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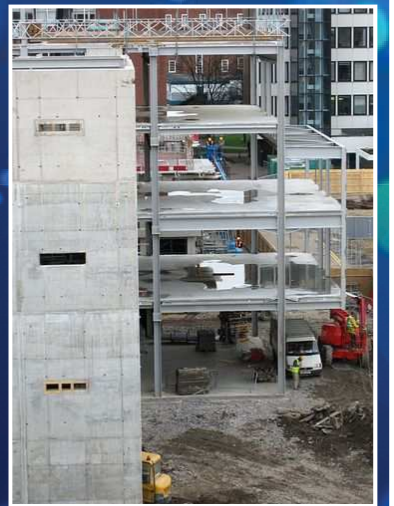



Photographs courtesy of Nicholas J Higham (c) 2006

The University of Manchester
Photon Science Institute

MANCHESTER 1824

ZEKE Rydberg states in a crowd and Condensed Rydberg Clusters: a new state of matter?

10th October 2008

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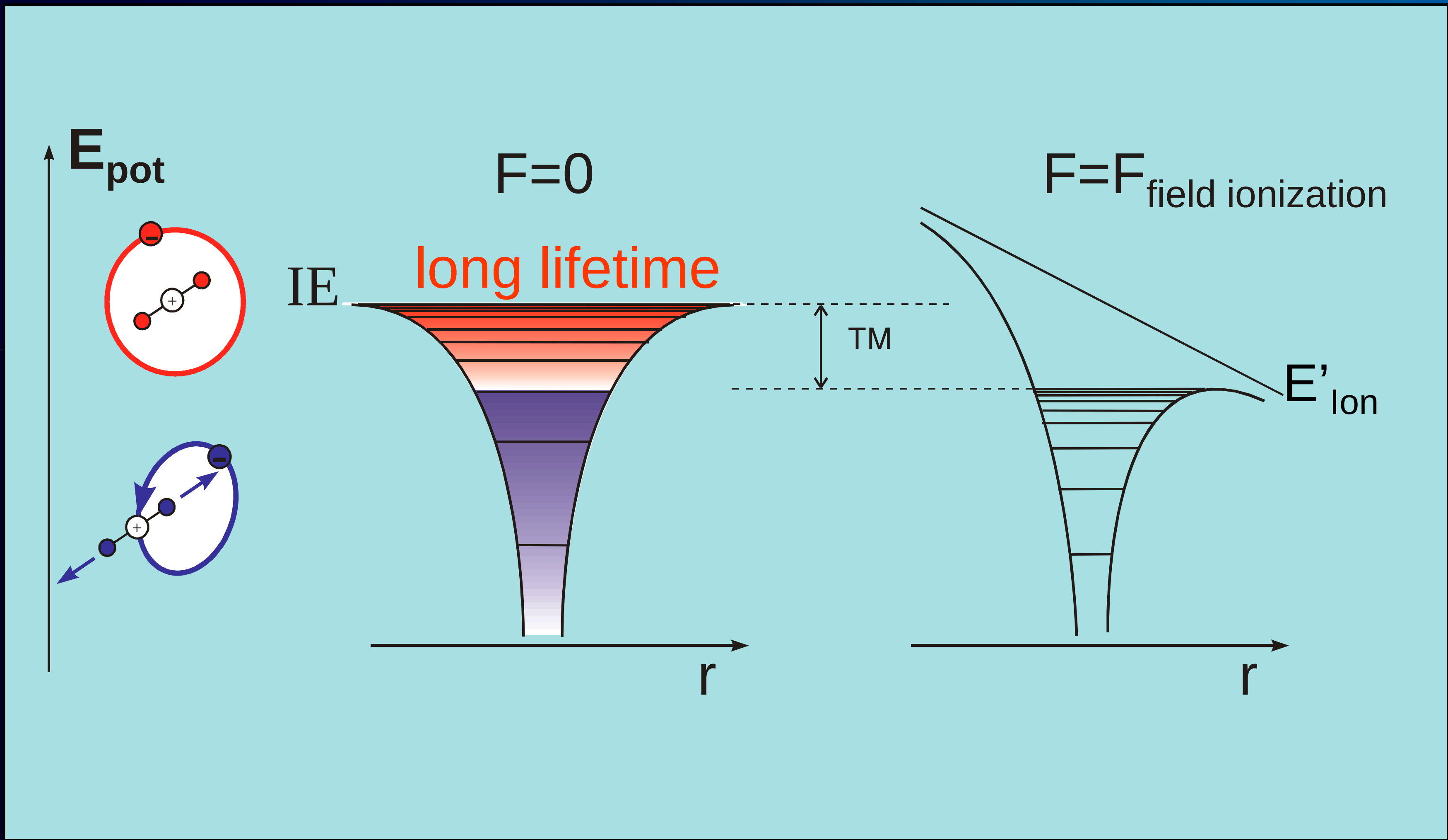
Pulsed Field Ionisation of ZEKE Rydberg States



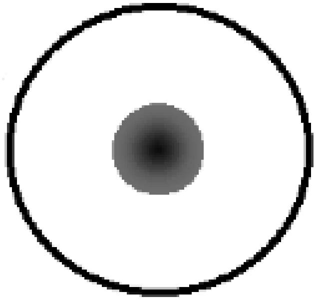
KMD et al CPL 1984, CPL 1988

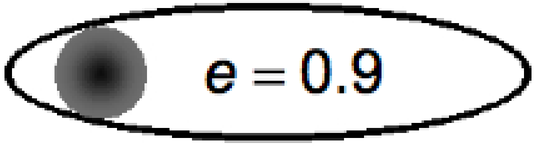
Stabilization via Angular Momentum Enhancement, Equal to Ultra-long Lifetimes

$$e = \sqrt{1 - \ell^2 / n^2}$$

Eccentricity: It gives the shape of the orbit

$e = 0$





Large ℓ orbit: no collisional energy exchanges between the Rydberg electron and the core

Small ℓ orbit: many collisional energy exchanges between the Rydberg electron and the core

Long Rydberg Lifetime ($\sim n^5$)

Lifetime due to core-collisions ~ n^3

Radiative lifetimes are also longer for large ℓ orbits)

Energy States of H-atom

$$E = IE_H - R_H / n^2$$

Energy States of "H-atom like" Rydberg State

$$E = IE - R / (n-\delta)^2$$

n: principal quantum number

δ : quantum defect

Rydberg

Setting the Scene
for a half day experiment

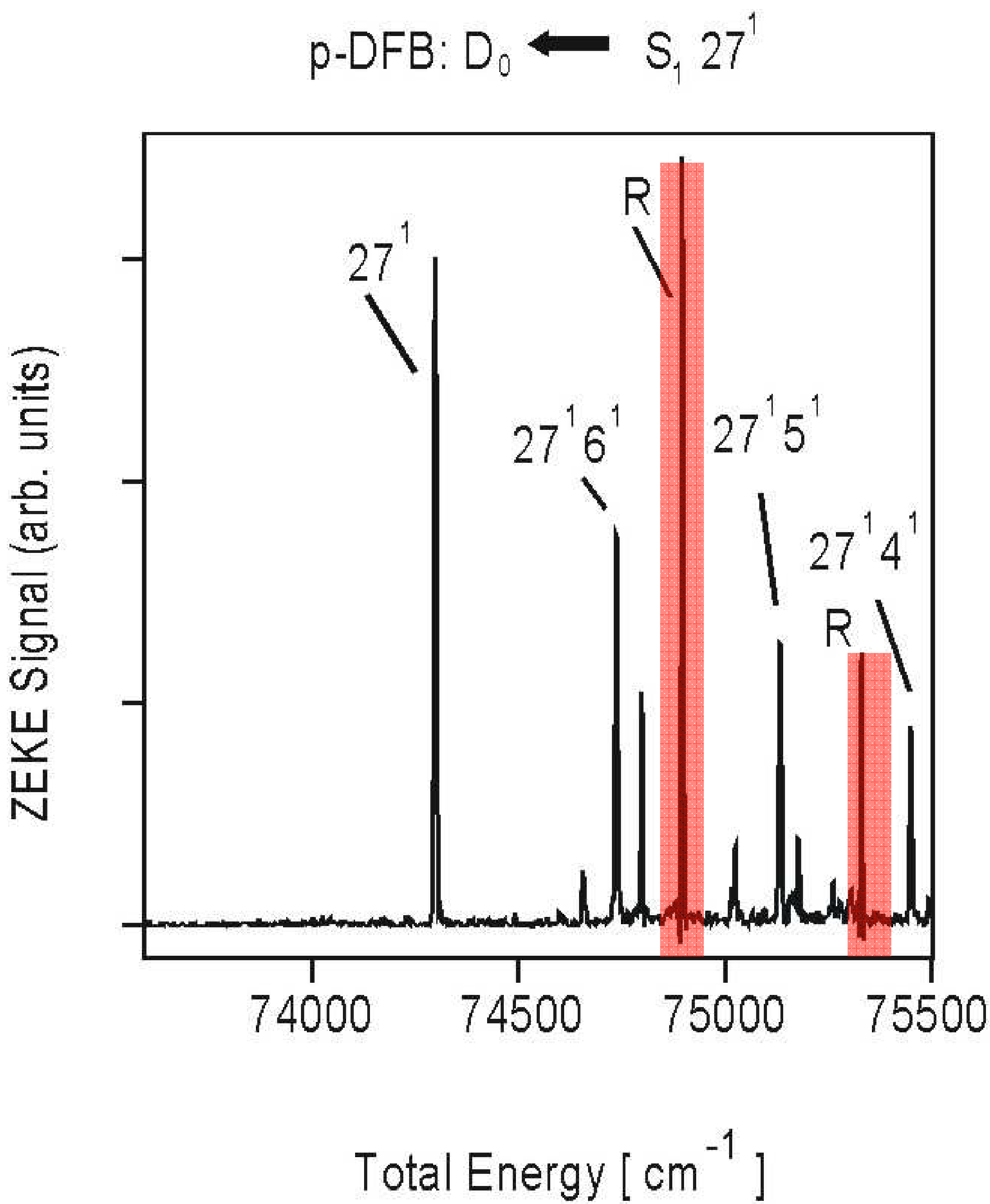
- ZEKE Rydberg states
  - – one colour ZEKE Rydberg excitation
    - para-difluorobenzene
- Supersonic Jet Excitation
  - – close to nozzle at high density
  - – high collisional cooling
- Rydberg electron sees many ions!!
  - – electrons should be bound collectively!

Setting the Scene
for a half day experiment

- ZEKE Rydberg states
  - – one colour ZEKE Rydberg excitation
    - para-difluorobenzene (pDFB)

As shown by Reiser et al, *JPC* 1991,
pDFB shows some very strong one-colour transitions where the S_1 S_0 and the D_0 S_1 transition are simultaneously in resonance

So produce very highly excited ZEKE Rydberg states n > 200 with only one laser!!


p-DFB: D_0 ← S_1 27^1
27^1
$27^1 6^1$
R
$27^1 5^1$
$27^1 4^1$
R
ZEKE Signal (arb. units)
74000
74500
75000
75500
Total Energy [cm^{-1}]

Setting the Scene
for a half day experiment

- ZEKE Rydberg states
  - one colour ZEKE Rydberg excitation
    - para-difluorobenzene (pDFB)
- **Supersonic Jet Excitation**
  - **close to nozzle at high density**
  - **high collisional cooling**
- Rydberg electron sees many ions!!
  - electrons should be bound collectively!

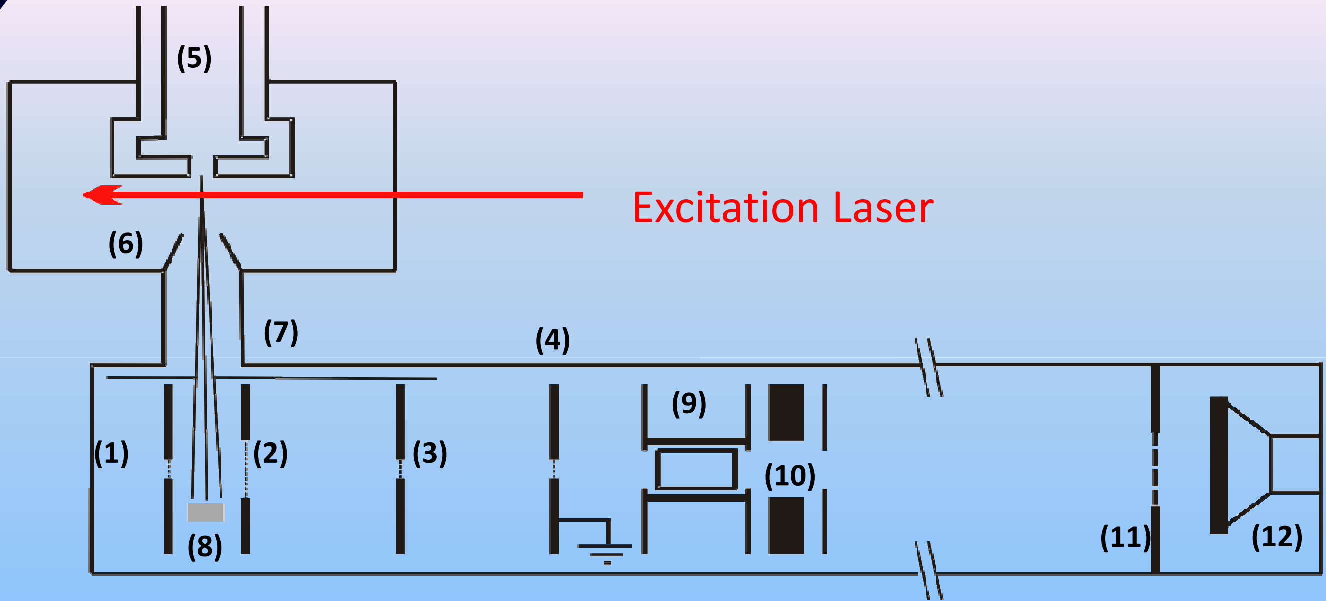
Jet characteristics:

at nozzle:	**2.5 10^{19} cm^{-3}**
pDFB density at nozzle:	**2.5 10^{17} cm^{-3}**
pDFB density at 1mm distance.:	**2.5 10^{15} cm^{-3}**
$pDFB^{+}$ maximum density:	**2.5 10^{15} cm^{-3}**
	10^{5} ions/cm
	10^{4} ions/mm
	10 ions/⌠m

$pDFB^{+}$ average distance: *ca.* hundreds of nm's

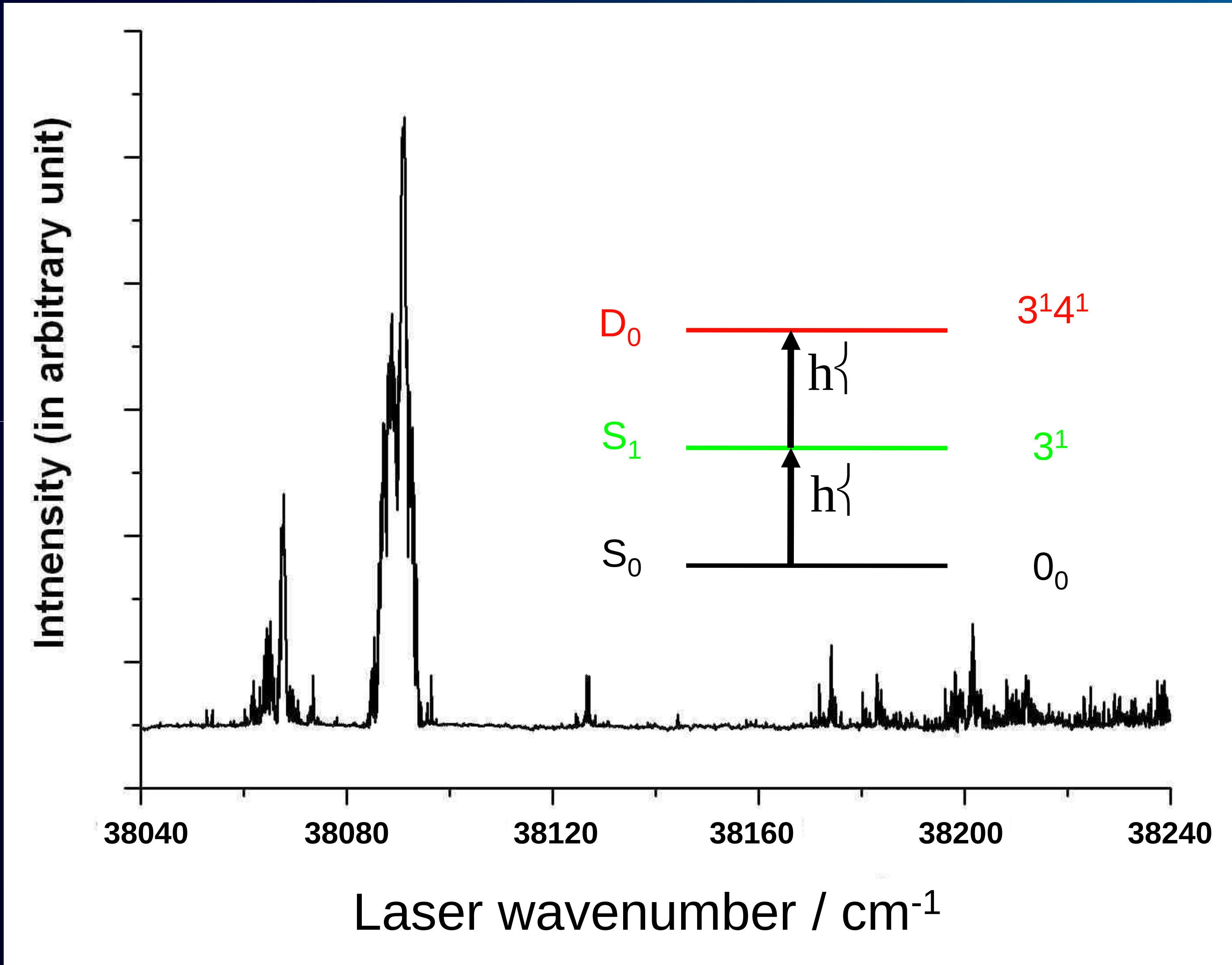
If something new such as *Condensed Rydberg Clusters* are formed, the expected distance between ion cores is expected to be around hundreds of nanometers, if δ_{pDFB} is ca. 10^{13} to 10^{14} cm^{-3}

Schematic diagram of the experimental set up for the TOF analysis of a molecular ultracold Rydberg plasma.

