

Methods in Spectroscopy and Dynamics

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Administration

Course: Wednesdays, 16-18

Exercises: Wednesdays, 18-19

TA: Pardis Naderasli

Moodle: CH-340

Course support: Scientific journals (mostly), Slides

General

The goal of this class is to introduce a number of modern methods for the investigation of spectroscopic (structural) and dynamic aspects of chemistry.

In the first part of the course I will introduce some of these methods myself, in the second part you will present some techniques yourself.

The exercise hours will be used for the preparation of the presentations.

Planning of the semester

My part:

- Introduction to key experimental techniques in Gas-Phase Spectroscopy and Dynamics research (Molecular Beams, Supersonic Expansions, Particle Detection Methods, ...)
- Guest lectures:
 - Prof. S.Y.T. van de Meerakker (Radboud University Nijmegen, NL):
Cold/controlled chemistry
 - Prof. S. Willitsch (U. Basel):
Cold Ions
 - Prof. M. Oppermann (U. Basel):
Circular Dichroism

Your part:

- * 45-min presentation on a selected topic

Your Presentations

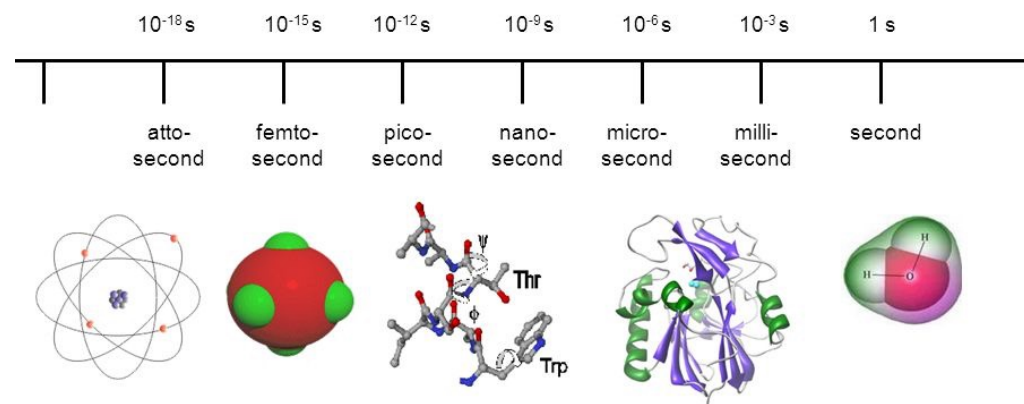
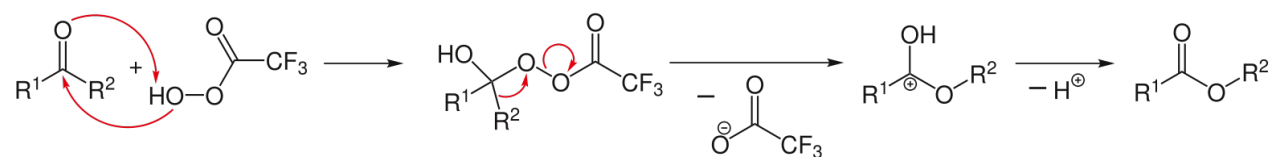
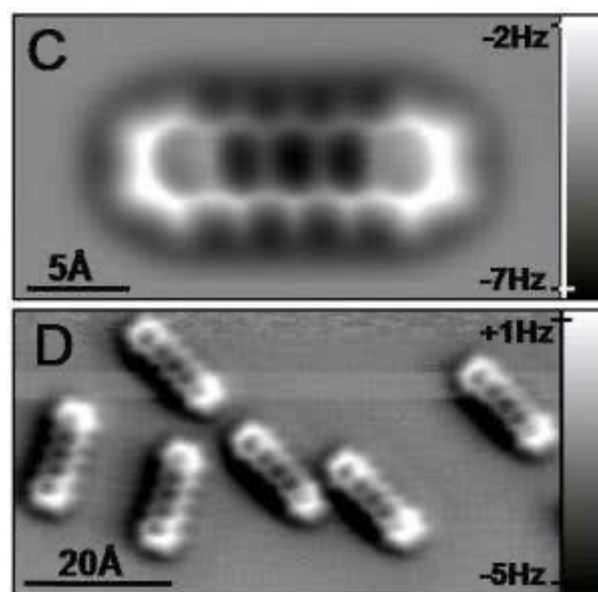
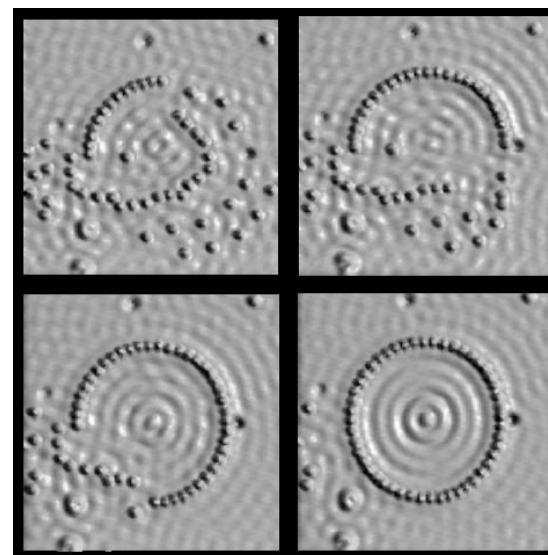
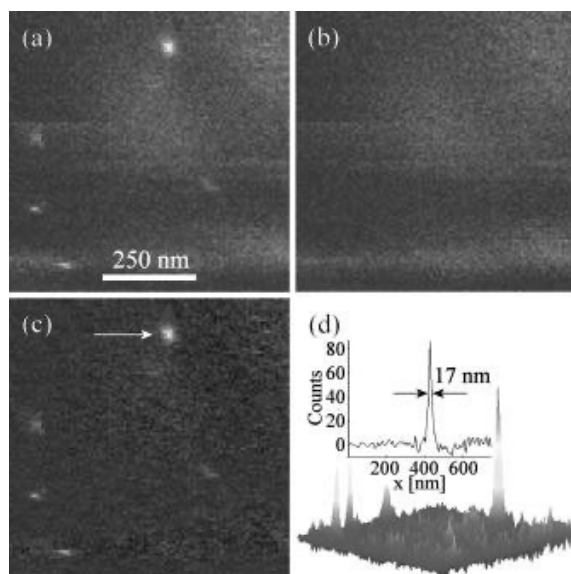
- pick a topic from a list I provide (or propose your own)
- I will provide a few papers for each topic, and you will use those as a starting point to find more information
- Perform literature research and prepare a 1-class presentation (i.e. about 40 minutes of talking, allowing time for questions)
- Pardis will help you with the technical aspects (finding papers etc.)

