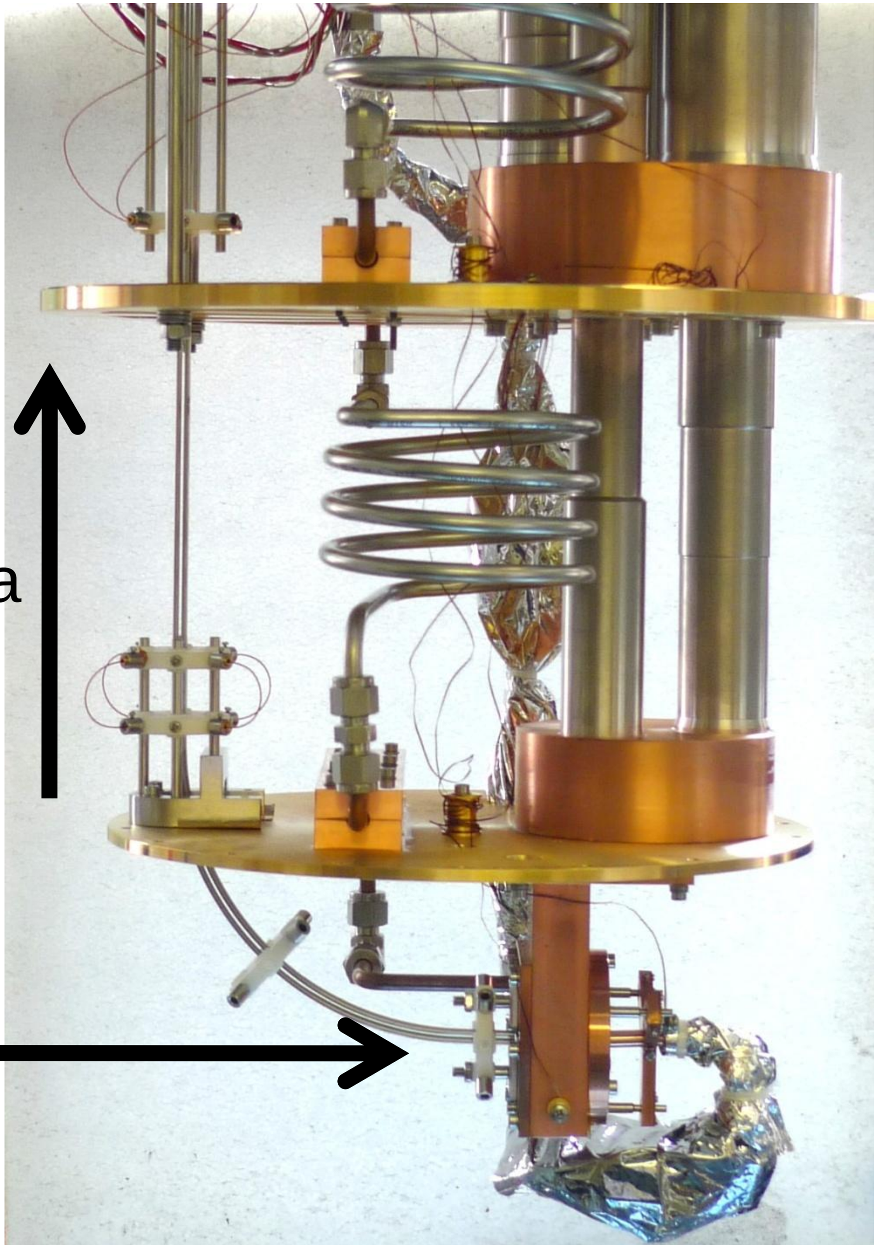
Based on design in: C. Sommer *et al.*,
Faraday Discuss., 203, **142** (2009)