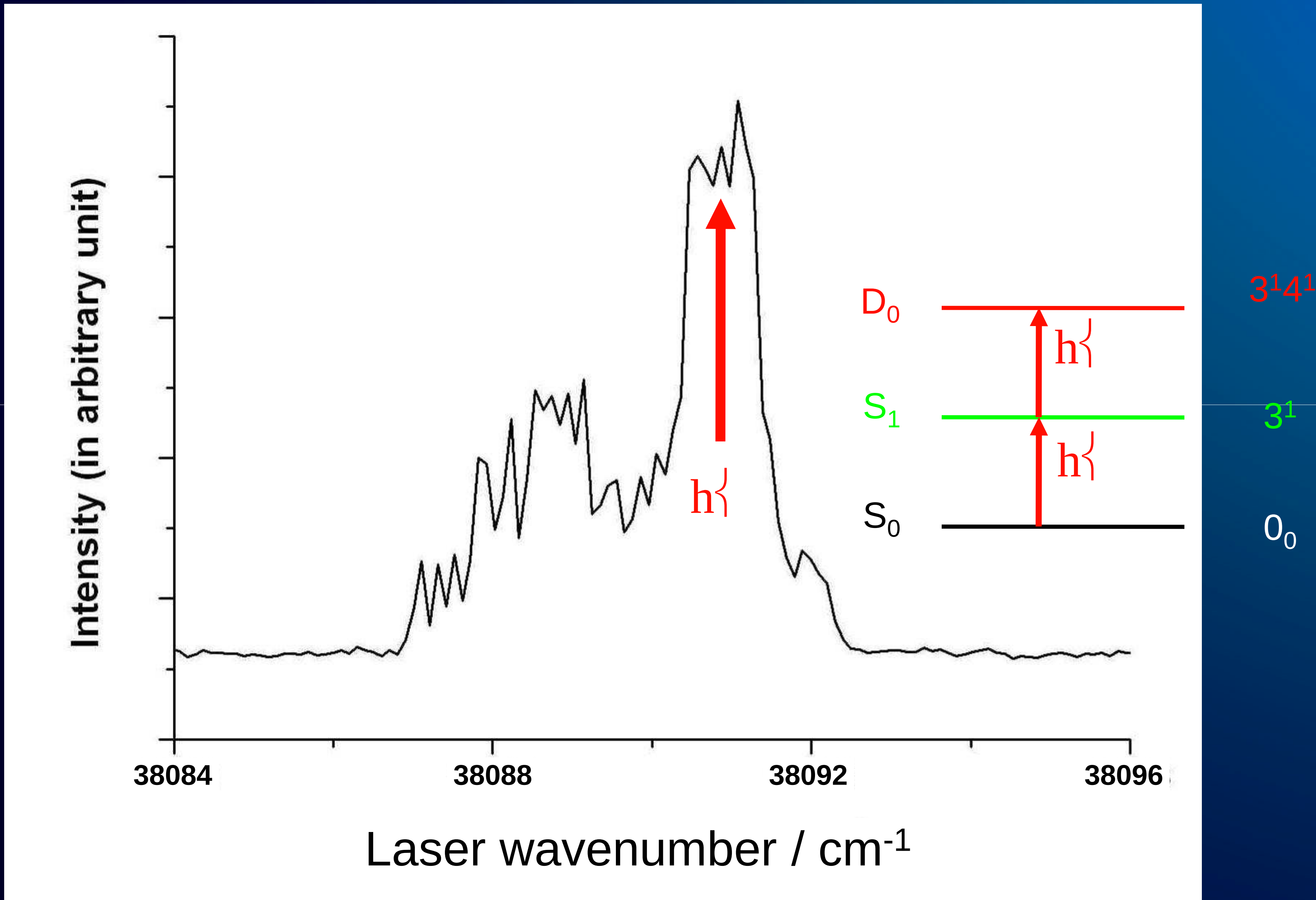


(1-4) Extraction plates
(5) General valve
(6) Skimmer
(7) Slit
(8) Molecular beam
(9) Deflector
(10) Lens,
(11) Grounded grid,
(12) MCP

Para-difluorbenzene (pDFB) one-colour spectrum with simultaneous S_1 S_0 and ZEKE Rydberg resonance



Para-difluorbenzene (pDFB) one-colour spectrum with simultaneous S_1 S_0 and ZEKE Rydberg resonance

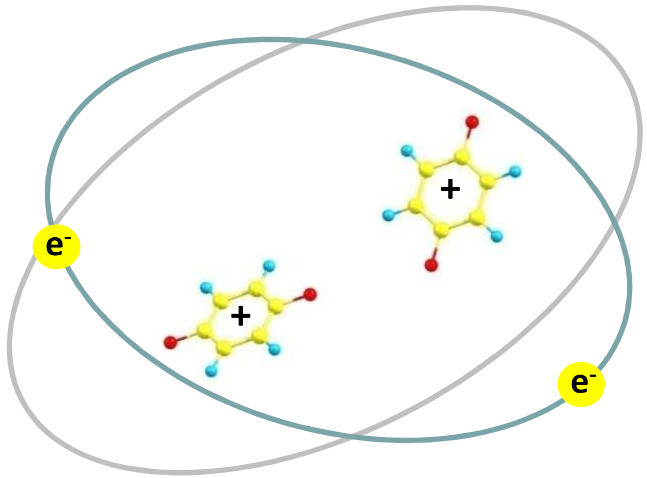


Setting the Scene
for a half day experiment

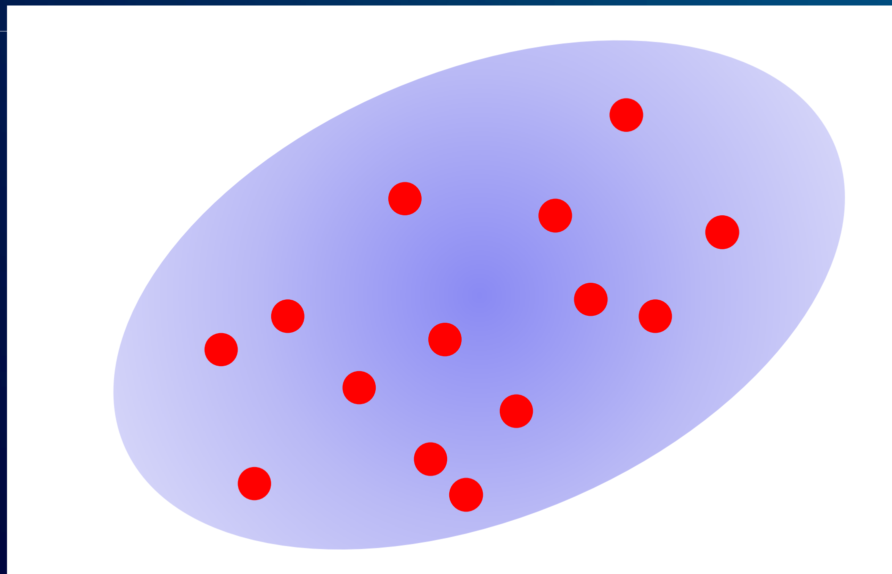
- ZEKE Rydberg states
  - – one colour ZEKE Rydberg excitation
    - para-difluorobenzene (pDFB)
- Supersonic Jet Excitation
  - – close to nozzle at high density
  - – high collisional cooling
- Rydberg electron sees many ions!!
  - – electrons should be bound collectively!

Concept of CRC

We postulate <u>C</u>ondensed <u>R</u>ydberg <u>C</u>lusters (CRC) as a moiety of n cations bound collectively by approximately the same number of electrons. The average distances between adjacent ionic molecular cores are assumed to be much smaller than the size of the Rydberg orbital, so that every Rydberg electron interacts with many cation cores.

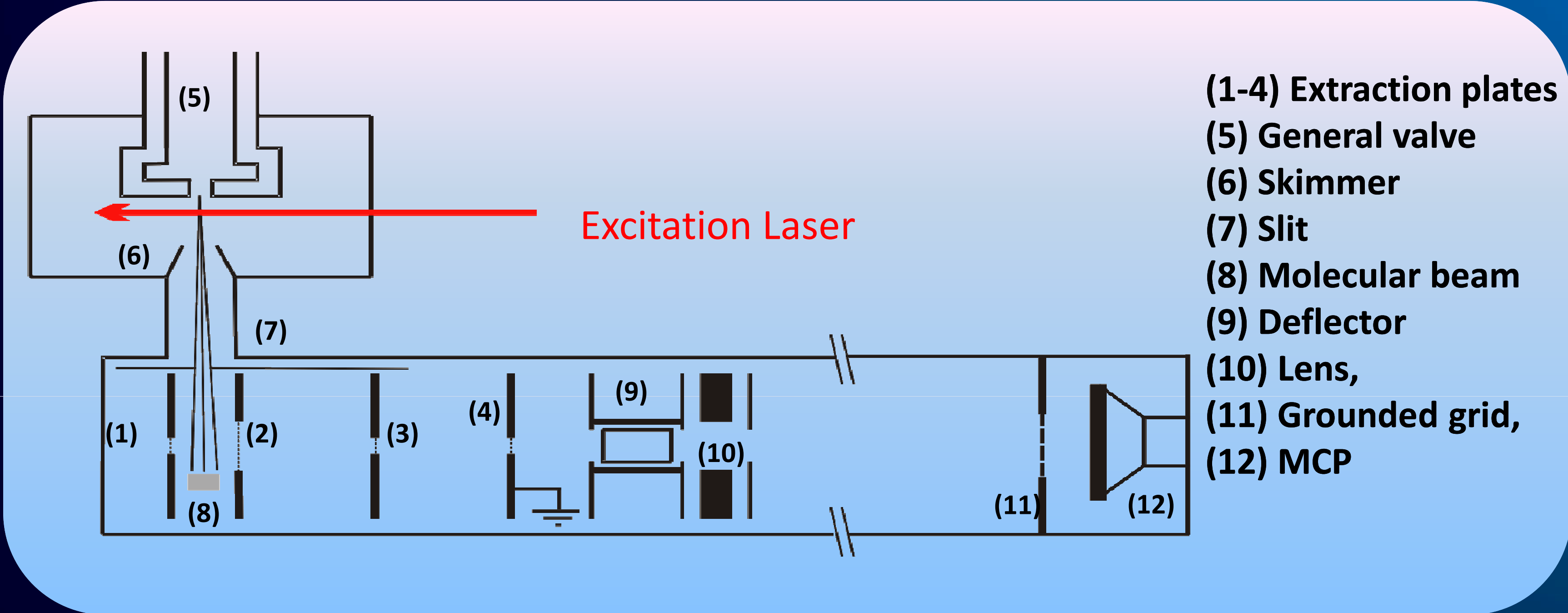


para-difluorobenzene (pDFB)



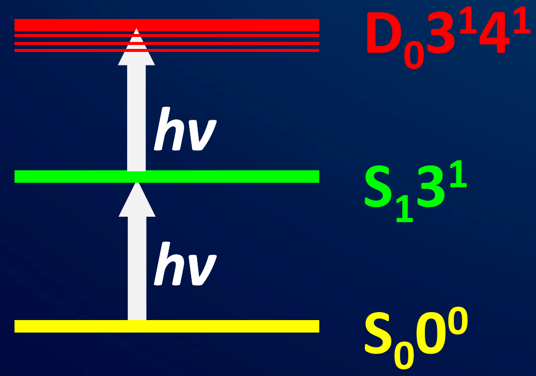
Condensed Rydberg Cluster

Generation of Ultracold Molecular Plasma and CRC

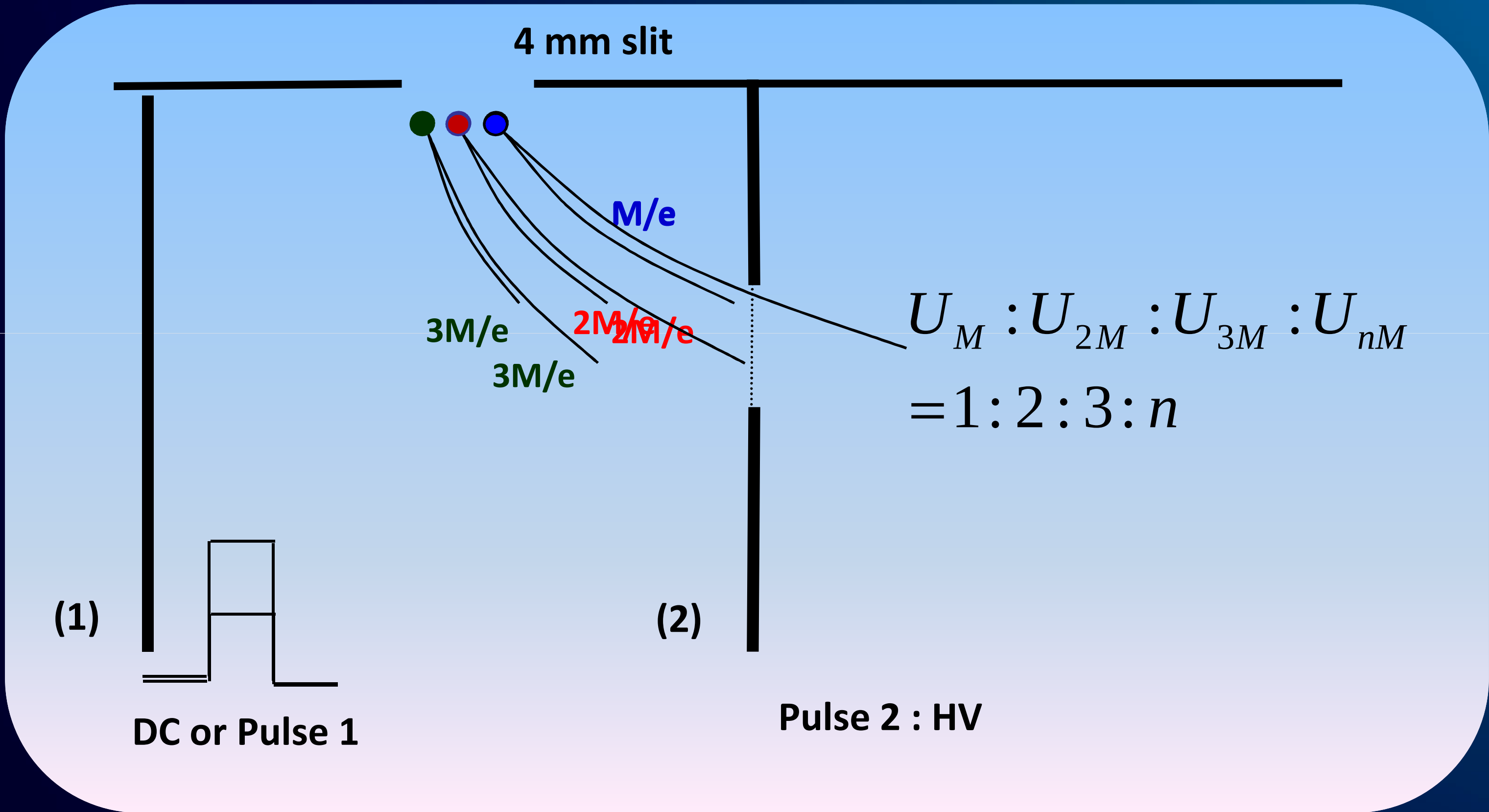


Density of pDFB$^+$ up to 10^{14}/cm^3
(Γ_{ion} >100, $\Gamma_{electron}$ > 40)

pDFB + 2 *hv* → pDFB* (*n* > 200)