General

Exam:

you will be writing a paper on a topic from a list of suggestions.

This will be fixed in due time.



Topics for you

1. Gas Phase Spectroscopy and Dynamics; Crossed/Merged Molecular Beams
2. Cold/Ultracold Molecules and Ions
3. Attoseconds (and applications)
4. Circular Dichroism
5. TR Circular Dichroism
6. (TR-)ARPES
7. Sum Frequency Generation
8. Ultrafast transient absorption
9. Single molecule imaging/spectroscopy
10. FRET
11. Electron Microscopy, Cryo-EM
12. Stimulated Raman scattering
13. X-Rays
14. Surface chemistry
15. Kinetics measurements
16. Microscopy (STM; AFM)

Exercise for next week

Do literature research and find three topics you would like to present in class.

Pick one from the list on the previous slide, or find one yourself.

We discuss the assignment in the next class.

Google can help to find websites of research groups in specific topics.

Journals (some examples; starting points):

Science

<https://science.sciencemag.org>

Nature

<https://www.nature.com>

Nature Chemistry

<https://www.nature.com/nchem/>

Nature Physics

<https://www.nature.com/nphys/>

Journal of Physical Chemistry A (also B and C)

<https://pubs.acs.org/journal/jpcafh>

Journal of Physical Chemistry Letters

<https://pubs.acs.org/journal/jpclcd>

Journal of the American Chemical Society (JACS)

<https://pubs.acs.org/journal/jacsat>

Journal of Chemical Physics

<https://aip.scitation.org/journal/jcp>

Physical Review Letters

<https://journals.aps.org/prl/>

Exercise for next week

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Pick one from the list on the previous slide, or find one yourself.