He/Ne buffer gas cooling in closed cycle cryostat

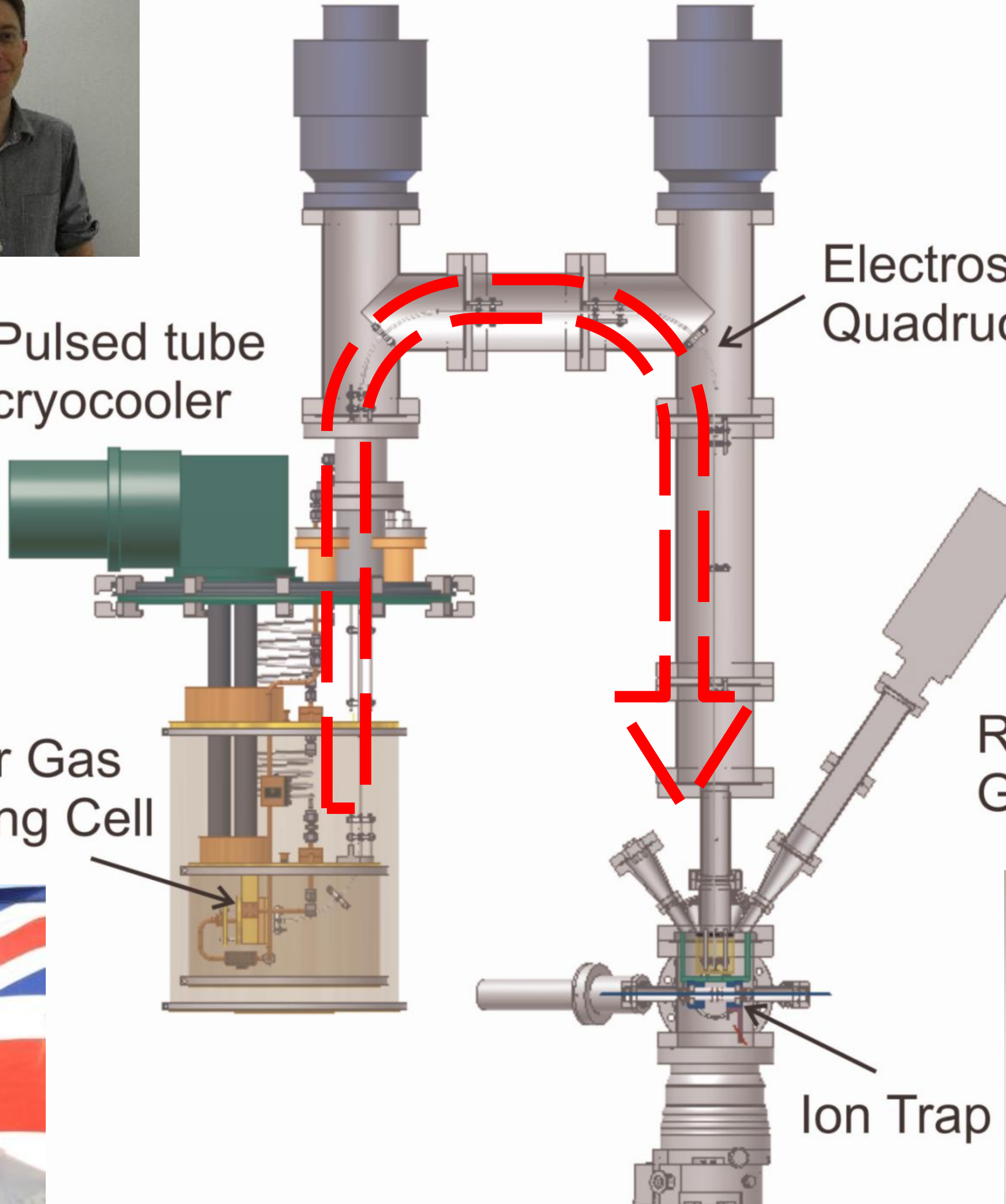
More intense beam
Rotationally cold

Extract cold molecules via quadrupole guide

Mix cold He at 5K with molecular gas



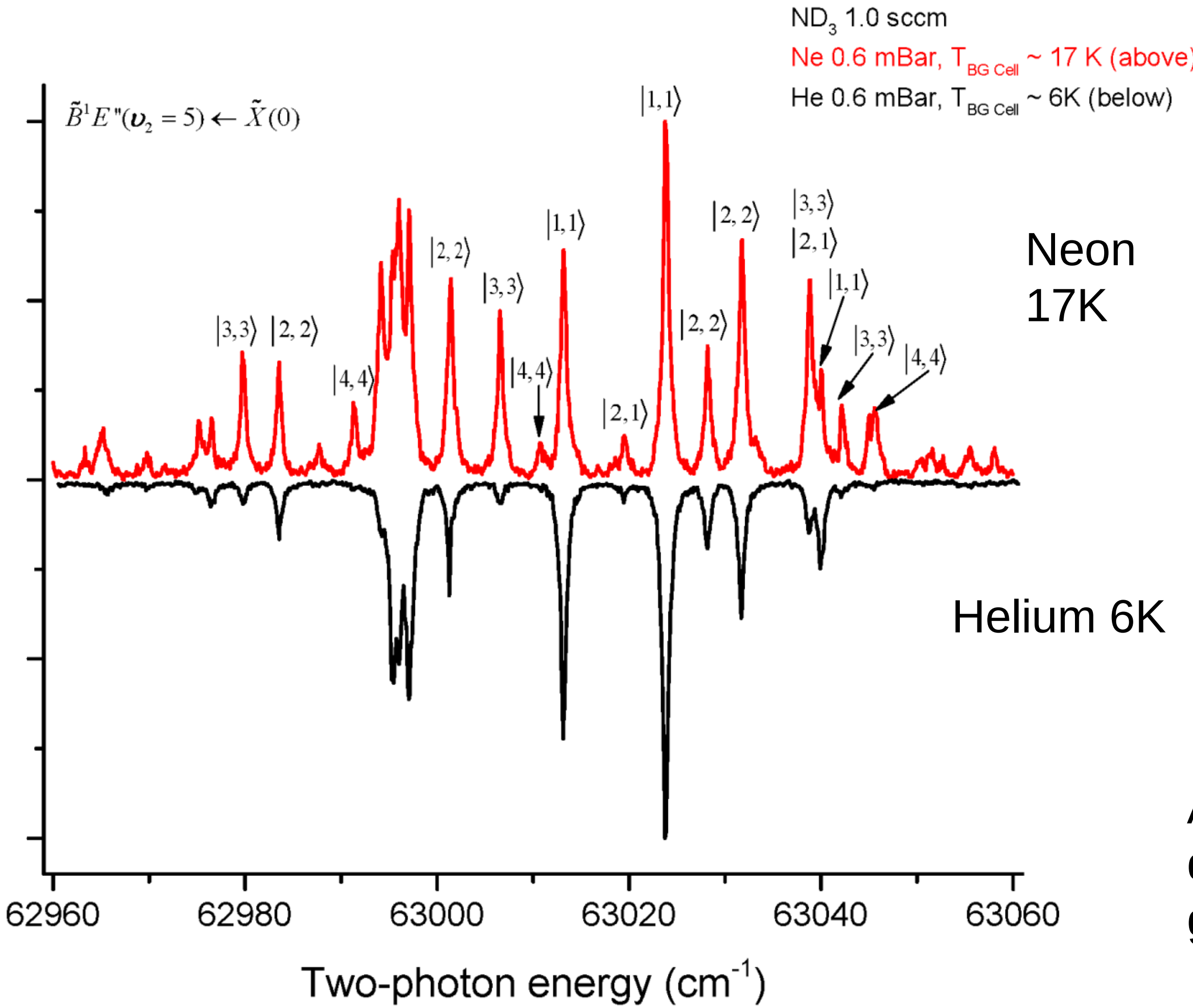
Based on design in: C. Sommer *et al.*, Faraday Discuss., 203, **142** (2009)