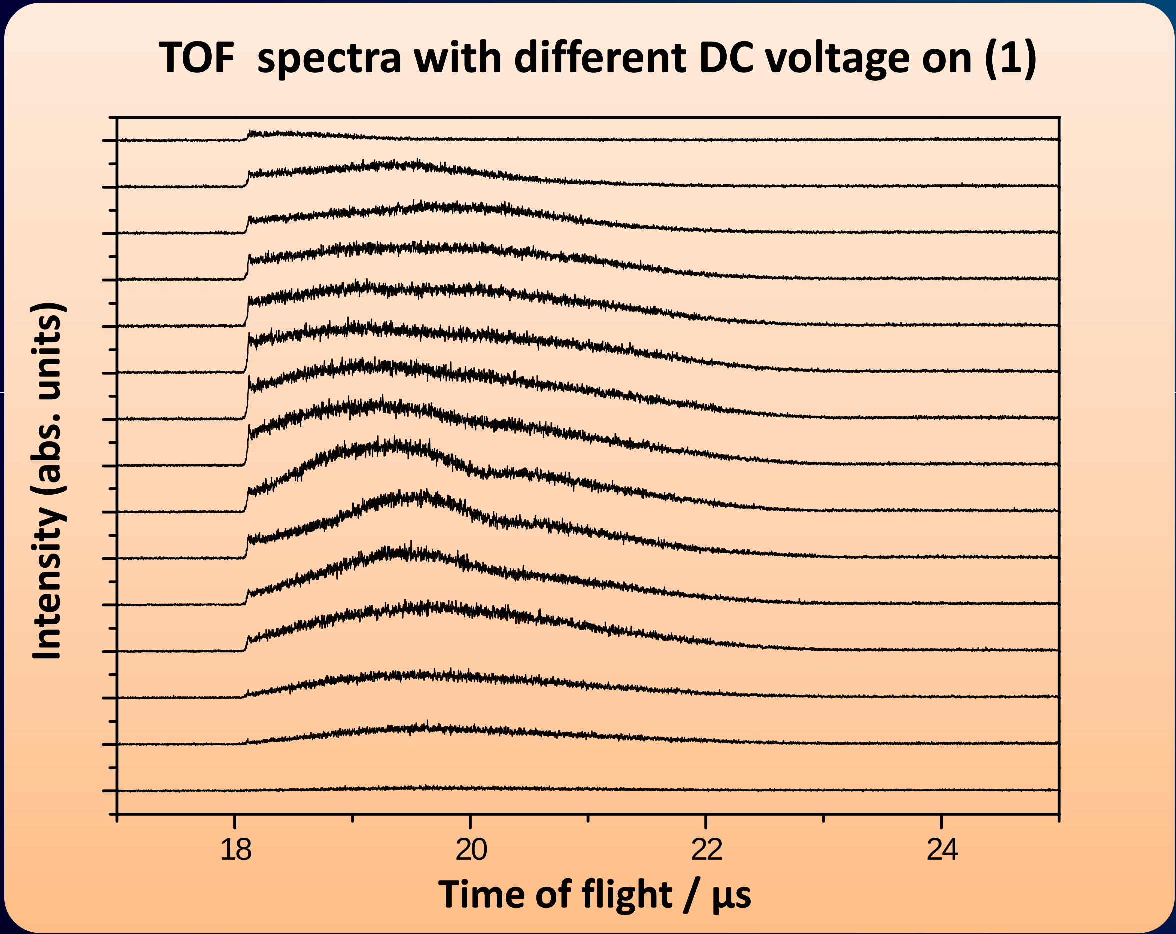
Detection of CRC
"Heavy Mass"

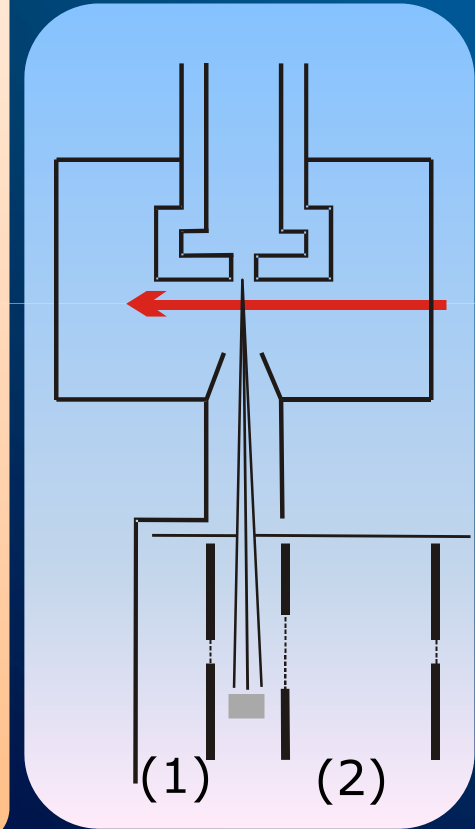


Method 1: Scan of dc voltage on aperture (1)

Detection of "Heavy Mass"

Results (1): Voltage scan on aperture 1





+4.8 kV pulse is applied on (2), pulse width is 1.22 µs, laser crosses with molecular beam at 6 mm from the nozzle

Possible signal source

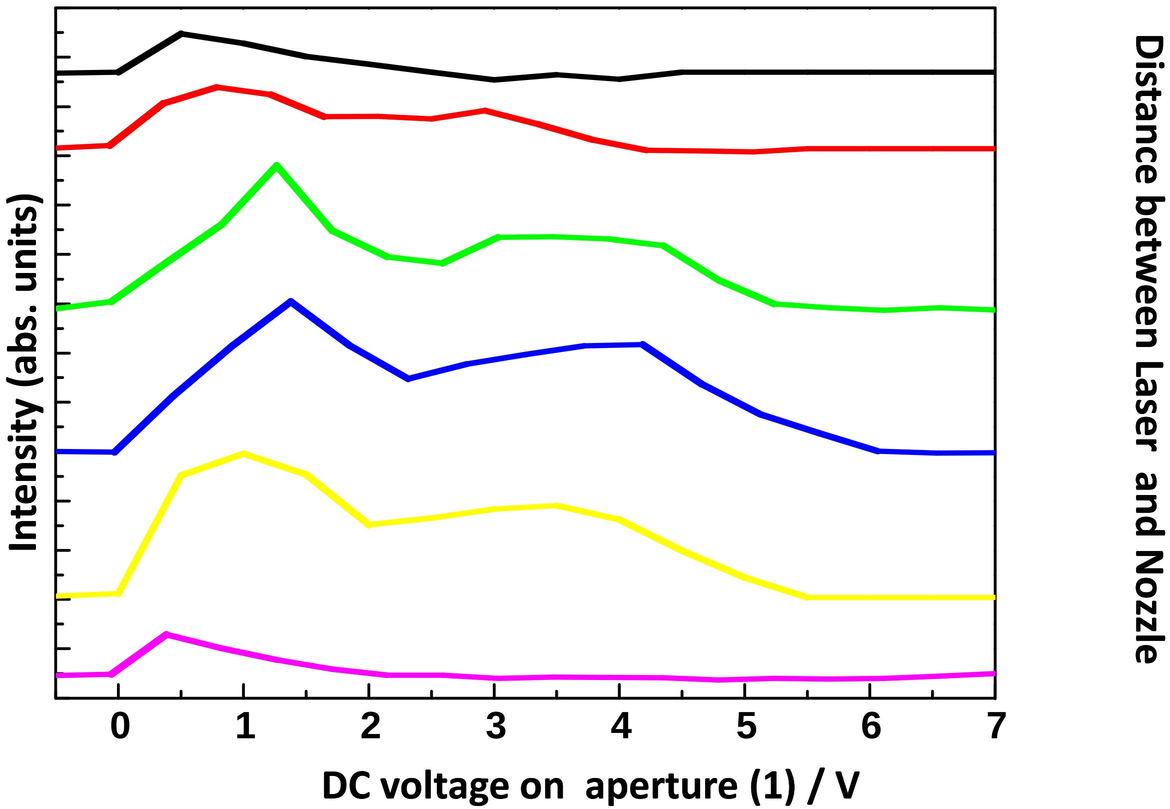
- Single pDFB cations ✗
- Single pDFB Rydberg's ✗
- Cations released from the plasma ✓
- something new released from or contained in the plasma: ✓

Condensed Rydberg Clusters *CRC*

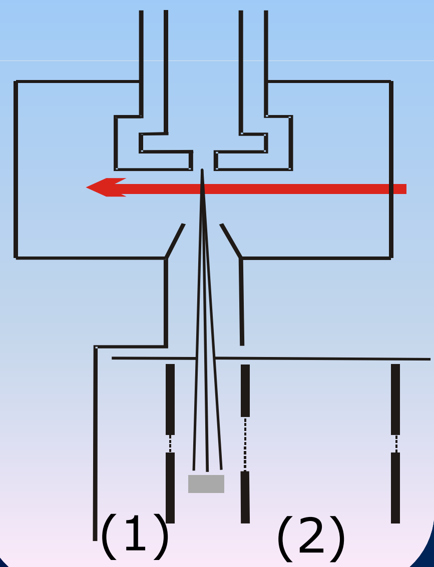
Detection of “Heavy Mass”

Laser in Jet Position Sensitivity

DC voltage on (1) scan with different laser positions



$$\Gamma =\propto \frac{D}{T}$$



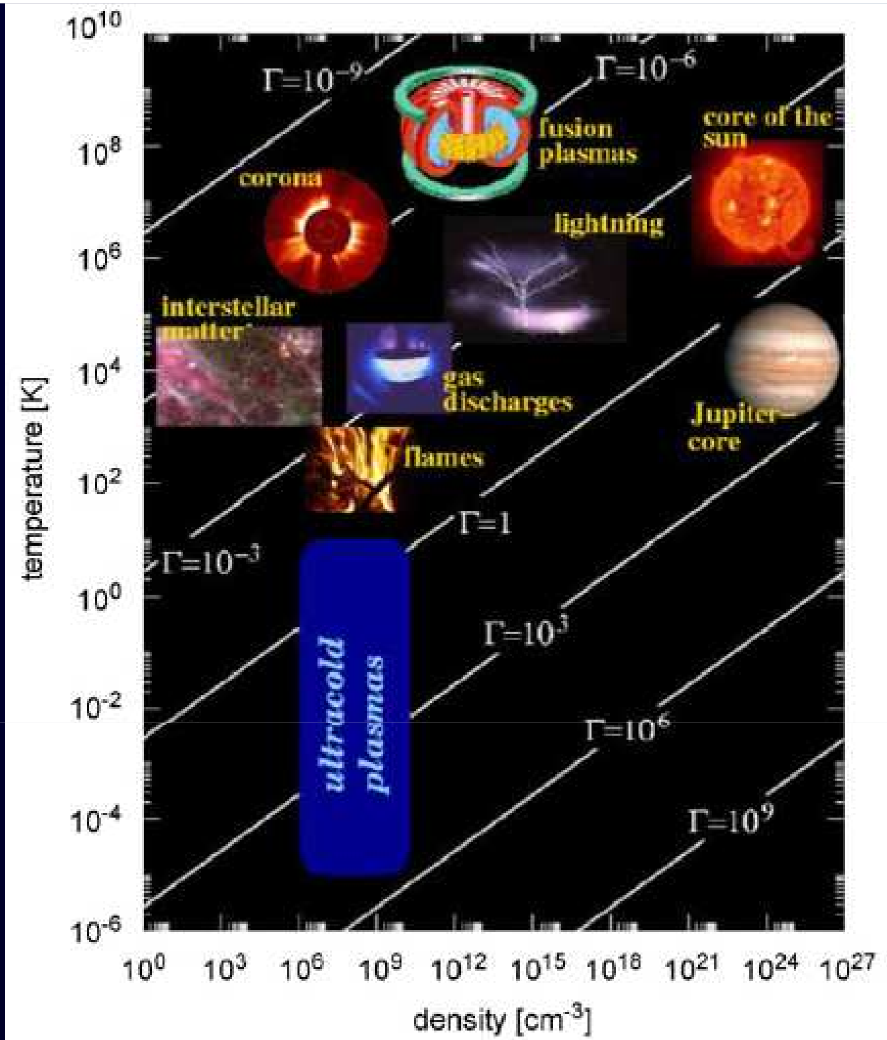
4.8 kV pulse is applied on (2), pulse width is 1.22 μs, the delay between laser and pulse is 450 μs.

Questions arising:

- Plasma Formation?!
- Can the “plasma” have a structure? ?
- Ultracold “condensate” of ***m* ions and *n* electrons** *($m \approx n$)* with periodic ion structure and electrons in a “conduction band”

Contrast this to

- Cold Plasmas from MOT plus Rydberg excitation
- van der Waals clusters



Overview of neutral plasmas in the density-temperature plane

T.C. Killian etc., Phys.Report 449 (2007) 77

T. C. Killian, Science, 316 (2007) 705

$$\Gamma = E_{interaction}/E_{thermal} = 2.69\times10^{-5}\left[\frac{n}{10^{12}\,cm^{-3}}\right]^{1/3}\left[\frac{T}{10^{6}\,K}\right]^{-1}$$

$E_{interaction}$: Coulomb interaction energy of the plasma; $E_{thermal}$: thermal energy of ions or electrons. n is number density of plasma.

How to obtain a *strongly coupled* Rydberg plasma

Plasma coupling parameter Γ

$$\Gamma = \frac{e^2}{4\pi\varepsilon_0 a} / k_B T$$

The experimental goal is to achieve strongly coupled plasma conditions for which the coulomb energy is much bigger than *kT*. Such a plasma could have a periodic shell structure and would have the characteristics of a metal

Lower temperature and/or increase density!!

Prediction is that Γ should be above 750 for crystalline phase

How to obtain a *strongly coupled* Rydberg plasma

Other efforts

(Killian, Gallagher, Pillet, Weidemüller...)

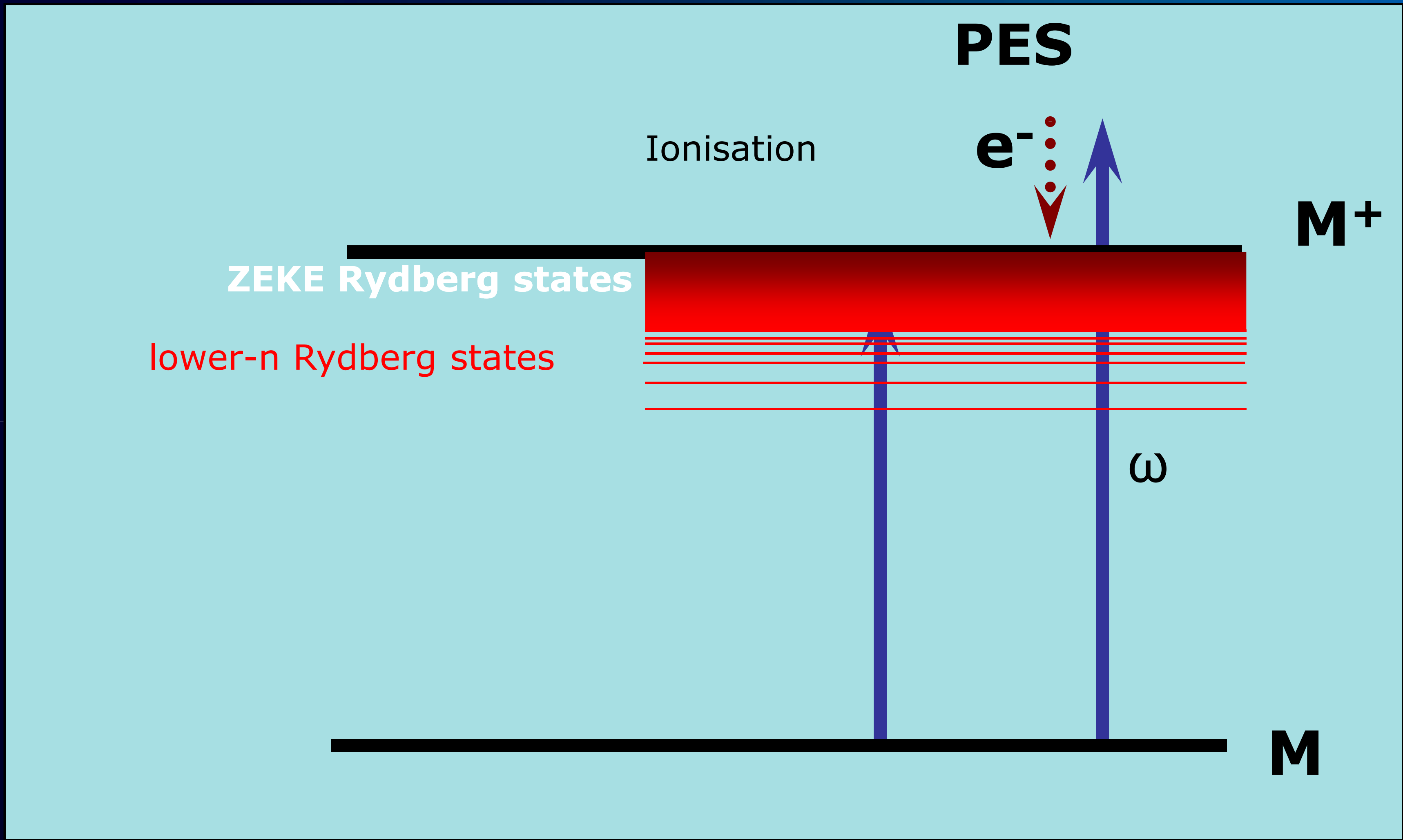
- Magneto-Optical trap to cool down atoms to microKelvin’s.
- Density of ions is only up to 10^9/cm^3
- Applies to atomic systems only

Our method

- Laser crosses with gas jet in the free expansion region (T ~ 0.1 K)
- Density of ions can be higher than 10^{14}/cm^3.
- Applies to molecular and atomic systems.