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Article databases

Google Scholar

Web of Science

<https://www.webofscience.com/wos/woscc/basic-search>

<https://scholar.google.com>

Gas-phase reaction dynamics and spectroscopy

Questions; Experimental difficulties

Experimental techniques

1. Spectroscopy

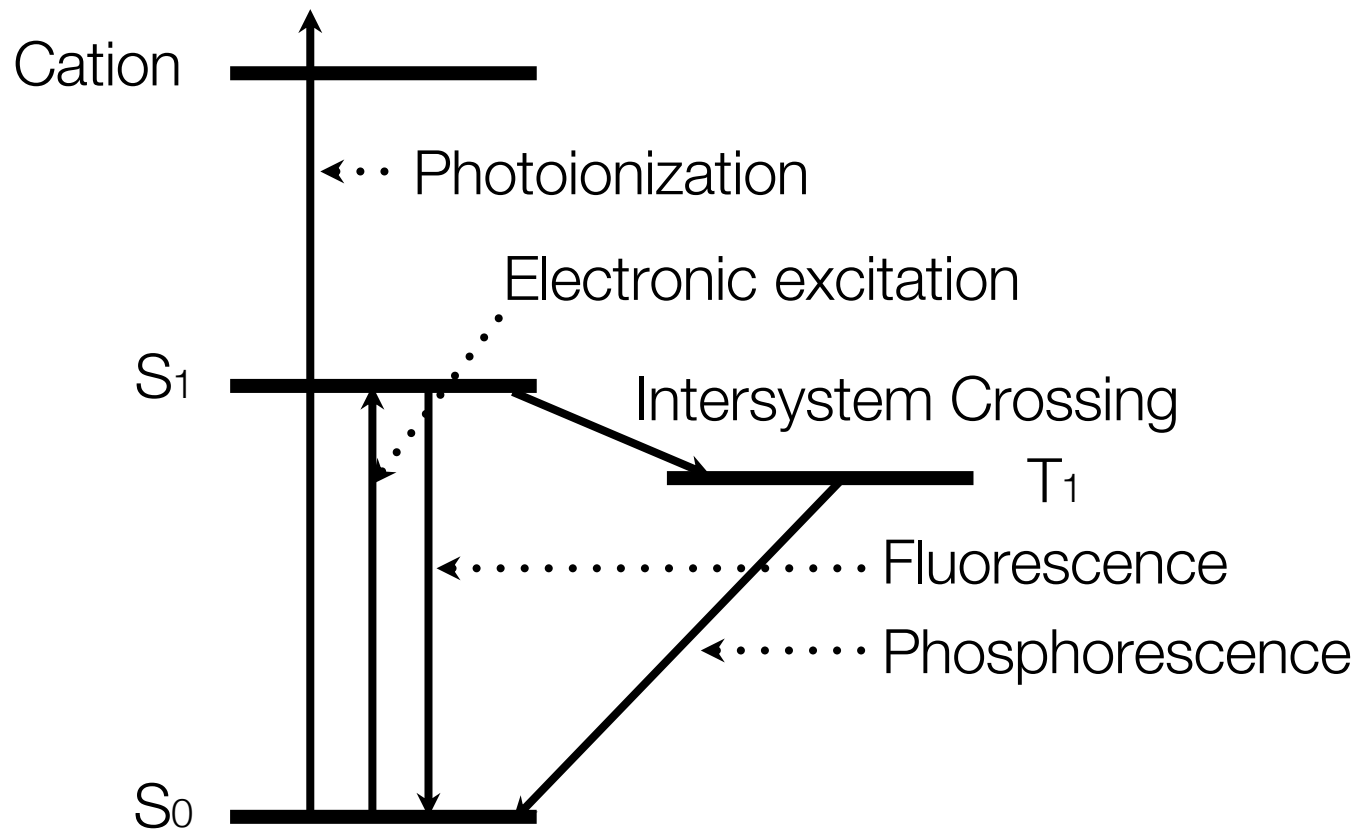
Electronic spectroscopy

Absorption

Emission (Fluorescence)

Laser ionization (in particular: REMPI)

Jablonski diagram



Energy Scales

Time scales?

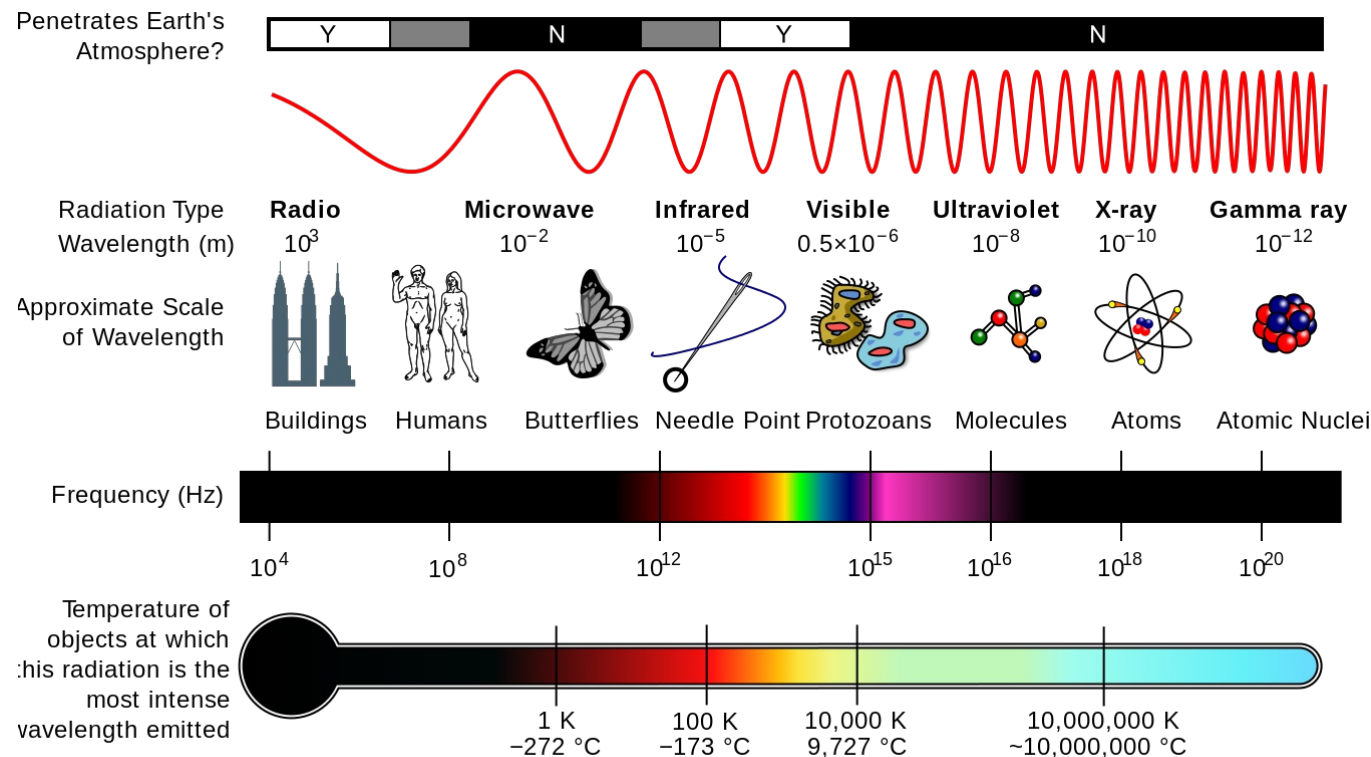
	eV	cm ⁻¹	WL	Hz
Ionization energies	10	100000	<100 nm	
Electronic states	1	10000	100's nm	
Vibrational	0.01	100	μm	THz
Rotational		1	cm	10 GHz
Hyperfine				>MHz