Kathryn Twyman

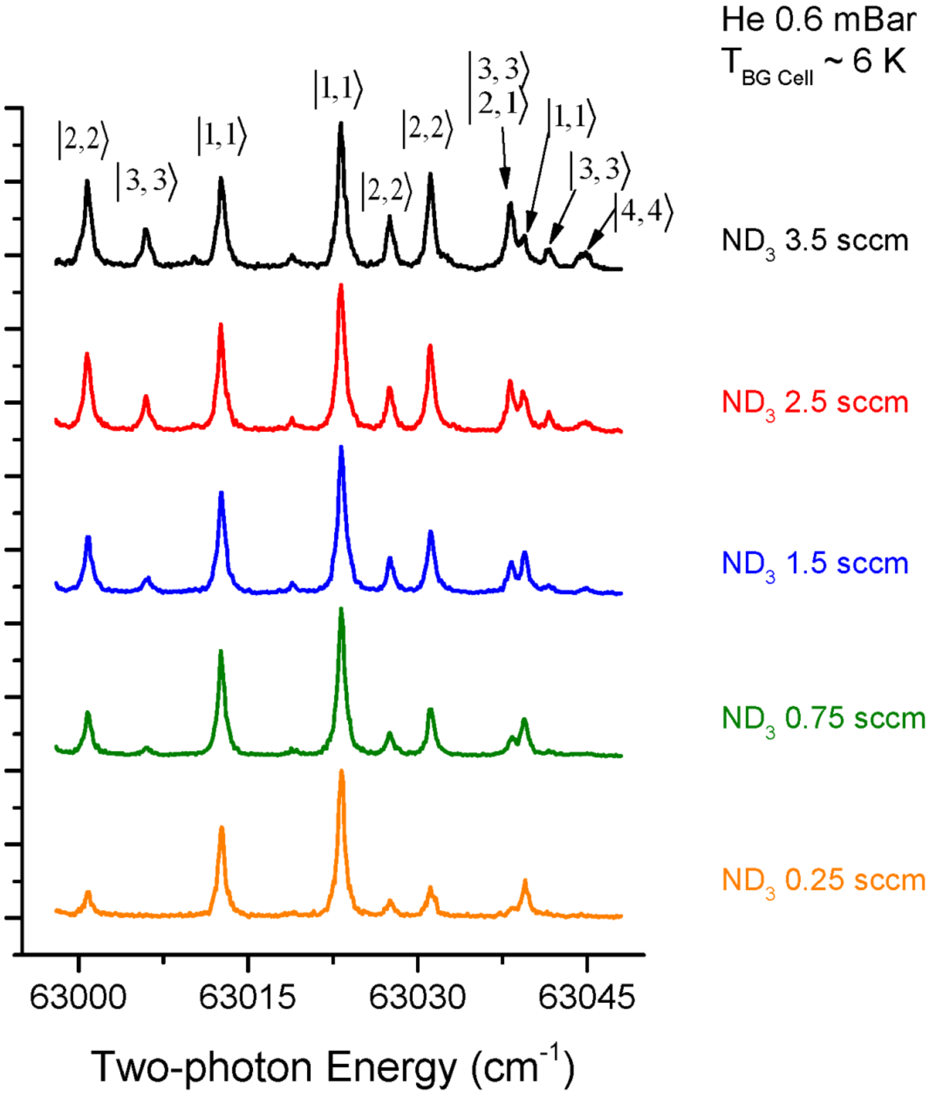
Laura Pollum

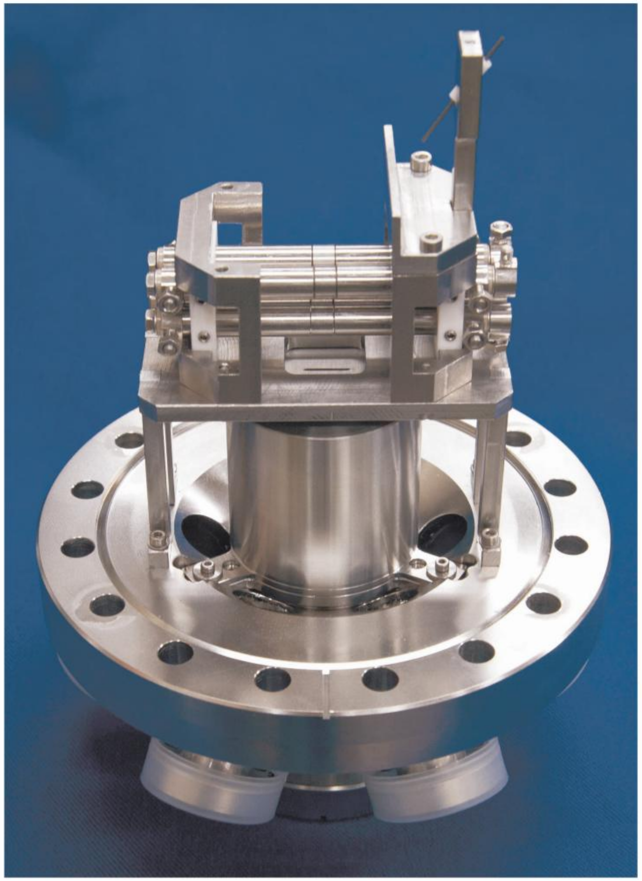
2+1 REMPI of transmitted ND_3

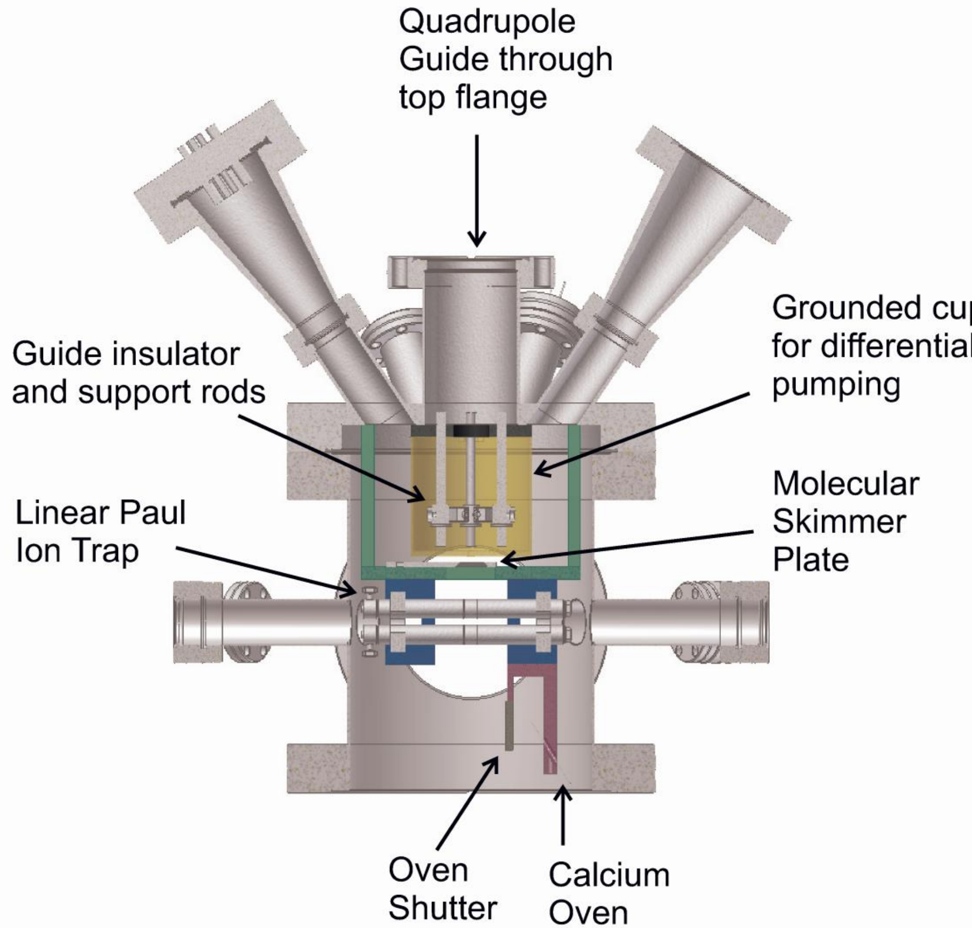