References:
S. Kulin, T. C. Killian, S. D. Bergeson, and S. L. Rolston, Phys. Rev. Lett., 85 (2000) 318.
T. C. Killian, M. J. Lim, S. Kulin, R. Dumke, S. D. Bergeson, and S. L. Roston, Phys. Rev. Lett., 86 (2001) 3759.
T. C. Killian, S. Kulin. S. D. Bergeson, L. A. Orozco, C. Orzel and S. L. Rolston, Phys. Rev. Lett., 83 (1999) 4776.

Adjust the energy of the electron and hence the electron temperature



Questions arising:

- Plasma Formation?!
- Can the “plasma” have a structure?
- Ultracold “condensate” of **_m_ ions and _n_ electrons** *(m≈n)* with periodic ion structure and electrons in a “conduction band”

Contrast this to

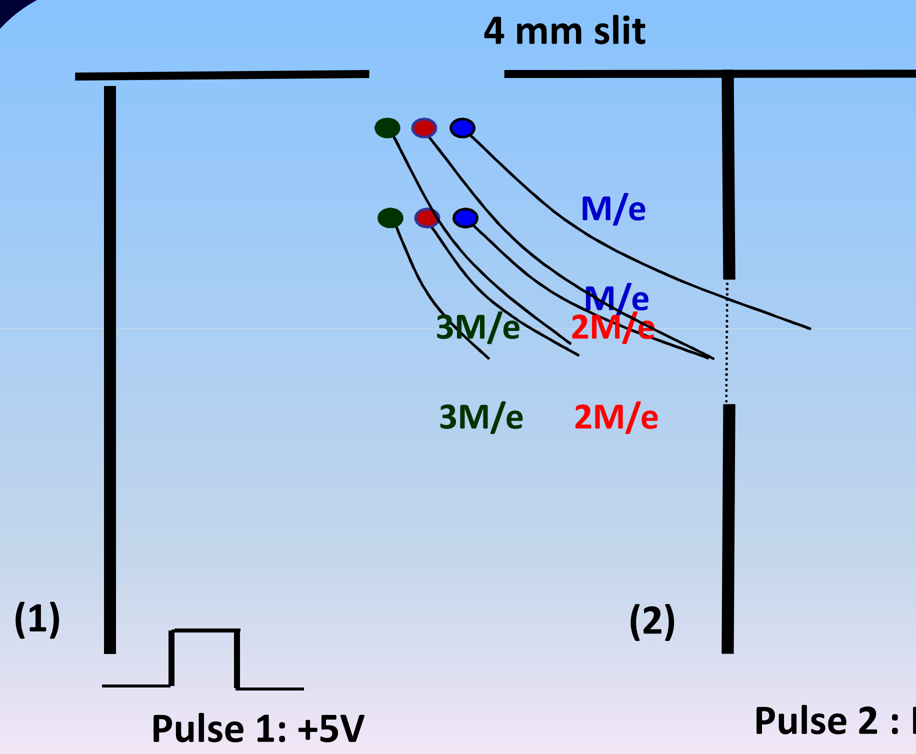
- Cold Plasmas from MOT plus Rydberg excitation
- van der Waals clusters

Detection scheme

- First, a weak pulsed electric field ionises the (neutral?) CRC's into partially charged CRC's
- Second, a strong electric field completely ionises the partially charged CRC's into single cations.
- The time-of-flight of the (heavy) CRC to aperture 2 is used for its mass (M/e) determination. Detection is by pulsed field ionisation in the strong field (between apertures 2 and 3) and detection at the time-of flight of the ***single cation*** to detector

Detection of CRC

Method 2: Time Scan of delay between pulse 1 and pulse 2

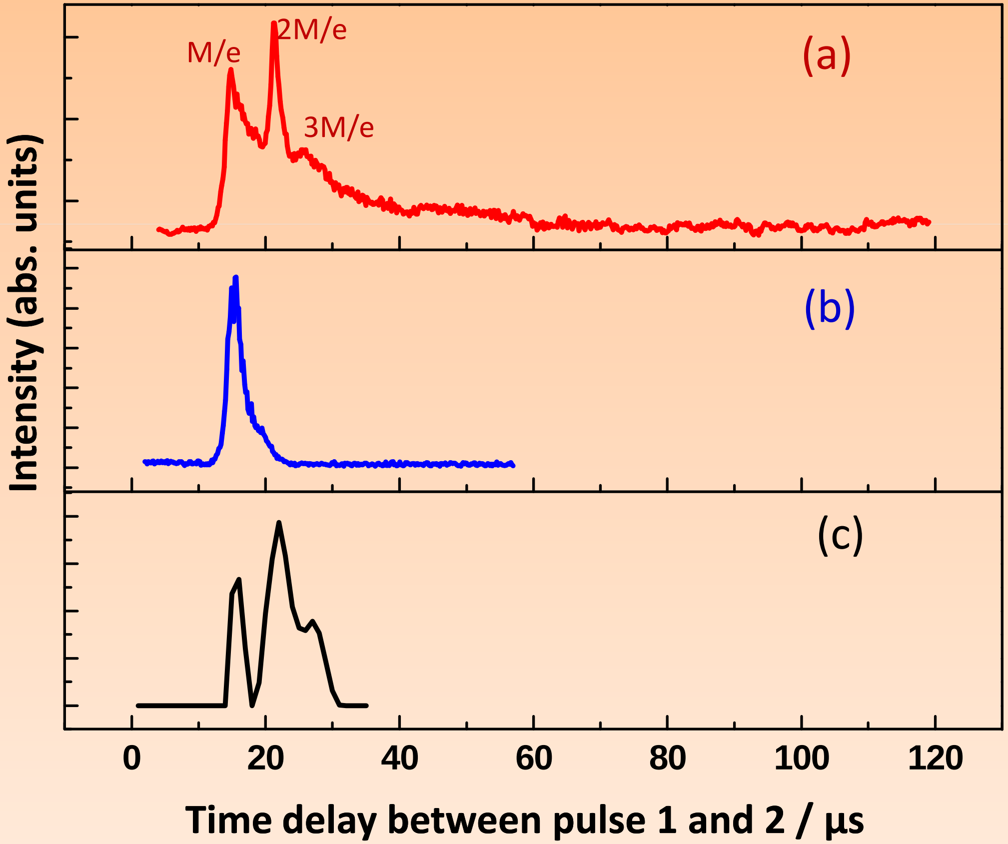


$$t_M : t_{2M} : t_{3M} : t_{nM} = 1 : \sqrt{2} : \sqrt{3} : \sqrt{n}$$

Detection of CRC

Results : Time Scan

Time scan for different positions of crossing the laser and molecular beam



Pulse 1 = 5 V, pulse width=210 µs; pulse 2 = 4.8 Kv, pulse width = 1.22 µs.

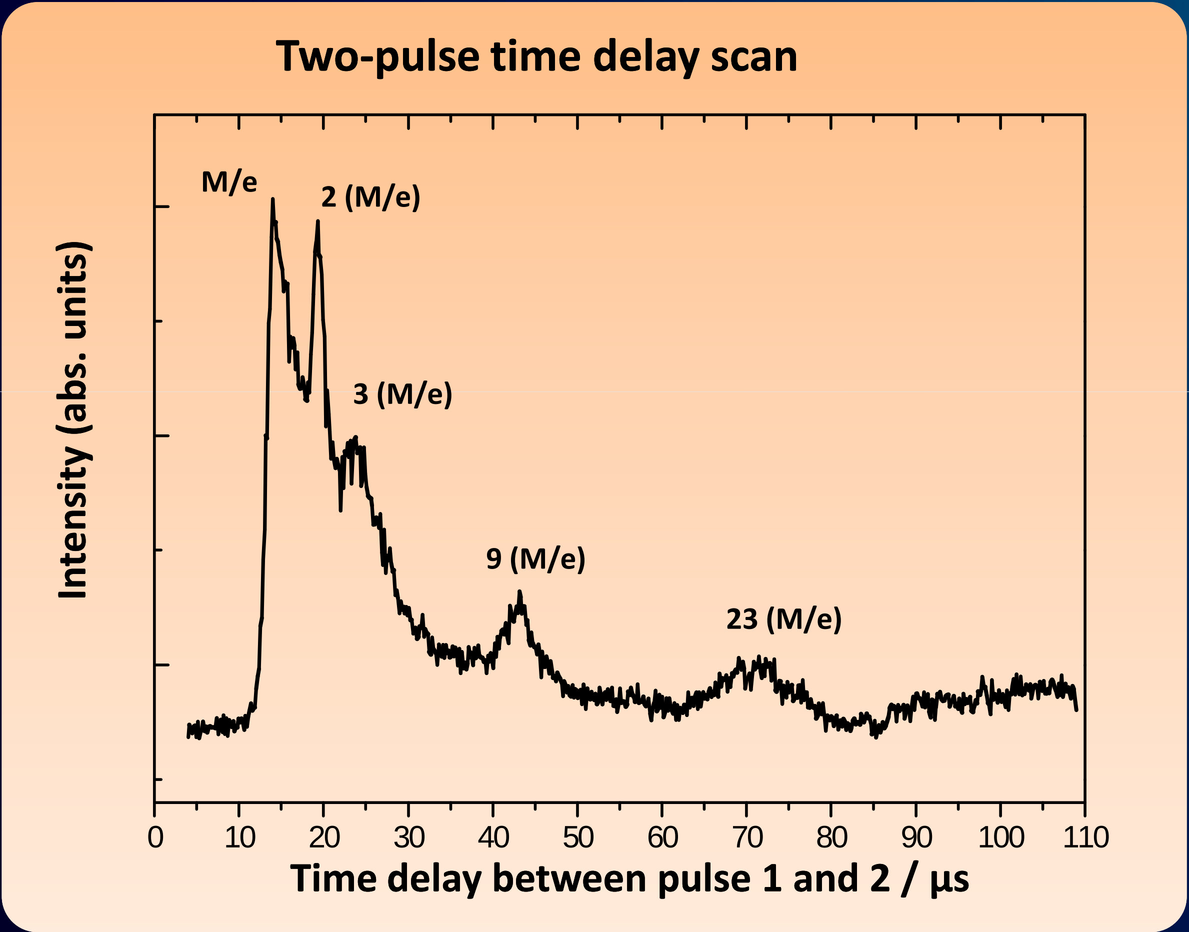
(a) experimental result, laser crosses with molecular beam 2 mm from the nozzle

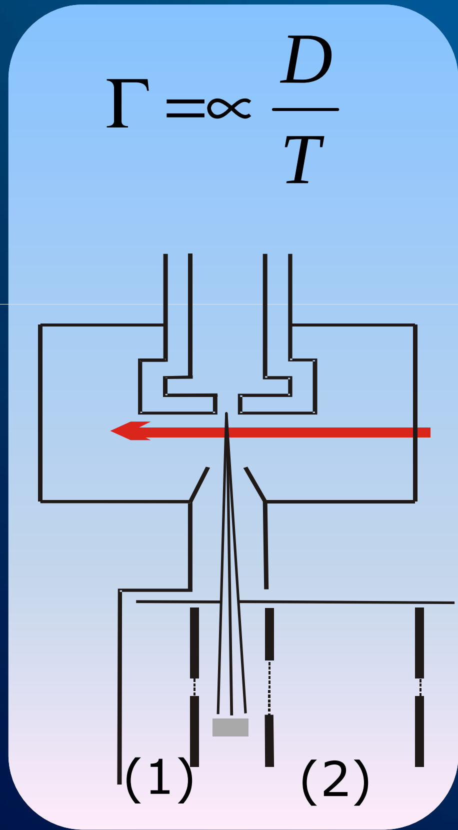
(b) experimental result, laser crosses with molecular beam at 15 mm from the nozzle

(c) simulations for (a)