Sources of EM radiation:

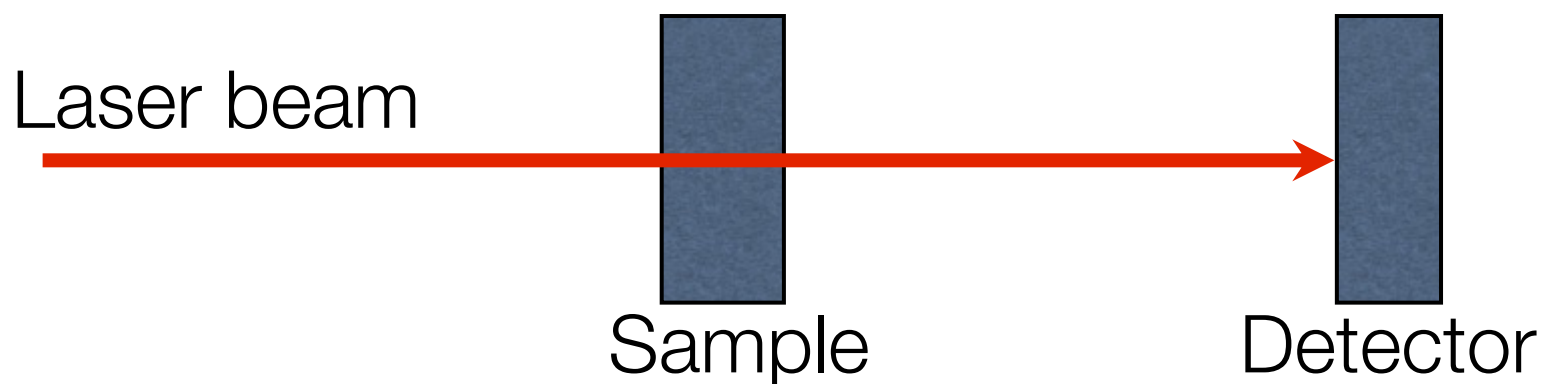
Lamps; Lasers; Free electron lasers; Synchrotron;
MW sources; RF sources

Wavelength regions

- IR Spectroscopy (mostly vibronic structure)
- Microwave Spectroscopy (rotational)
- UV/VIS (electronic)
- VUV/EUV/X-Ray (ionisation)



Absorption spectroscopy



Often not applicable in gas phase studies
(low densities)

Sensitivity-estimate (by comparison with condensed phase):

Lambert-Beer: $A = \epsilon \ell c$

Absorption spectroscopy

Sensitivity-estimate (by comparison with condensed phase):

Lambert-Beer: $A = \epsilon \ell c$

For a pure gas, in a cell, at room temperature.
There are reasons why we may not want this:

Einstein Coefficients

Recall

B₁₂: absorption

$$B_{12} = \frac{e^2}{4\varepsilon_0 m_e h \nu} f_{12}$$

B₂₁: stimulated emission

$$B_{21} = \frac{e^2}{4\varepsilon_0 m_e h \nu} \frac{g_1}{g_2} f_{12}$$

A₂₁: spontaneous emission

$$A_{21} = \frac{2\pi \nu^2 e^2}{\varepsilon_0 m_e c^3} \frac{g_1}{g_2} f_{12}$$

Sample preparation

Options

Gas cells



Uniformly filled cell
containing the gas

Molecular beams



Collimated, directed, dense beam of
molecules inside a vacuum chamber

Sample preparation

Options

Gas cells



Uniformly filled cell
containing the gas

Problems:

Collisions (mean free path)

Doppler shifts

$$\lambda \propto \frac{1}{p}$$

Mean free path of molecules in air at different pressures

Vacuum range	Pressure in mbar	number density (Molecules / cm ³)	Mean free path
Ambient pressure	1013	2.7×10^{19}	68 nm
Low vacuum	300 – 1	$10^{19} - 10^{16}$	0.1 – 100 μm
Medium vacuum	$1 - 10^{-3}$	$10^{16} - 10^{13}$	0.1 – 100 mm
High vacuum	$10^{-3} - 10^{-7}$	$10^{13} - 10^9$	10 cm – 1 km
Ultra-high vacuum	$10^{-7} - 10^{-12}$	$10^9 - 10^4$	1 km – 10^5 km
Extremely high vacuum	$<10^{-12}$	$<10^4$	$>10^5$ km

Sample preparation

Options

Gas cells



Uniformly filled cell
containing the gas

Problems:

Collisions (mean free path)