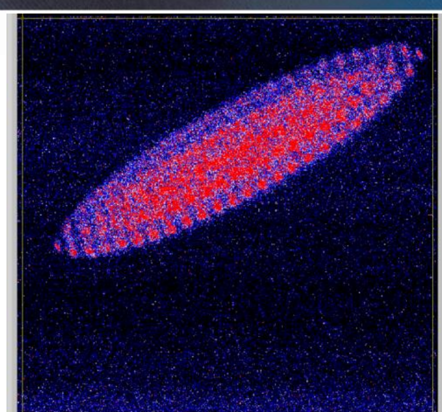
After 2 metre quadrupole guide

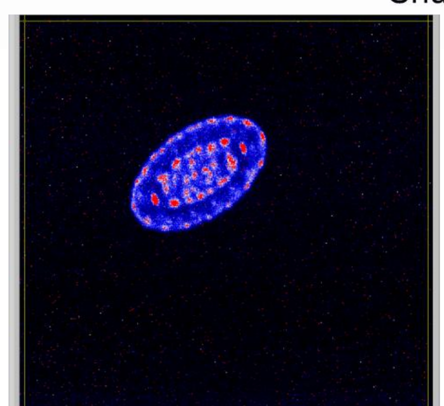
Variation with ND_3 flow rate

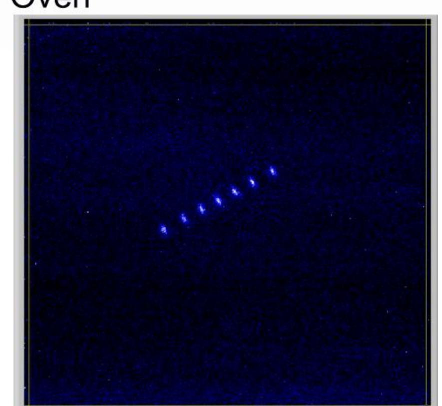




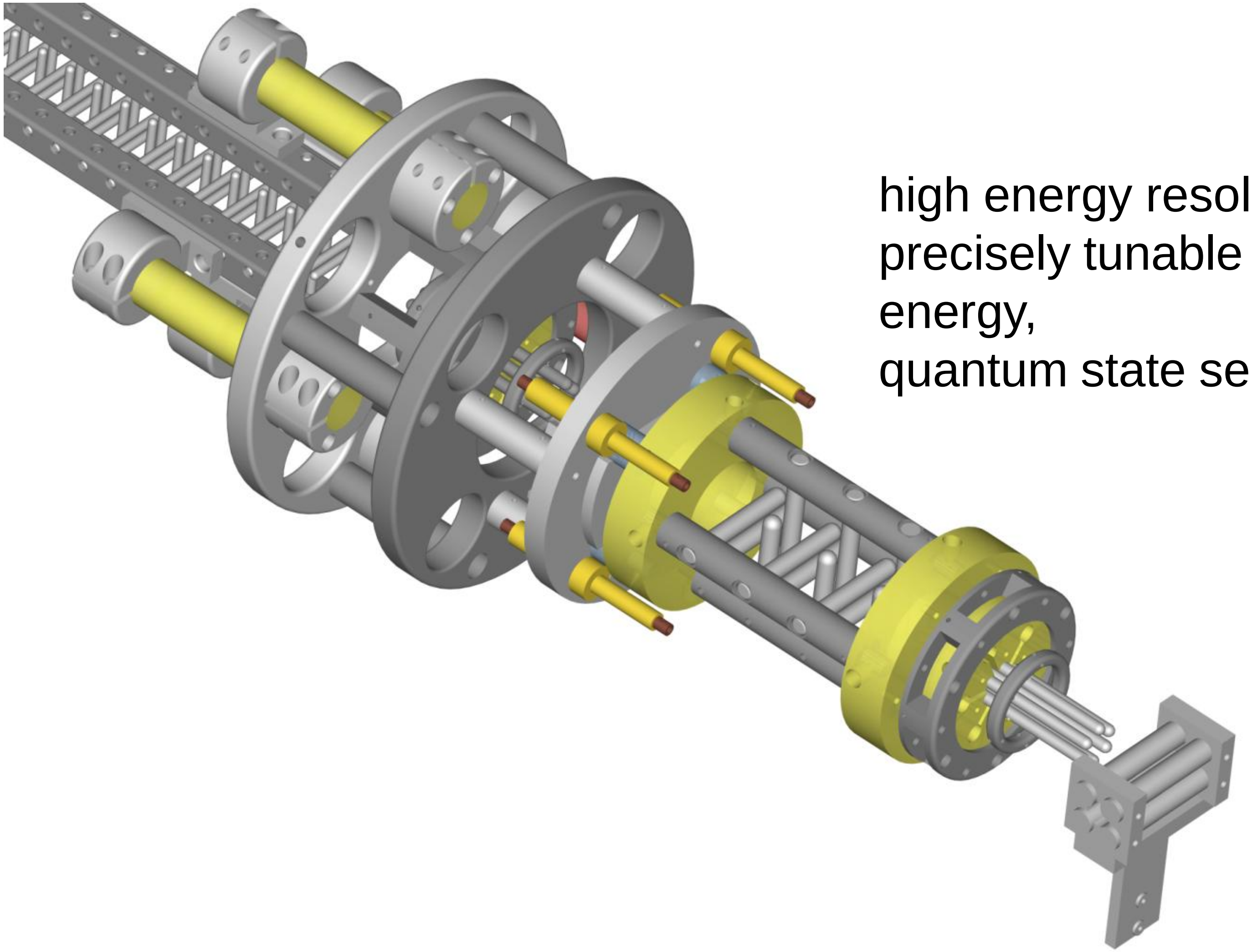

Quadrupole Guide through top flange
Grounded cup for differential pumping
Guide insulator and support rods
Molecular Skimmer Plate
Linear Paul Ion Trap
Oven Shutter
Calcium Oven