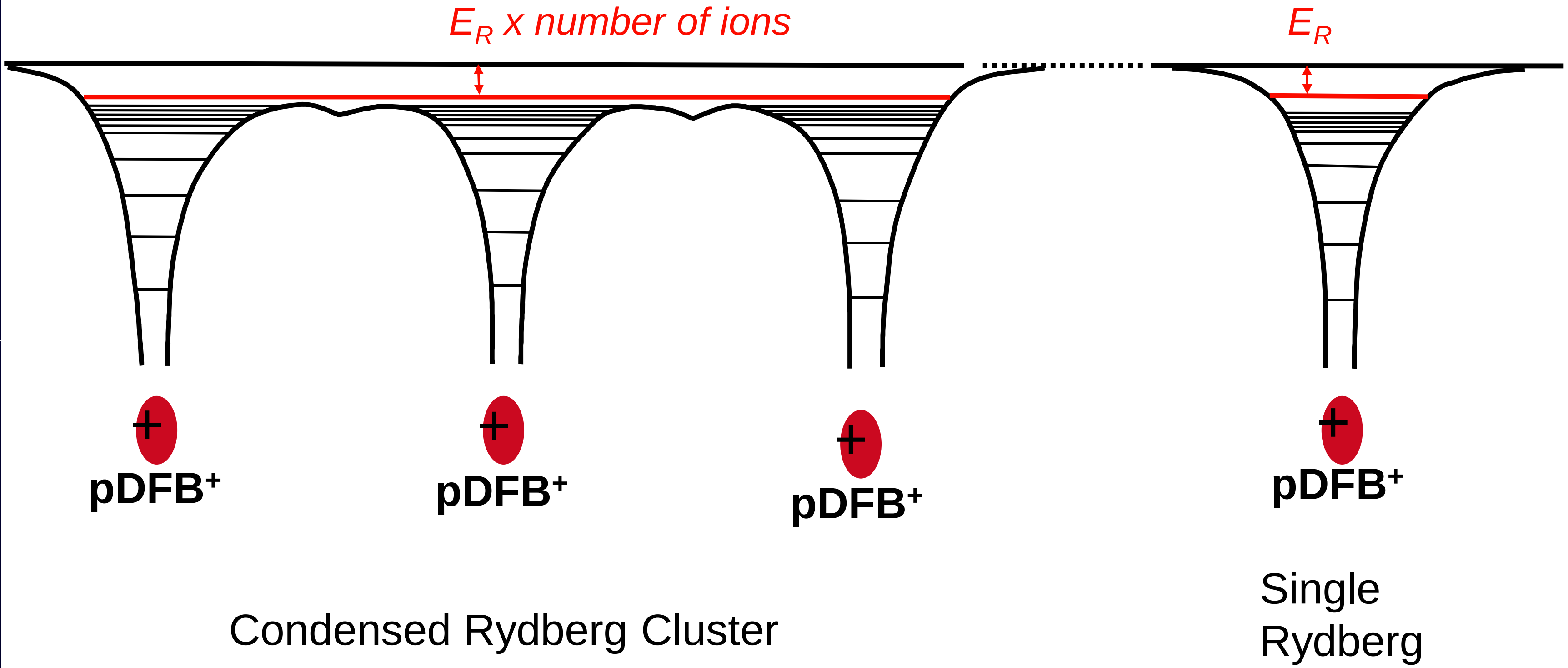
Detection of CRC

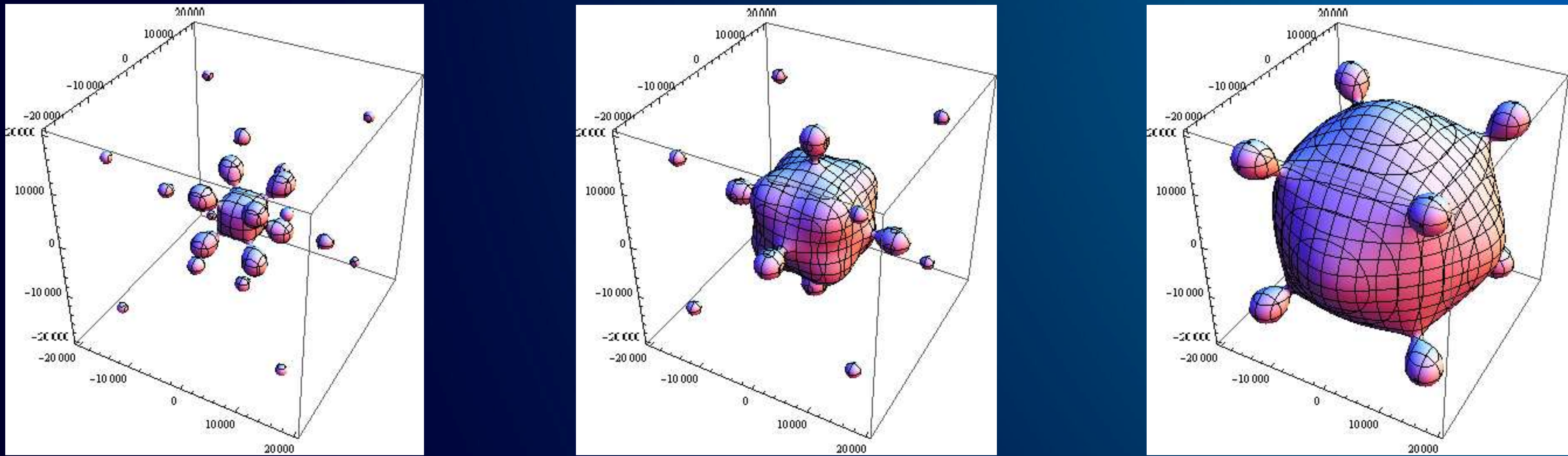
Results: Looking for High CRC





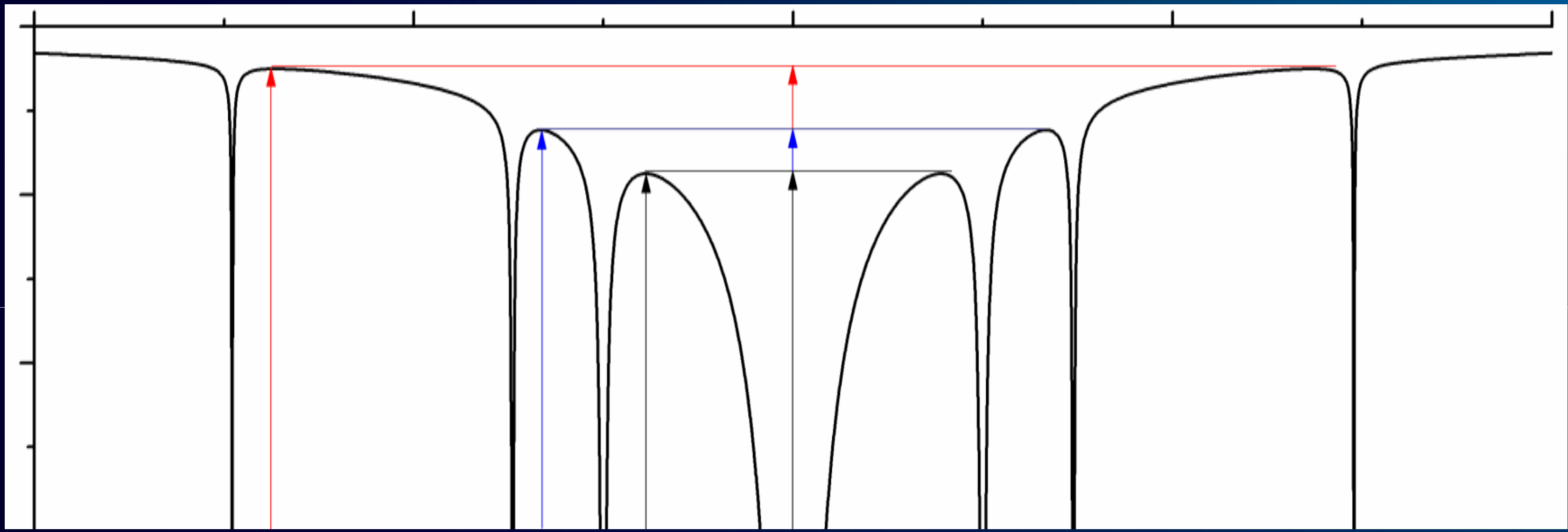
Laser crosses molecular beam at 6 mm from nozzle


E_R x number of ions
E_R
pDFB+
pDFB+
pDFB+
pDFB+
Condensed Rydberg Cluster
Single Rydberg



a b c

Proposed equipotential shell structure of CRCs with *M/e*= 23, where (a) is the first shell (cube structure); (b) is the second shell (octahedron structure) and (c) is the third shell (cube structure). All dimensions are in atomic units.



Conclusions

- Found a novel way to generate an ultracold (near) neutral strongly coupled plasma (applicable to molecules)

- Found that the life-time of the plasma is extremely long (milliseconds)

- Found a new state of matter

  "Condensed Rydberg Clusters"

  and the condition for its formation.

- Found the mass/charge ratio of ***CRC*** to be *2M/e, 3M/e, 9M/e* and *23M/e* (*M* is the mass of pDFB).

- ***What are Condensed Rydberg Clusters?***

Ultracold “condensate” of
***m* ions and *n* electrons** *(m≈n)* with periodic ion structure and electrons in a “conduction band”

- ***Proposed properties of Condensed Rydberg Clusters***

1. Under weak electric field conditions CRC will form from break-up of cold Rydberg plasma.
2. Under strong electric field conditions CRC will loose all electrons and fragment into single cations.

Condition for the formation of CRC

- High density in Rydberg region
- Large ion Coulomb coupling parameter – choose the cross point of laser and molecular beam
- Large electron Coulomb coupling parameter– tuning laser to excite molecules into highly excited Rydberg region: low electron temperature

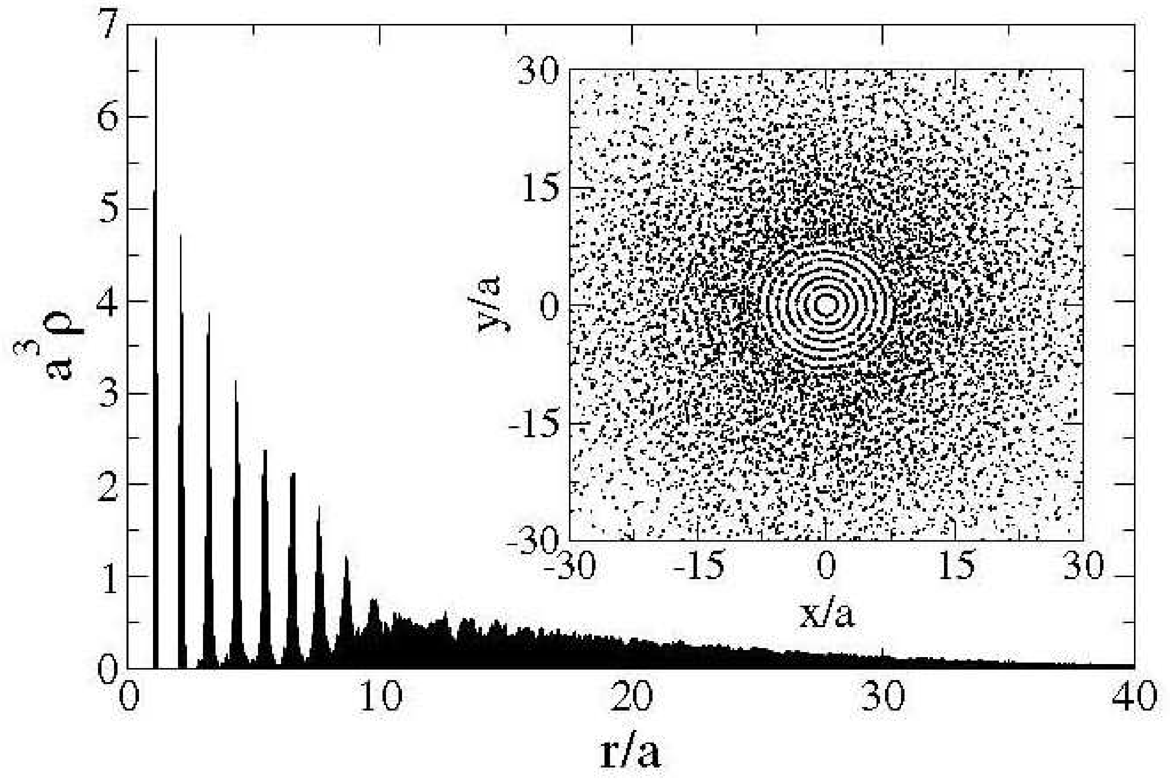


FIG. 3. Radial density after a time of $t = 24\ \mu s$ ($\omega_{p0}t = 110$). The inset shows a two-dimensional cut through the plasma cloud, clearly revealing the formation of concentric shells. (For better contrast, cuts with $x = 0$, $y = 0$, and $z = 0$, respectively, have been overlayed.)

T. Pohl, T. Pattard and J. M. Rost
Phys. Rev. Letts. 92 (15), 2004

Outlook

Evaporative cooling in plasma expansion?

ca 10^{-4} of all cations can be described with a Maxwell Boltzmann velocity distribution at very much lower temperature (i.e. 10µK)

i.e. the coldest molecular ions concentrate in the centre of the plasma

Starting with 10^{14} ions/cm^3 there would be 10^{10} cations at 10 µK in 1 cm^3, *i.e.* 10^7 cations at 10 µK in 1 mm^3 ; with the plasma expanding by 10^3, the coldest ions remain in the centre and there would still be 10^7 cations in 1 mm^3 in the centre, bound by the electron gas:

This could be useful for BEC of molecules

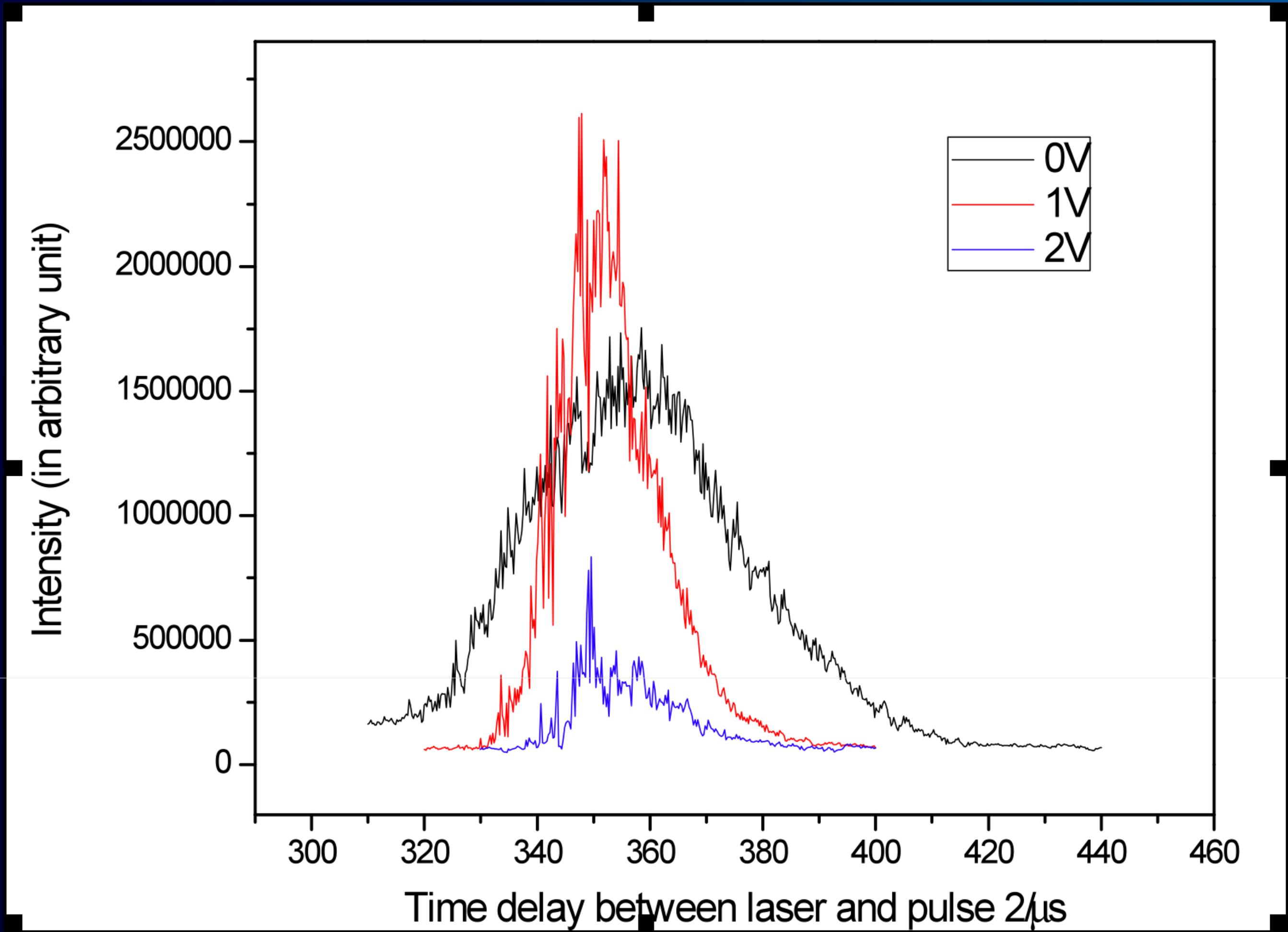
Outlook

Choose NO as molecule:

Density of NO^+ can be as high as 10^{17} cm^{-3}
All molecular cations in the plasma can be in the same rotational state by using rotationally selective two-photon, two-colour excitation *via* the A state:
$N^+ = 0, 1, 2$, etc

How are the rotational angular momenta coupled?
What about parity?

NO^+ is a Boson



Signal from plasma, as a function of delay between laser and pulse 2, for a DC voltage of 0, 1 and 2 V applied to aperture 1 and a 3.6 KV pulse applied to aperture 2

Co-workers

£££

Engineering and
Physical
Sciences
Research
Council

The Royal Society

PSI

The University of Manchester

- **Dr Jingwei Guo**
- **Mervash Varnasseri**
- Dr Xin Tong
- Professor Chris Greene
  (VMP and U Colorado)
  Visiting Miller Professor,
  UC Berkeley

Proposed Mechanism

- pDFB + 2 $h\nu$ $\rightarrow$ pDFB* (n > 200)
  $\rightarrow$ pDFB$^+$ + e- (no kinetic energy)

- The size of Rydberg orbital is proportional to n^2
  so Rydberg orbit is several μm

- Density of pDFB up to $10^{16}/cm^3$

- Even if only 0.1% pDFB are Rydberg excited, the average distance between adjacent Rydberg is much smaller than the average Rydberg orbital

CRC need strongly-coupled plasma environment

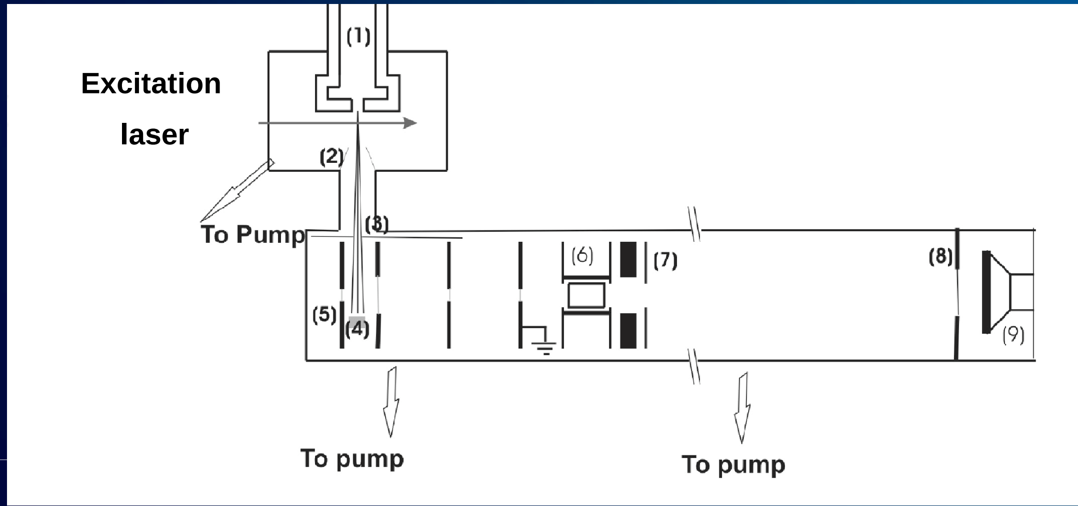
For the ions

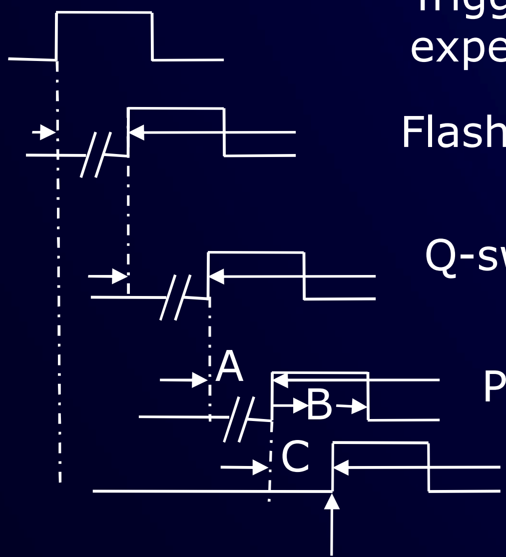
- Free expansion cools down the translational temperature of ions to 0.1 Kelvin
- Density of ions decreases rapidly with distance from the nozzle.
- combining these two factors, Coulomb coupling parameter Γ for ions can be bigger than 100

For the electrons

- Resonant ionisation of pDFB generates ZEKE photoelectron (electron with very small negative or positive energy *around* cm^{-1})
- Coulomb coupling parameter for electrons can be bigger than 40.