Doppler shifts

$$f = \left(1 + \frac{\Delta v}{c} \right) f_0$$

Example:
Electronic transition in NH_3

$$\Delta \tilde{\nu}_{obs} = \frac{\Delta v}{c} \tilde{\nu}_{real}$$

$$\tilde{\nu}_{real} = 68000 \text{ cm}^{-1}$$

$$\Delta v = 500 \text{ m/s}$$

$$\tilde{\nu}_{obs} = 0.11 \text{ cm}^{-1}$$

Molecular Beams



Molecular
beam

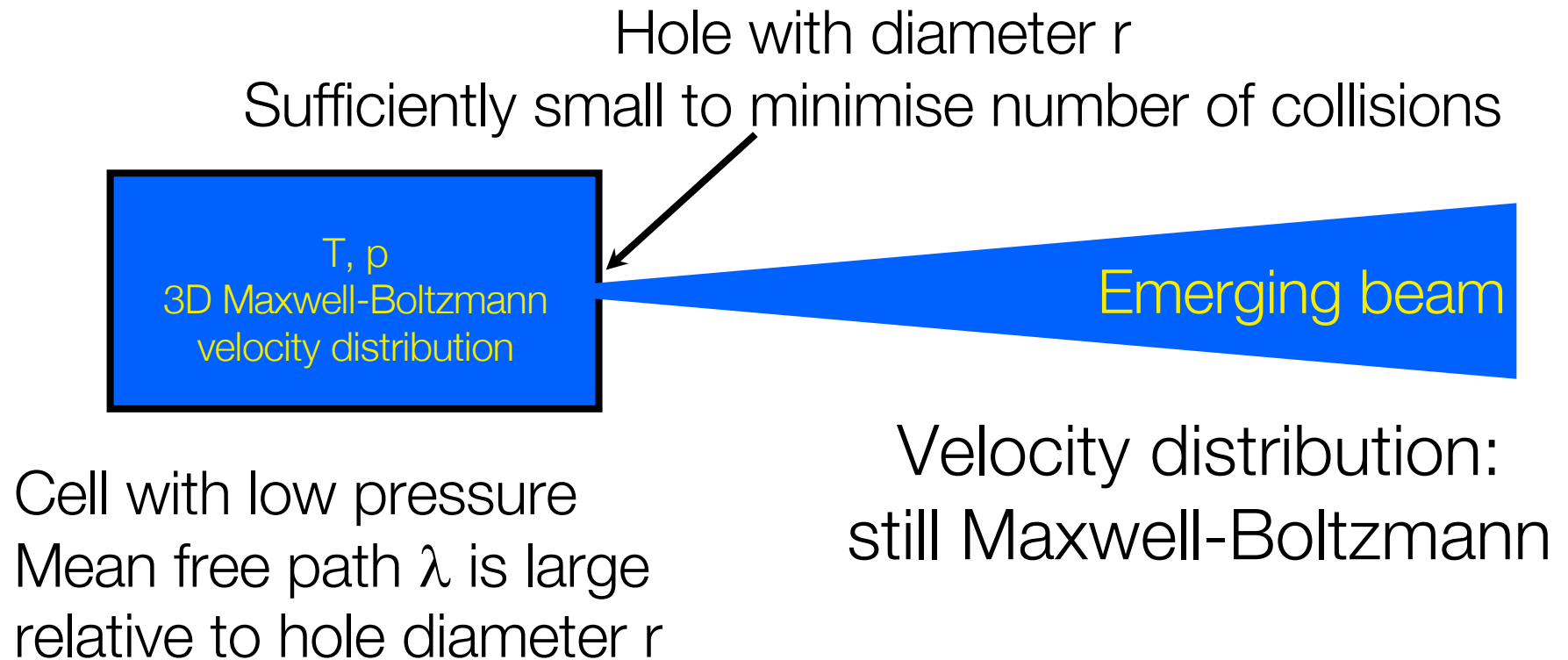


Effusive source