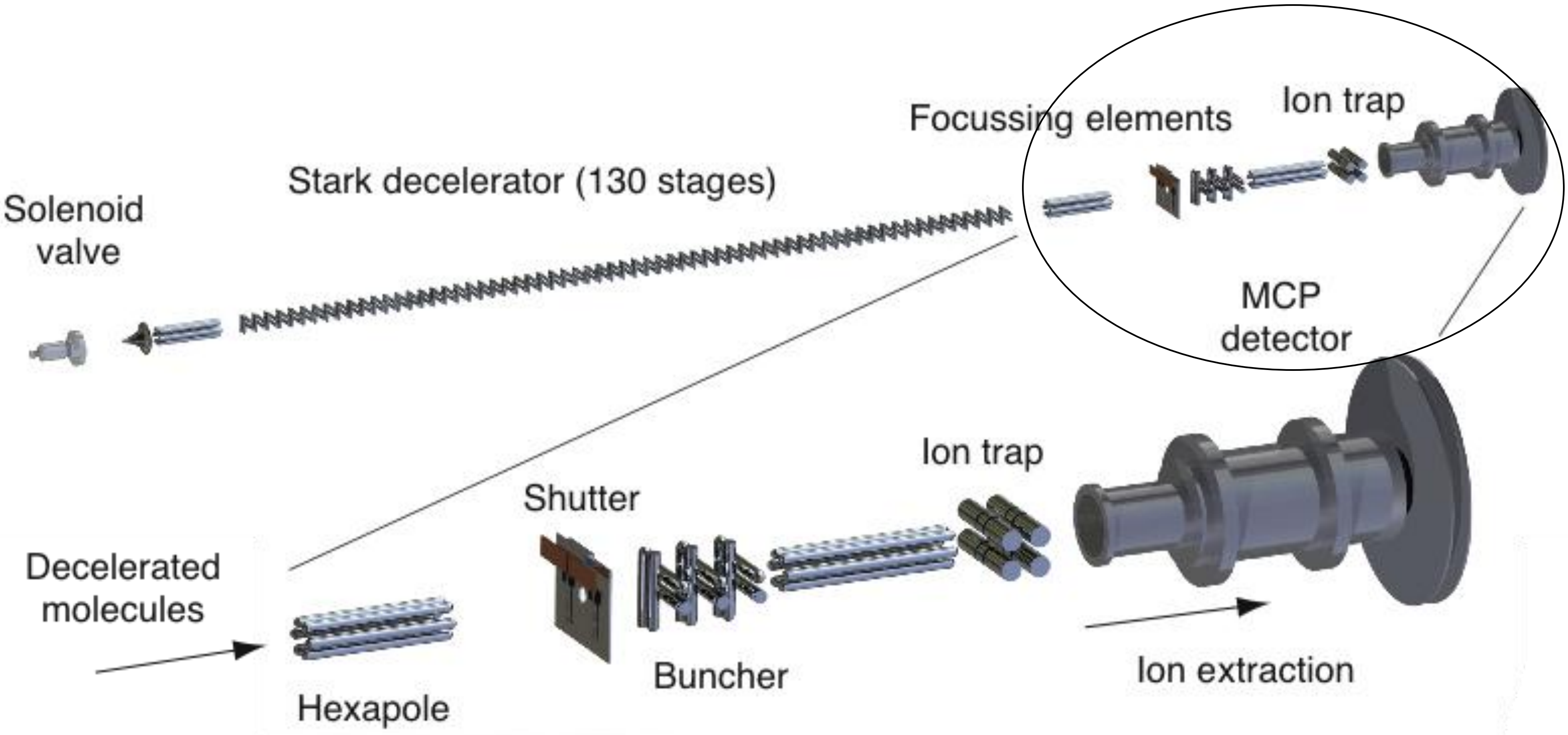


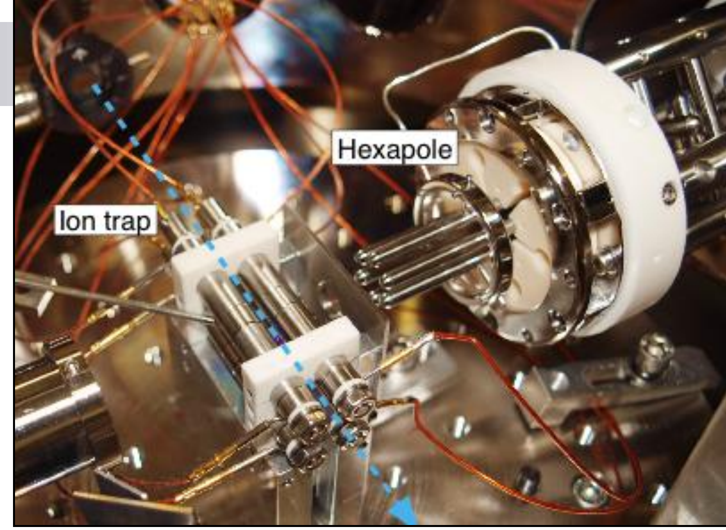
(2) Stark decelerator plus ion trap combination