Schematic diagram demonstrating the synchronization of the TOF detection of Condensed Rydberg Cluster experiment





Trigger to the general valve controller (time 0 for the whole experiment

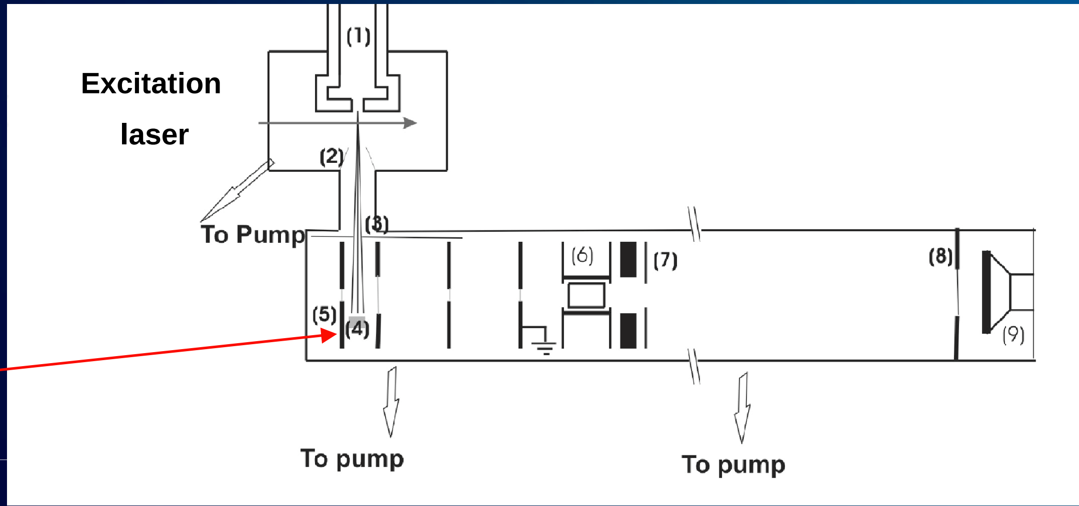
Flashlamp discharge of the YAG laser 200 – 400 *μs* delay

Q-switch of the YAG laser, 300 *μs* delay

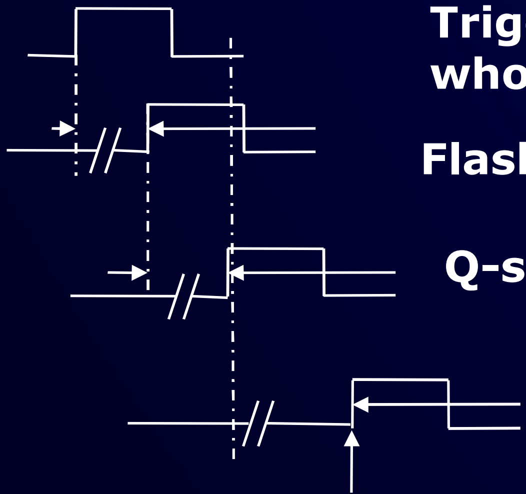
Pulse 1, 450 – 600 *μs* delay

Pulse 2, 10 – 140 *μs* delay

Schematic diagram demonstrating the synchronization of the TOF detection of Condensed Rydberg Cluster experiment



Small DC voltage on aperture 1



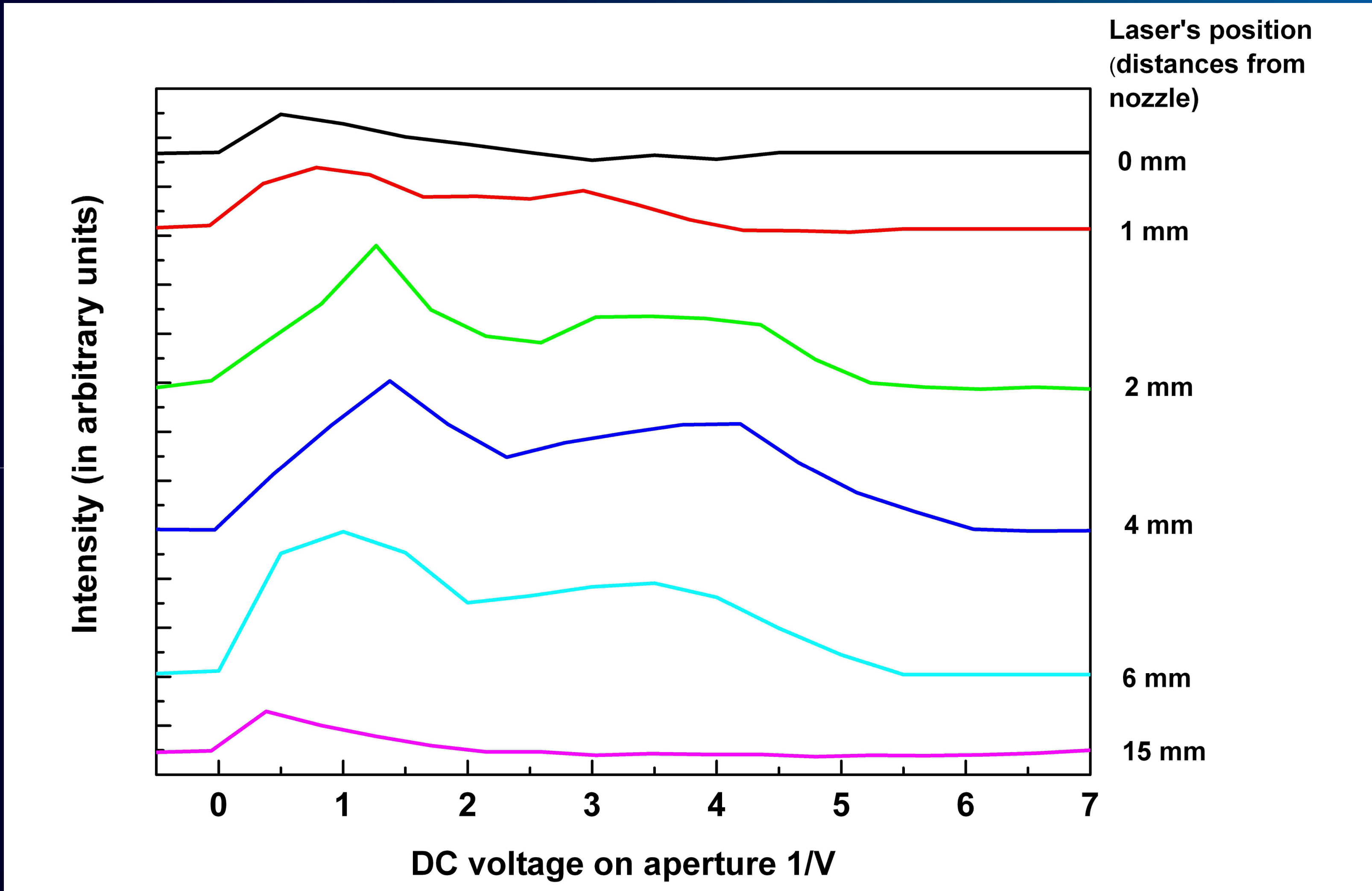
Trigger to the general valve controller (time 0 for the whole experiment

Flashlamp discharge of the YAG laser 200 – 400 μs delay

Q-switch of the YAG laser, 300 μs delay

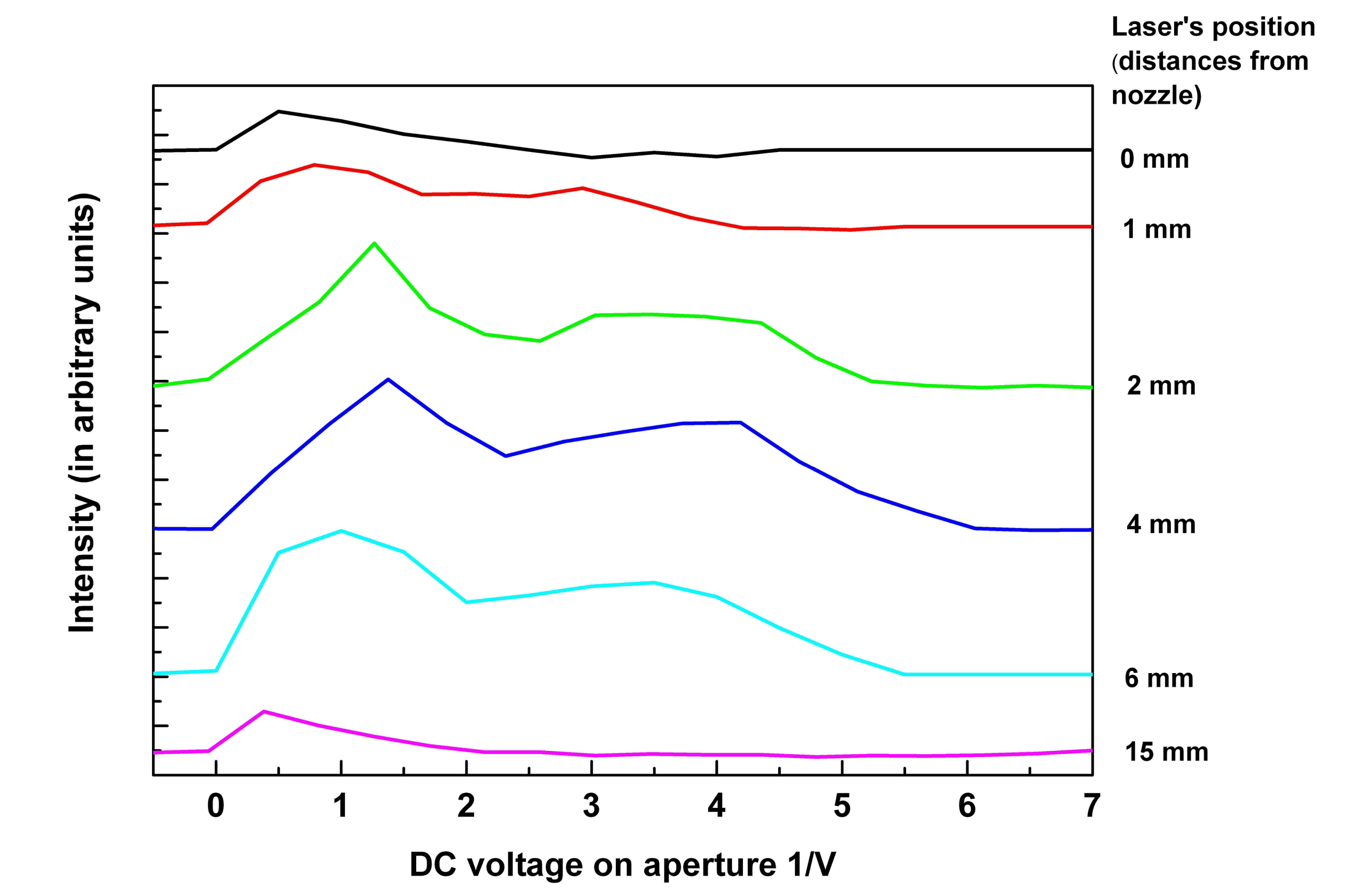
4.8 kV pulse on aperture 2, 450 μs delay after laser pulse.

DC (on aperture 1) voltage scan



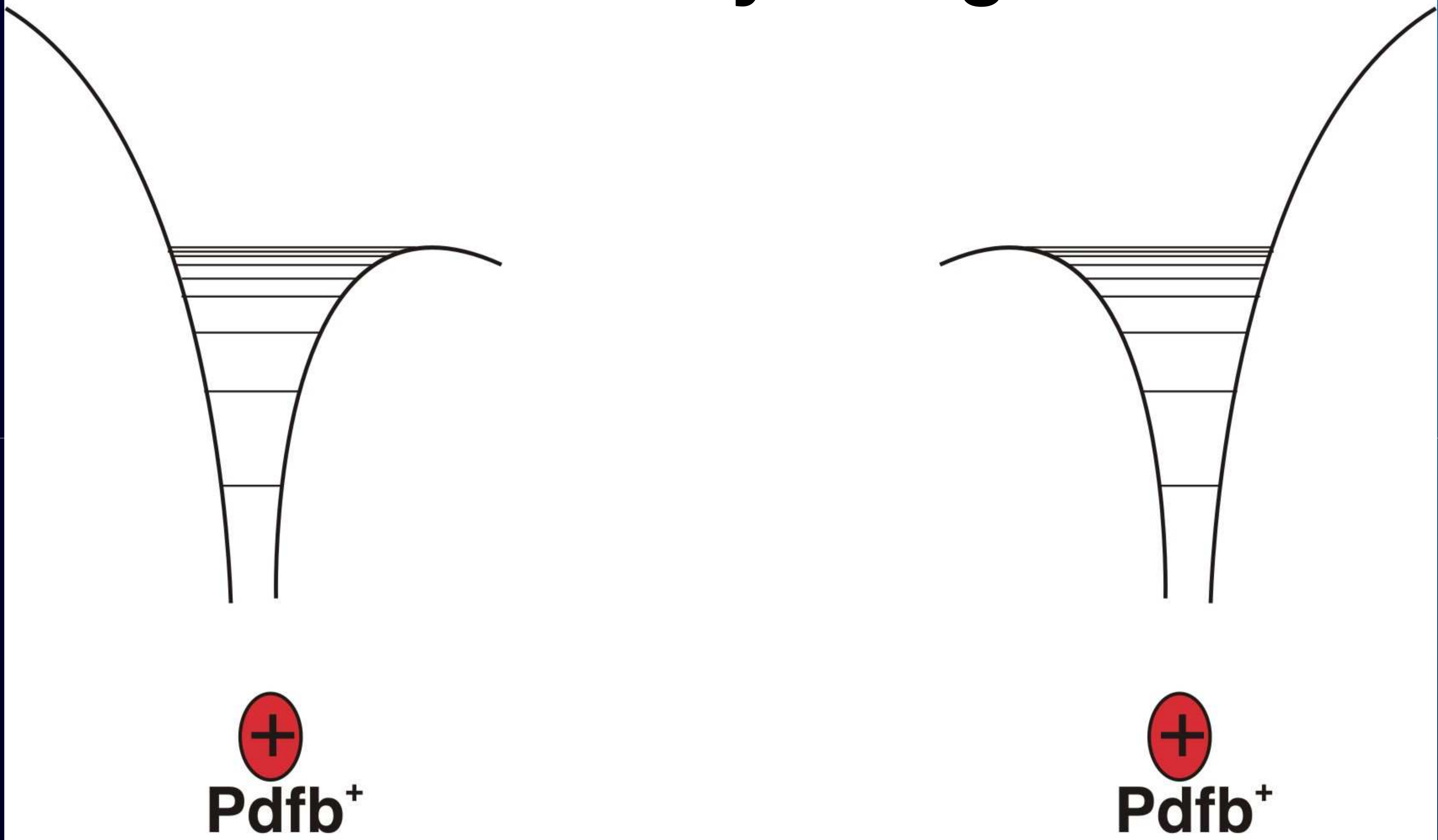
+4.8 kV pulse is applied on aperture 2, pulsewidth is 1.22 μs. The delay between laser pulse and ionisation pulse on aperture 2 is 450 μs