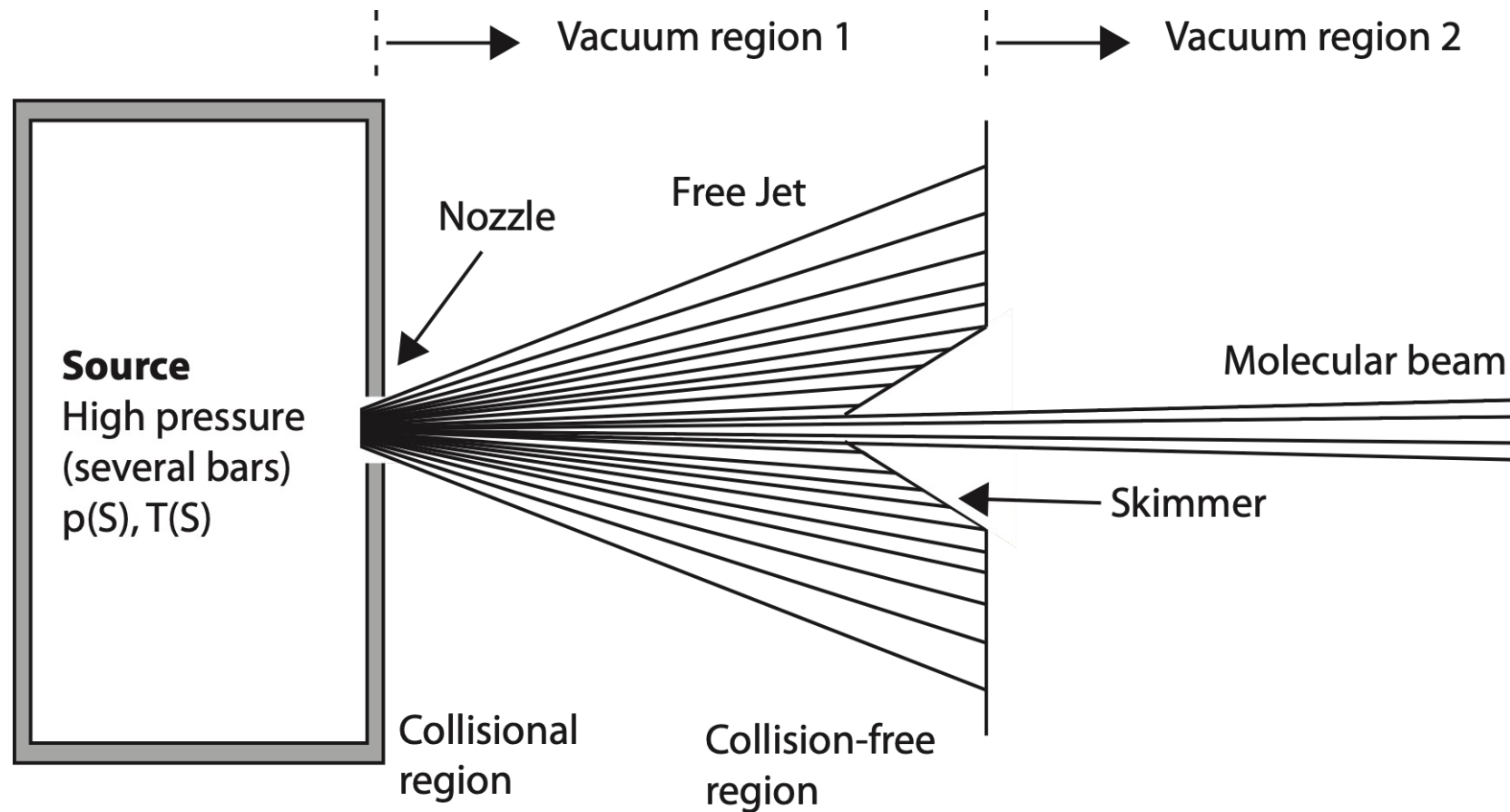
Oven

Supersonic expansion

Effusive sources



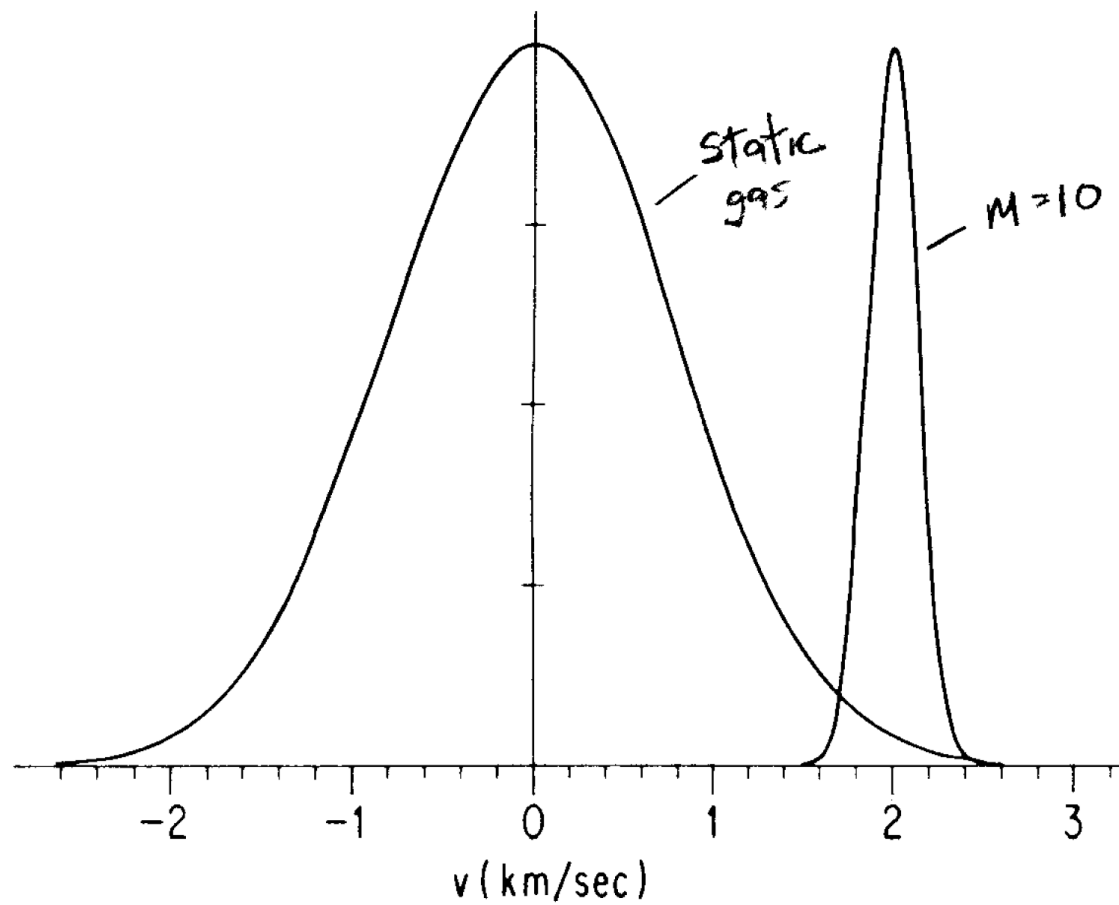
Supersonic expansions



Dynamics in supersonic expansions

- Conversion of random motion into forward motion
- Translational cooling by collisions
- Internal cooling by collisions
- loss of thermal equilibrium: $T_{\text{trans}} < T_{\text{rot}} < T_{\text{vib}}$ in general
- Increased average velocity