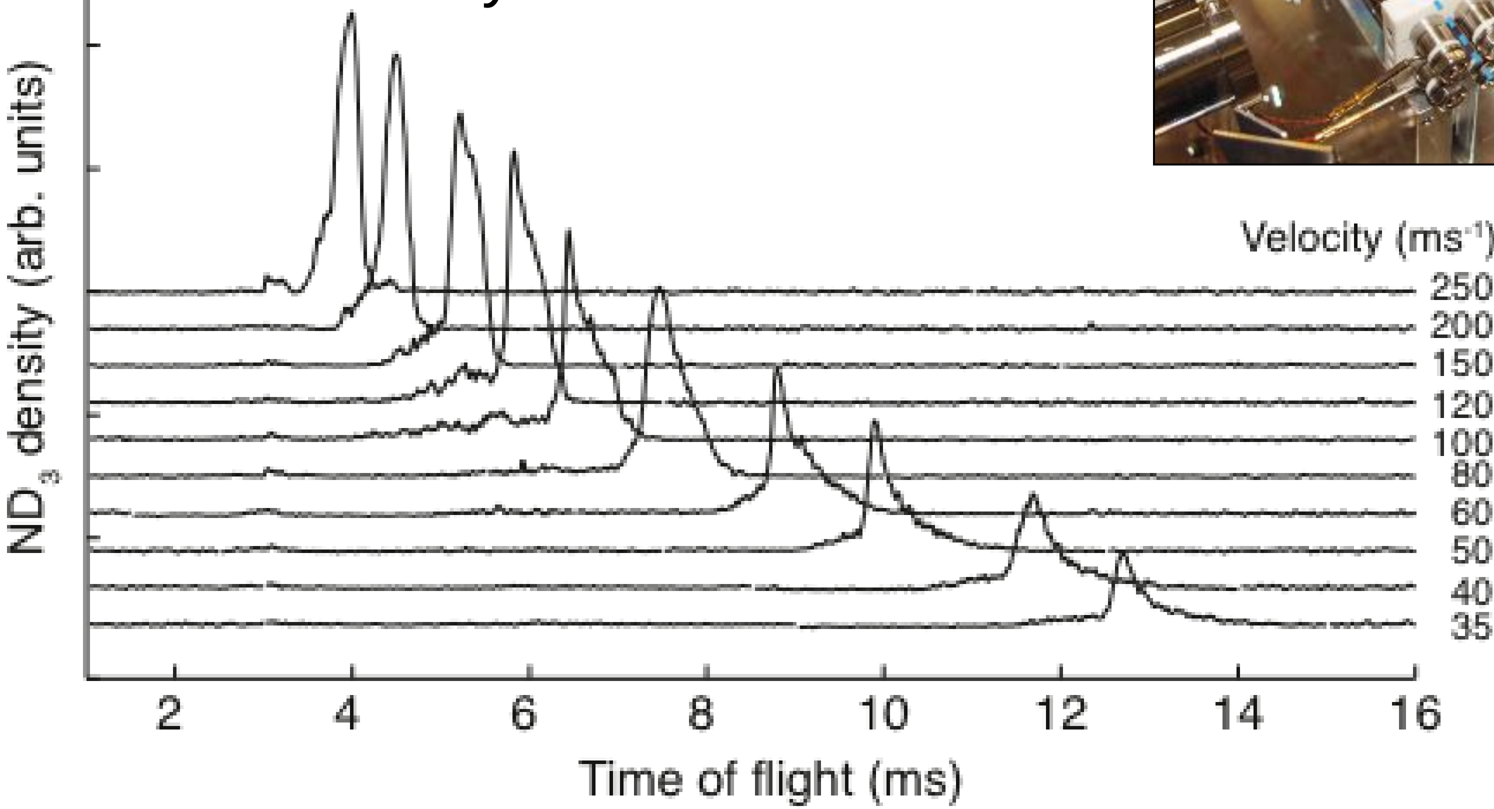
high energy resolution,
precisely tunable collision energy,
quantum state selective.