DC (on aperture 1) voltage scan



4.8 kV pulse is applied on aperture 2, pulsewidth is 1.22 μs. The delay between laser pulse and ionisation pulse on aperture 2 is 450 μs

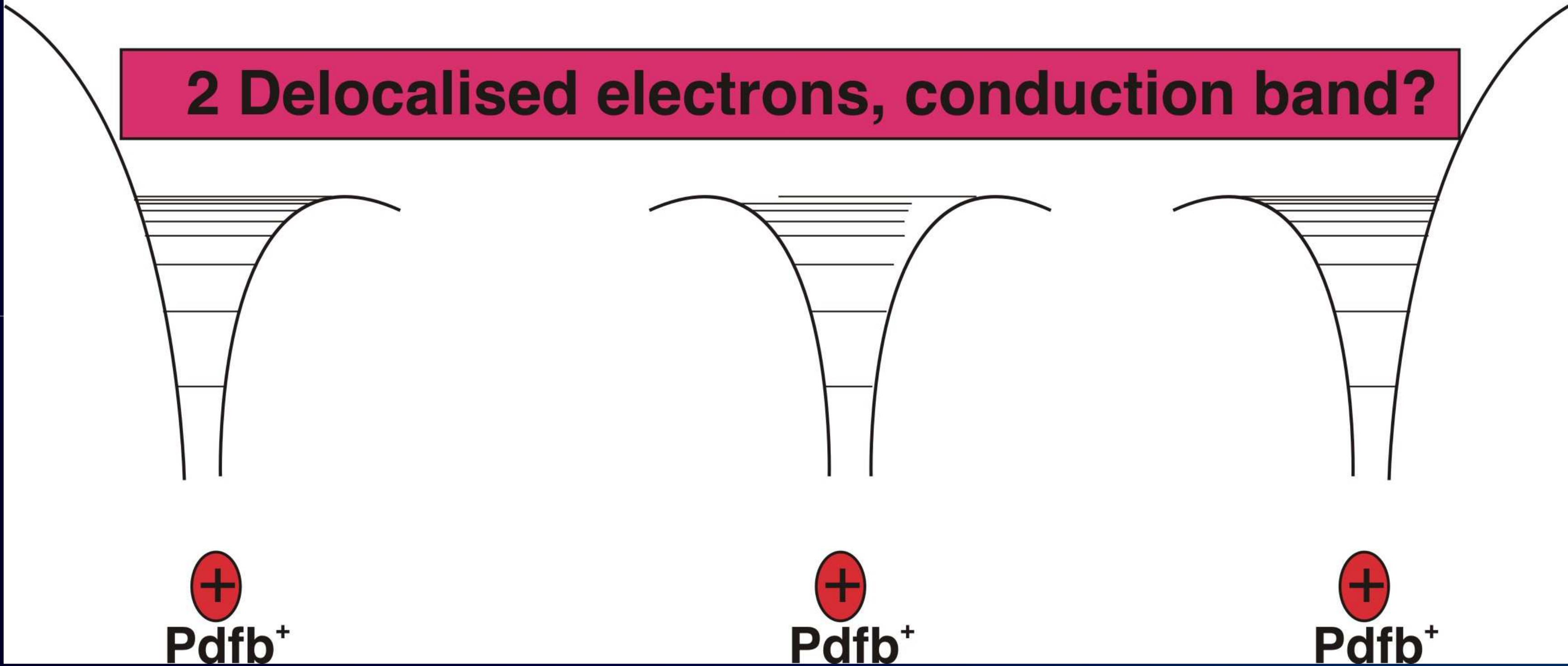
Condensed Rydberg Dimer



A few hundred nanometers

Condensed Rydberg Cluster

Trimer$^+$



Plasma expansion

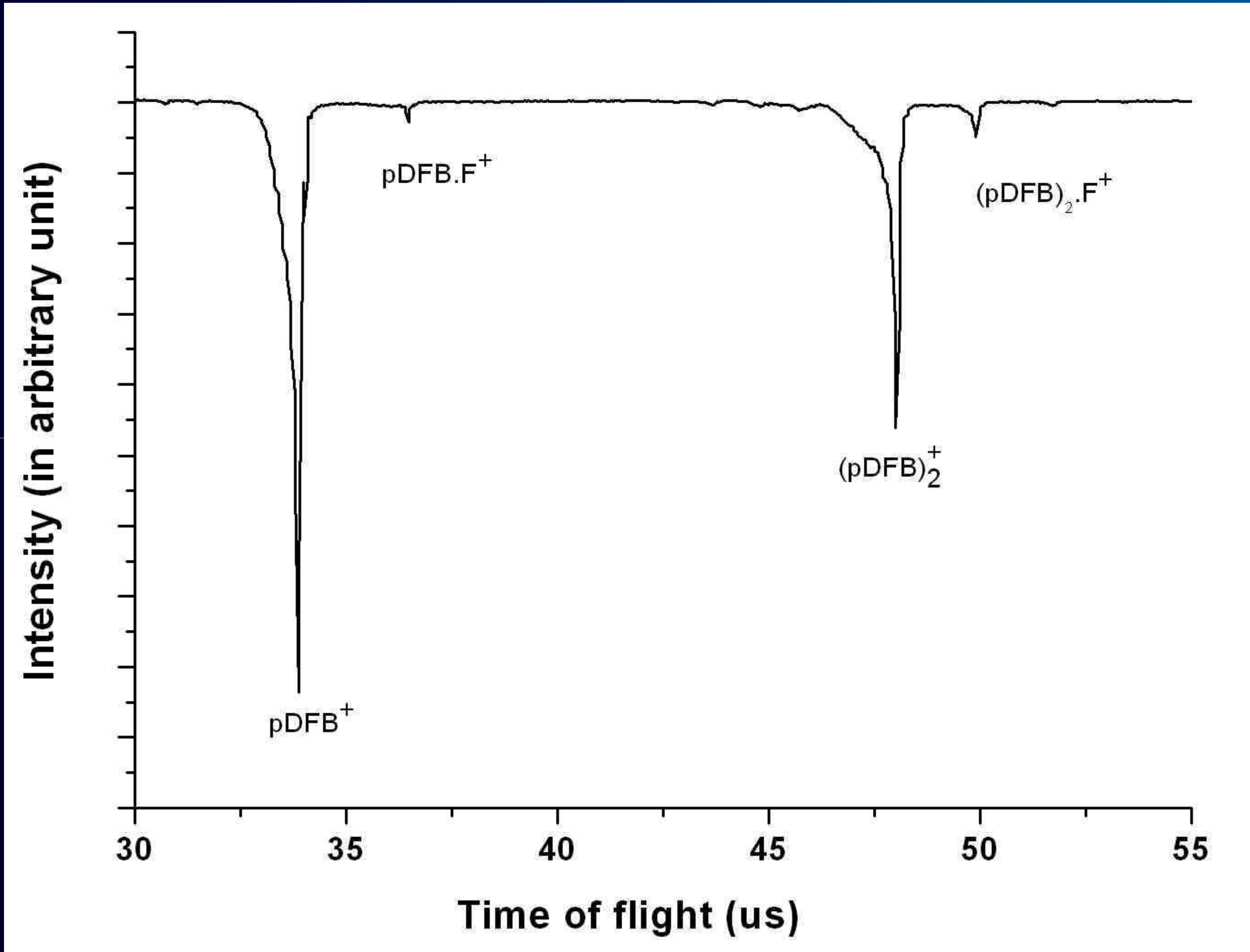
- Electron heat is the driving force of plasma expansion.[1]

$$v_{expansion} = \sqrt{k_B T_e / m_i}$$

- Electron inelastic collision and three-body recombination is the major process to control the electron temperature.[2]

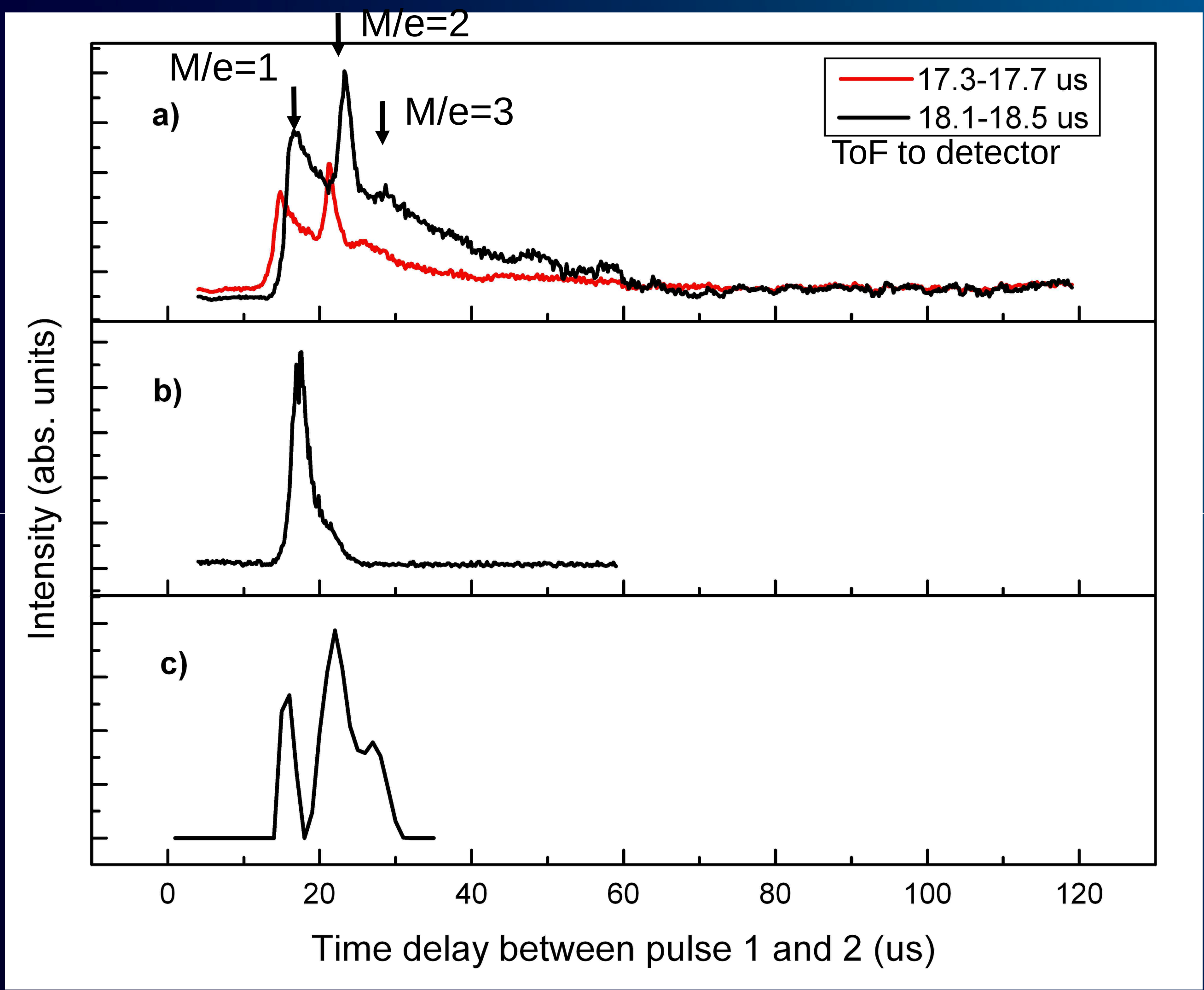
1.R. S. Fletcher, X. L. Zhang and S. L. Rolston, Phys. Rev. Lett., 96 (2006) 105003.

2. P. Mansbach and J. Kech, Phys. Rev. **181** 275 (1969).



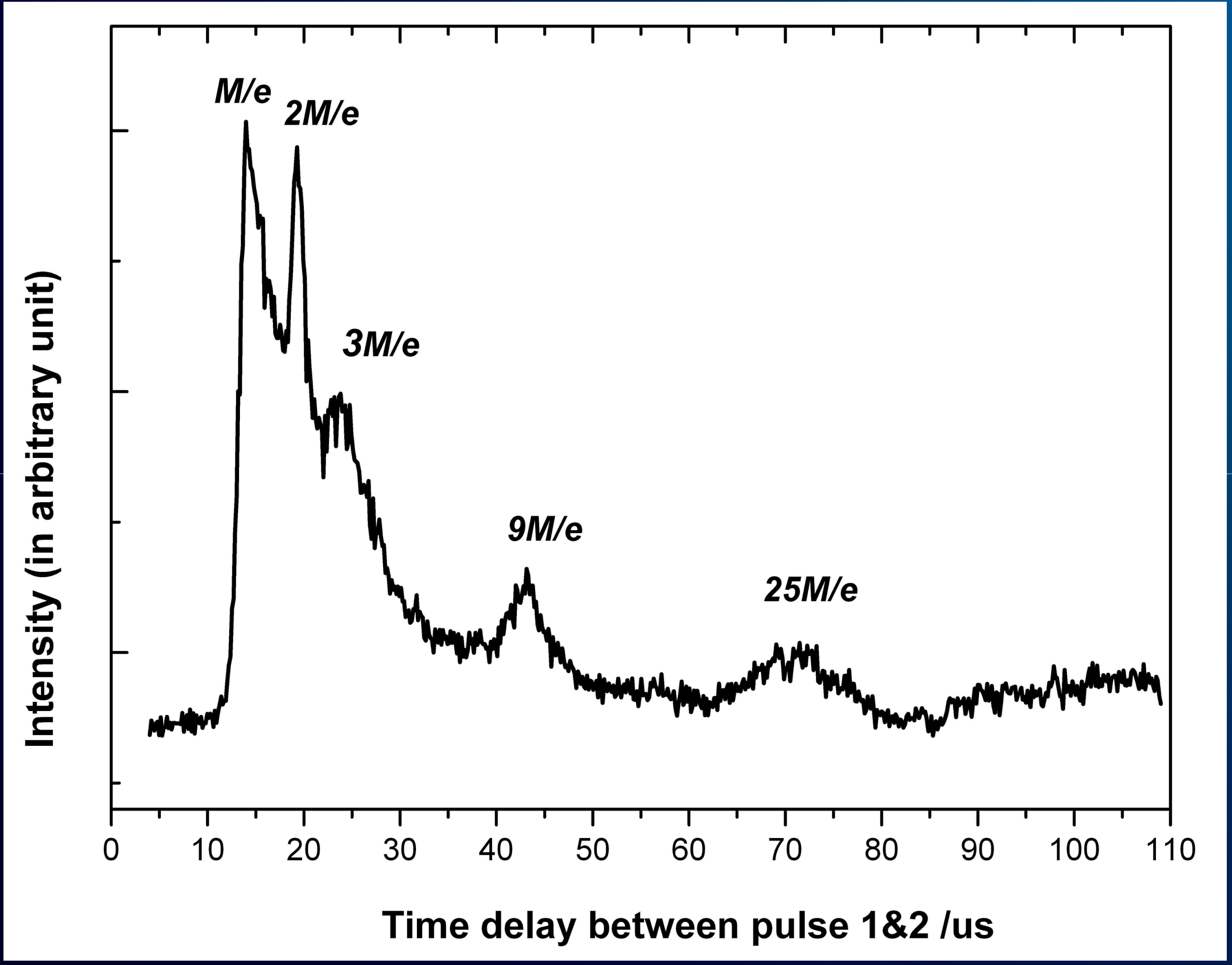
pDFB.F^{+}
$(pDFB)_2.F^{+}$
$(pDFB)_2^{+}$
pDFB^{+}
Intensity (in arbitrary unit)
30
35
40
45
50
55
Time of flight (us)