Velocity distribution



Velocity distribution

Inside reservoir:

$$f(v_z) = \left(\frac{m}{2\pi kT} \right)^{1/2} \exp \left\{ -\frac{mv_z^2}{2kT} \right\}$$

Maxwell distribution

Average velocity is zero

Velocity distribution

In the expansion:

Fast molecules accelerate slow ones.

The resulting distribution is narrower and centered at a non-zero velocity v_s :

$$f(v_z) \propto v_z^3 \exp \left\{ -\frac{(v_z - v_s)^2}{\alpha_s^2} \right\}$$

Width of the distribution

$$\alpha_s = \left(\frac{2kT_s}{m} \right)^{1/2}$$

Speed ratio

$$S = \frac{v_s}{\alpha_s}$$

Example:
50 m/s wide velocity distr.
in O₂ corresponds to < 5 K

Supersonic?

Speed of sound in an ideal gas

$$a = \sqrt{\gamma RT/m} \quad \gamma = \frac{C_p}{C_v} = 5/3$$

Mach number

$$M \equiv v/a$$

These expansions are called supersonic because $M \gg 1$
This is the case mostly because T is low, so the speed of sound is low.

Supersonic expansions

Adiabatic and isentropic
(no friction, no heat exchange)

Enthalpy:

$$h_0 = h - v_S^2/2$$
$$v_S^2 = 2(h_0 - h) = 2 \int_T^{T_0} C_p dT$$

$$v_{S,\infty} = \sqrt{\frac{2k}{m} \left(\frac{\gamma}{\gamma - 1} \right) T_0}$$

Supersonic expansions

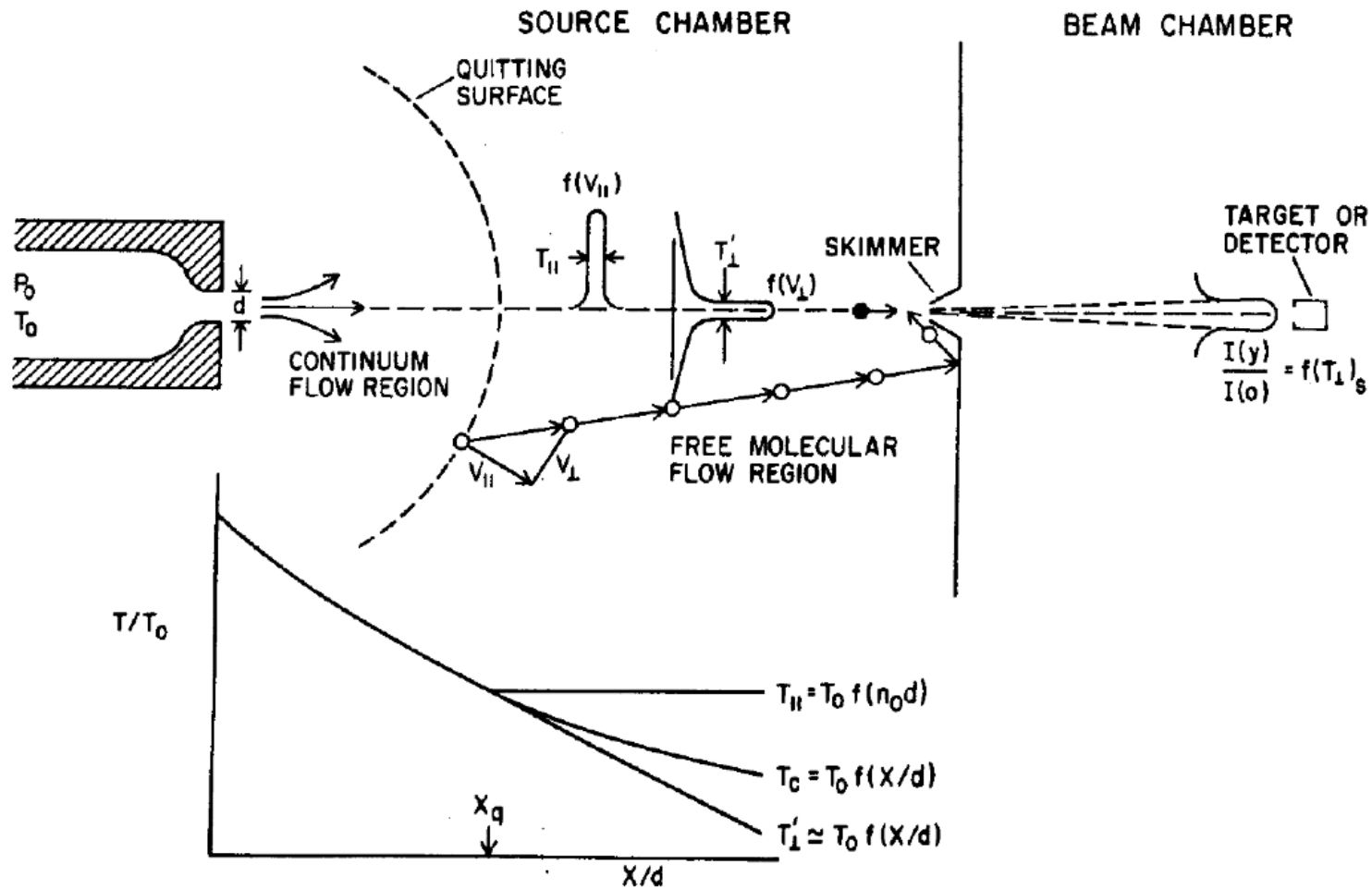
$$v_{s,\infty} = \sqrt{\frac{2k}{m} \left(\frac{\gamma}{\gamma-1} \right) T_0}$$