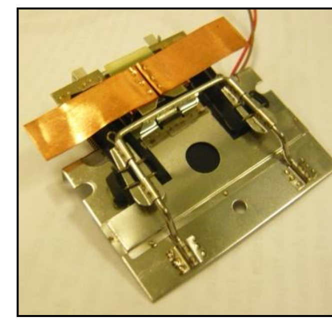
Stark decelerator ion trap combination





ND_3 beam: decelerated beam isolated from fast beam by a shutter



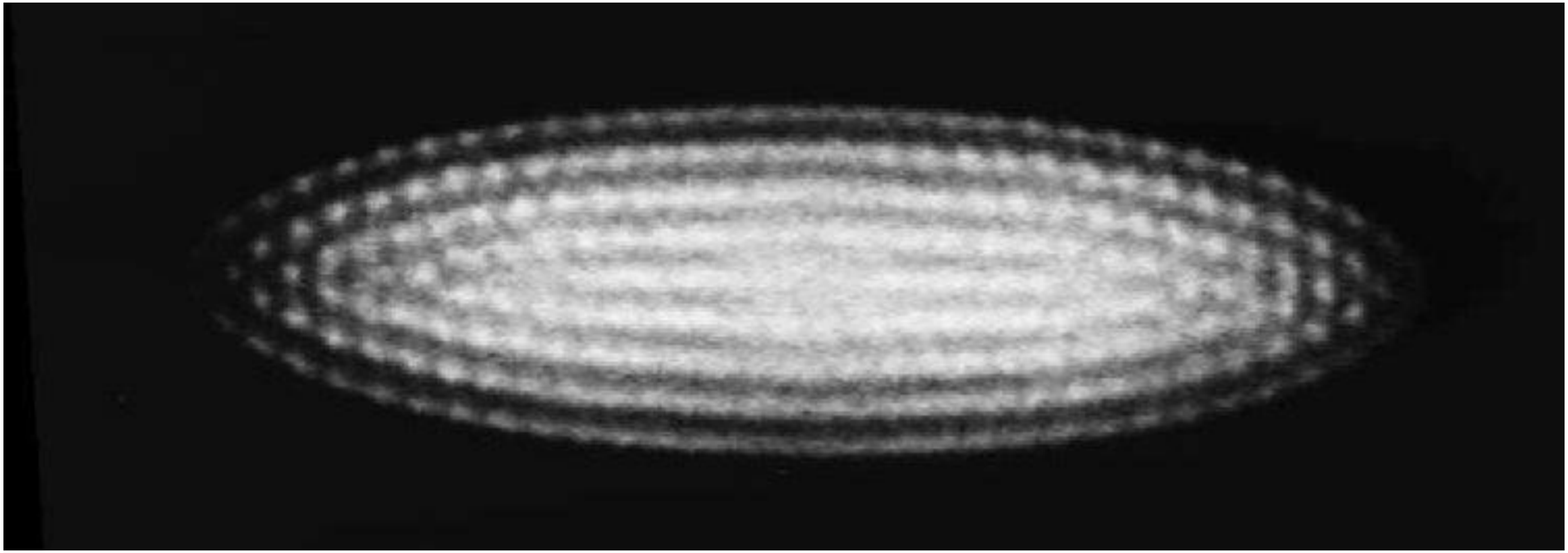


Effective collision energies from around 75 K down to close to 1 K

[See also: C. E. Heiner *et al.*, PCCP **8** 2666 (2006)]

Reaction of Xe^+

$$Xe^+ (^2P_{3/2}) + ND_3 \longrightarrow ND_3^+ + Xe$$



1. Prepare Coulomb crystal of Ca^+ ions
2. Load Xe^+ ions into the trap by laser multiphoton ionisation of carrier gas
3. Focus ammonia beam into the ion trap (Stark decelerator electrodes held at ±8 kV for focusing, no deceleration)

A range of reactions should be possible with ND_3 or NH_3 and sympathetically cooled ions

- $ND_3 + Xe^+ \rightarrow ND_3^+ + Xe$

- $ND_3 + NH_3^+ \rightarrow$
- $ND_3 + C_2H_2^+ \rightarrow$
- $CH_3F + Ca^+ \rightarrow$

Stark decelerator versus buffer-gas cooled velocity selector

- Stark decelerator
  - Pulsed source
  - Velocity control and high energy resolution
  - Single quantum state (or very few quantum states)
- Buffer gas cooled velocity selector
  - Continuous source
  - Variable rotational temperature 6 to 20K
  - More flexibility in molecules useable
  - no issue with undecelerated molecules.

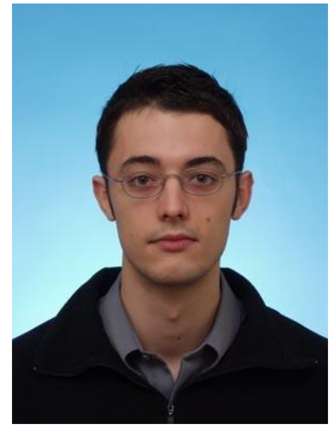
Summary

- We take advantage of the very high sensitivity of the Coulomb crystal setup to study the reaction of an energy-tuneable, translationally-cold neutral beam with trapped laser-cooled ions.

- Results have been reported for e.g., Ca^+ + CH_3F at ~1K and other reactions with a quadrupole guide
- Wide range of possible reactions by sympathetic cooling
- Developments towards internal state control using Stark decelerator and buffer gas cooling
- Operation of a Zeeman decelerator
- Promising new approach to cold radicals e.g., halogens

Thanks to… the ion trappers

Martin Bell



Alex Gingell

Laura Pollum

Stefan Willitsch

(now Basel)

James Oldham

(now Wayne State)

Brianna Heazlewood

Nabanita Deb

The decelerators and guiders

Brianna Heazlewood

Martin Bell

Kathryn Twyman

Heather Lewandowski

Lee Harper

James Oldham

Katrin Dulitz

Edward Steeer

The PhotoStop Gang

Magnetic Trapping

Chris Rennick

Photostop Durham

Eckart Wrede

Adrian Rowland

David Carty

Jessica Lam

Will Doherty

Michael Drewsen (Aarhus)

Gerard Meijer (Berlin)

Gerhard Rempe (Garching)

Frederic Merkt (ETH)

Matthias Keller (Sussex)

EPSRC Programme Grant

The Final Credits