Two-pulse time delay scan



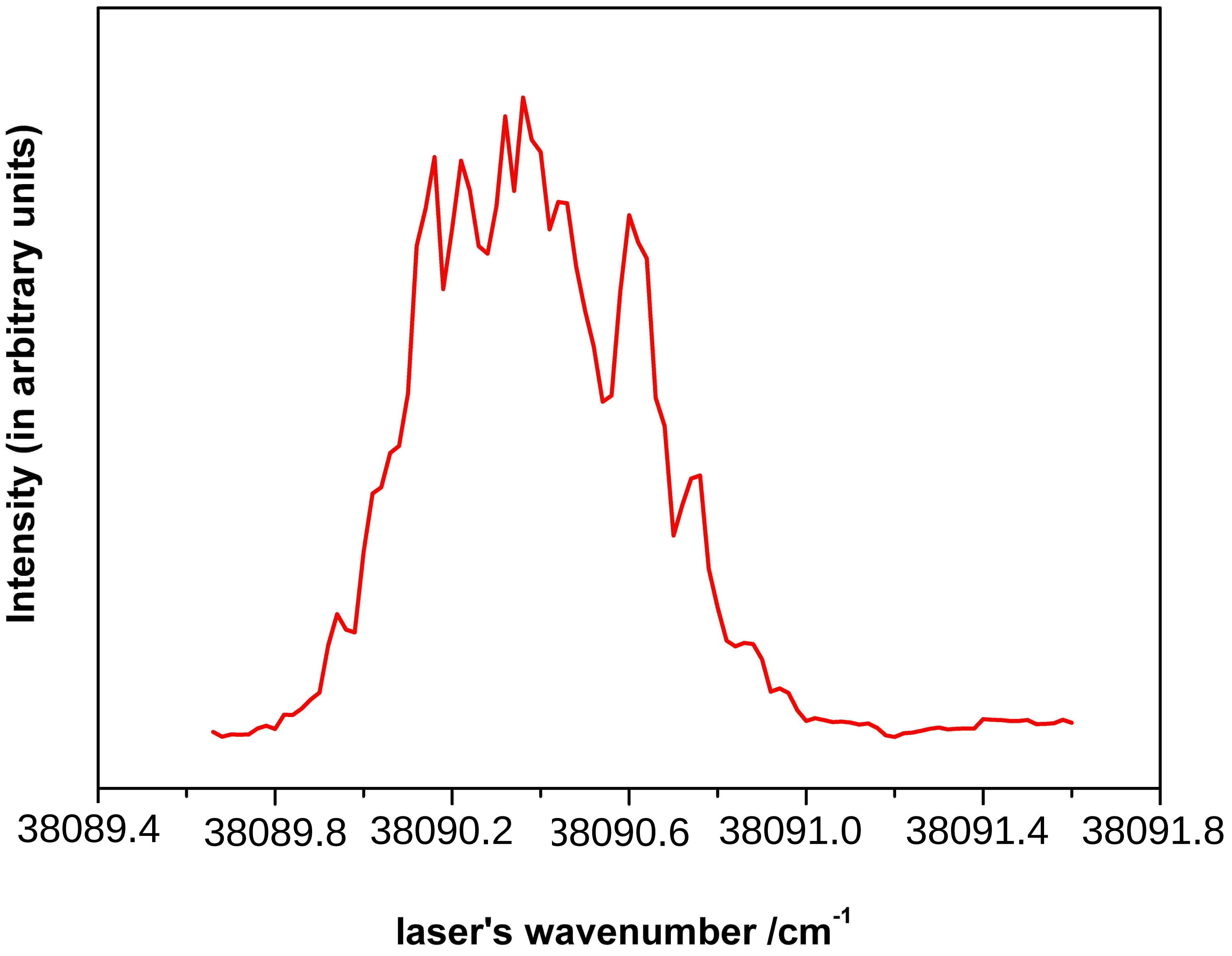
(a), the experimental result (with two different time gates), laser crosses with molecular beam 2 mm from the nozzle; (b) the experimental result, laser crosses with molecular beam at 15 mm from the nozzle; (c), simulations for (a).

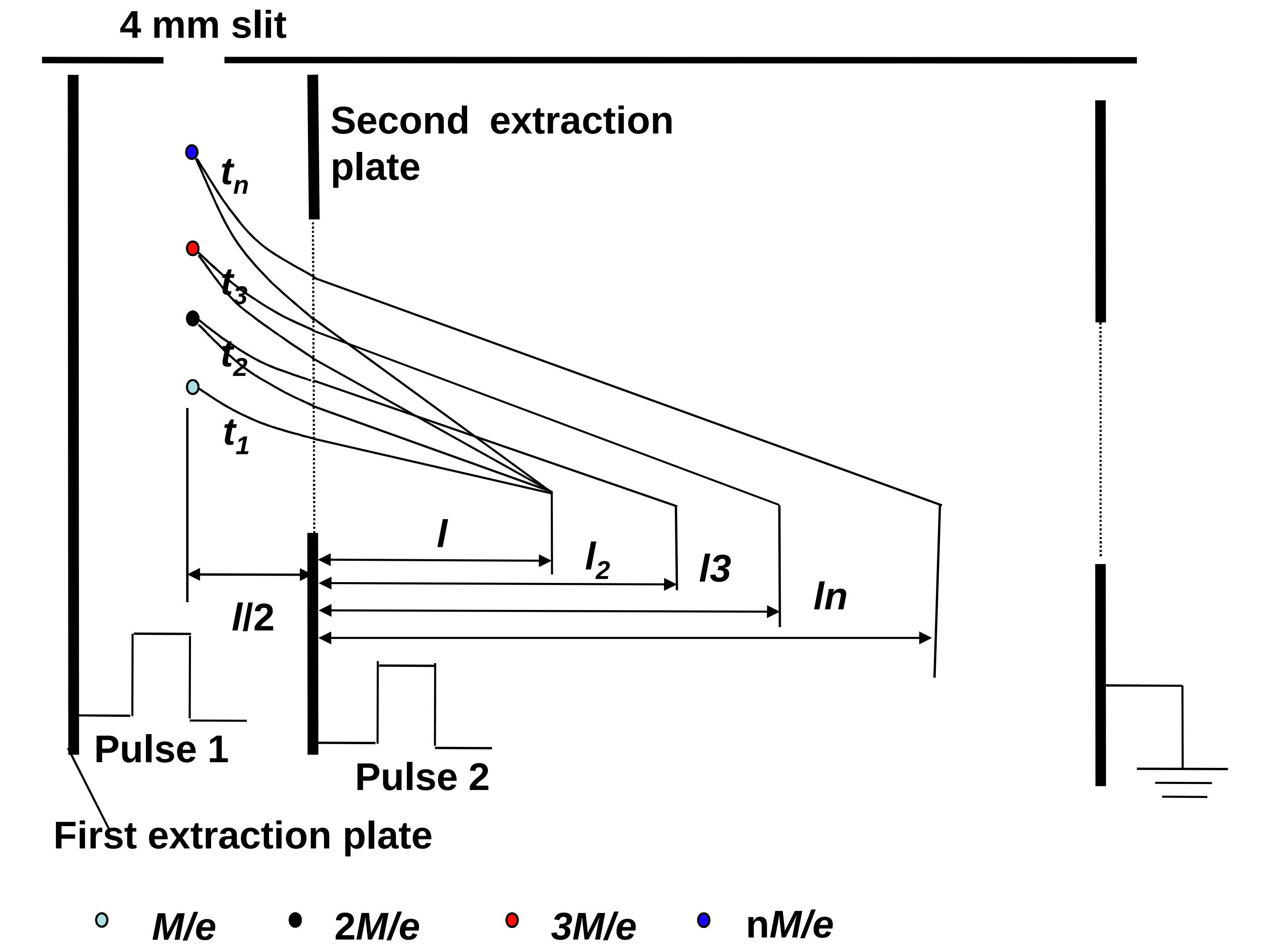
Two-pulse time delay scan



Laser crosses molecular beam at 6 mm from nozzle

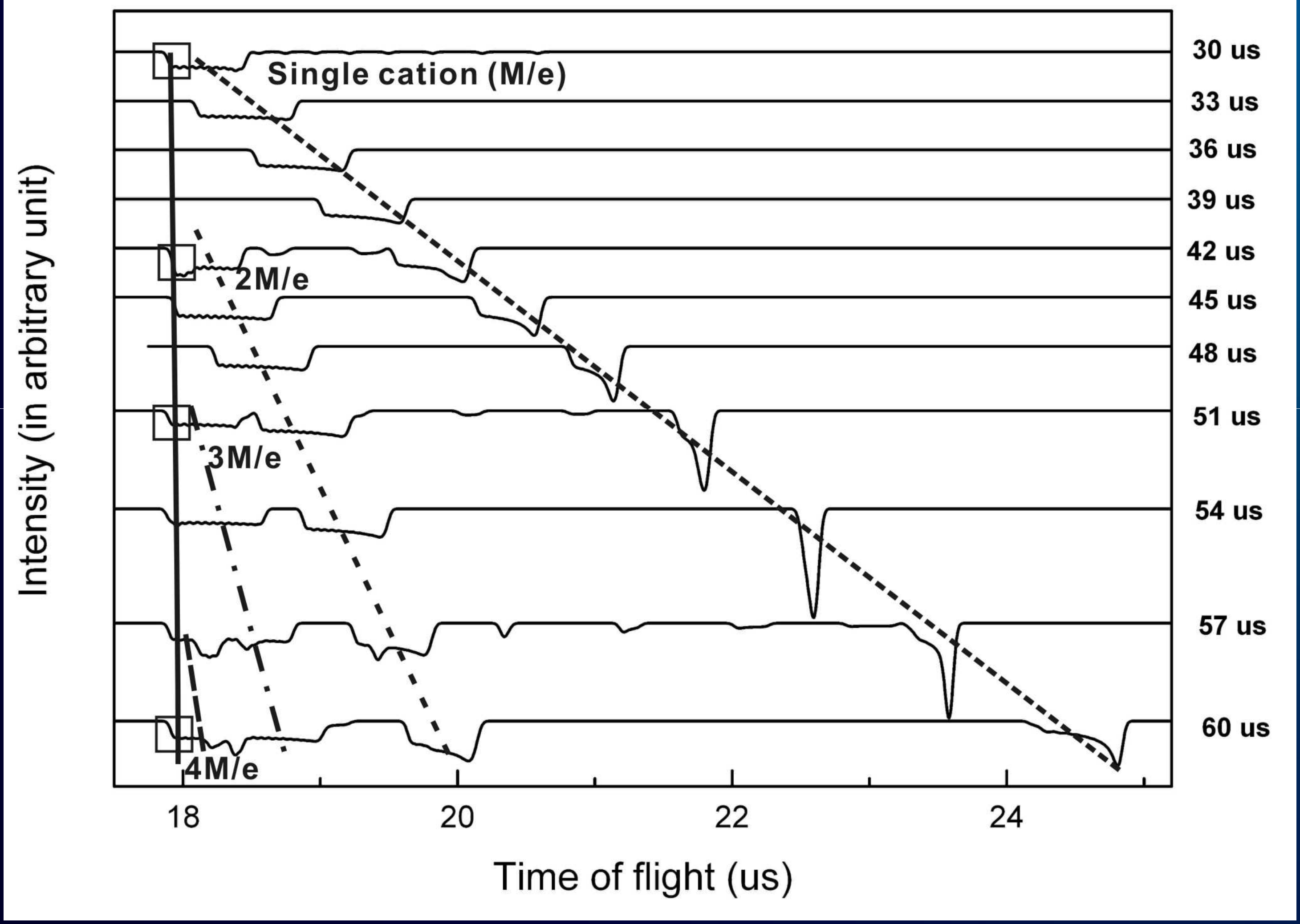
Spectral scan for signal at t_2-t_1=70⌠s





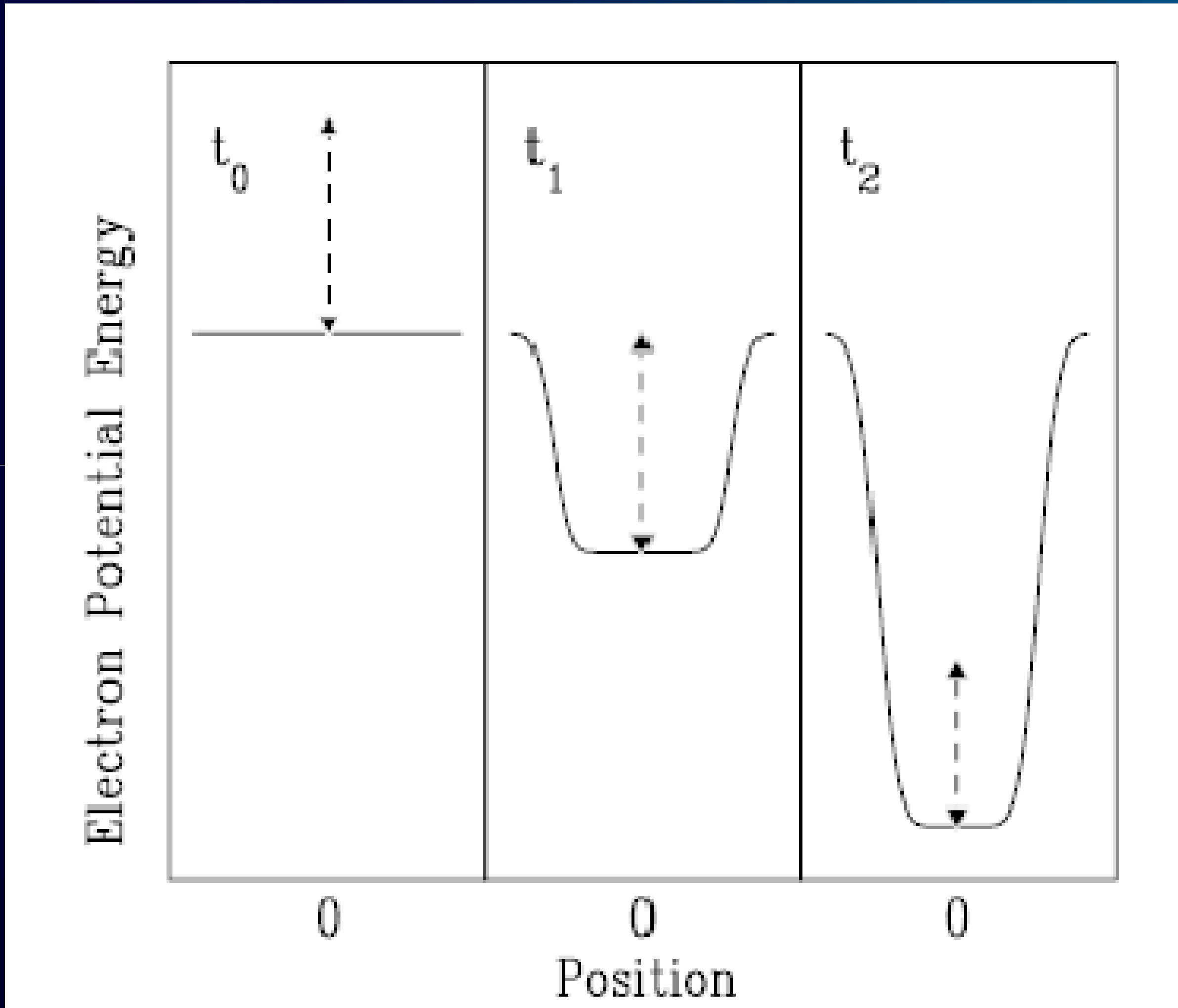
$$t_M : t_{2M} : t_{3M} : t_{nM} = 1 : \sqrt{2} : \sqrt{3} : \sqrt{n}$$

Simulation of the TOF spectra of pDFB+, with different delays between pulses 1 and 2 (labelled on the right hand site of each curve). Pulse 1 = 1.25 *V*, pulse 2 = 4.8 *kV*, both pulses are full energy extraction.



30: 42: 51: 60 = 1 : 1.4 : 1.7 : 2 = $t_M : t_{2M} : t_{3M} : t_{4M}$

Plasma potential well evolution



T. C. Killian, S. Kulin. S. D. Bergeson, L. A. Orozco, C. Orzel and S. L. Rolston, Phys. Rev. Lett., 83 (1999) 4776.

Excitation to Rydberg states in an ultracold cloud of atoms

Laser excitation using pulsed dye laser

A substantial part of the atoms is laser excited into Rydberg states (typically n around 80, but newer experiments also excite to higher n or above threshold).

Electron temperature control

- Three-body-recombination heat up electron ~ T(-9/2).
- Deexcitation of Rydberg molecules:

$$A_d = 7.2\rho_e (27.2eV / K_B T_e)^{0.17} v^{2.66} a_0 \alpha c$$

- Excitation of Rydberg including

$$A_e = 55\rho_e (K_B T_e / 27.2eV)^{0.83} v^{4.66} a_0 \alpha c$$

$$v = \sqrt{-13.6eV / E_R}$$

$$A_d / A_e = \frac{0.13E_R}{-13.6eV}\left(\frac{27.2eV}{K_B T_e}\right) = -\frac{0.26E_R}{K_B T_e}$$

Bohr length

the fine-structure constant

P. Mansbach and J. Kech, Phys. Rev. **181** 275 (1969).

Definition of CRC

Condensed Rydberg Clusters (CRC) can be defined as dense clusters of highly-excited Rydberg molecules. The average distance between adjacent ionic cores is much smaller than the average Rydberg orbit, so that every Rydberg electron interacts with many cations. *

Jingwei Guo, Klaus Muller-Dethlefs, in preparation to submit to *Science*