$$\frac{T_s}{T_0} = \left(1 + \left(\frac{\gamma-1}{2} \right) M^2 \right)^{-1}$$

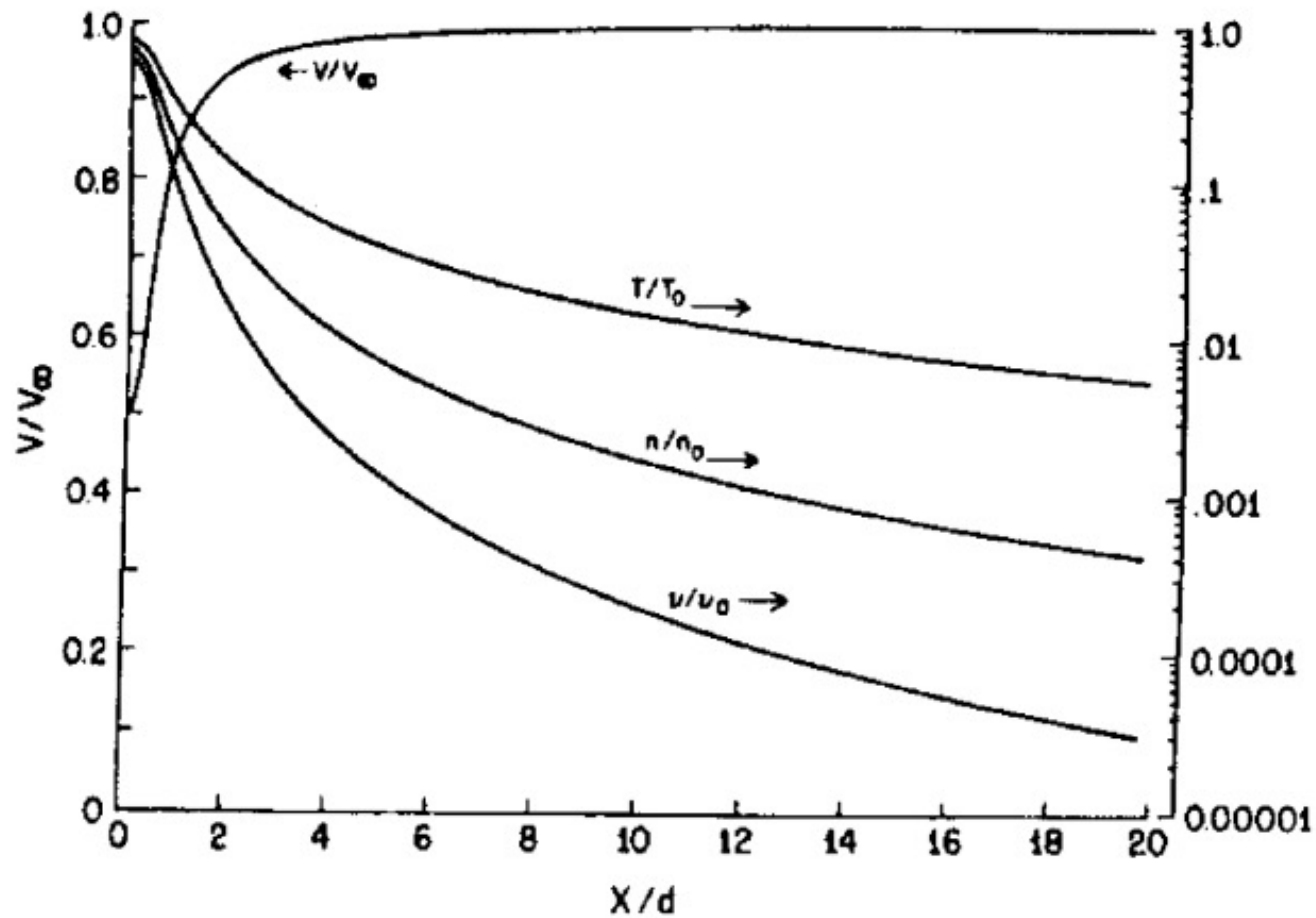
$$\frac{P}{P_0} = \left(1 + \left(\frac{\gamma-1}{2} \right) M^2 \right)^{\gamma/(1-\gamma)}$$

$$\frac{\rho}{\rho_0} = \left(1 + \left(\frac{\gamma-1}{2} \right) M^2 \right)^{1/(1-\gamma)}$$

Supersonic expansions

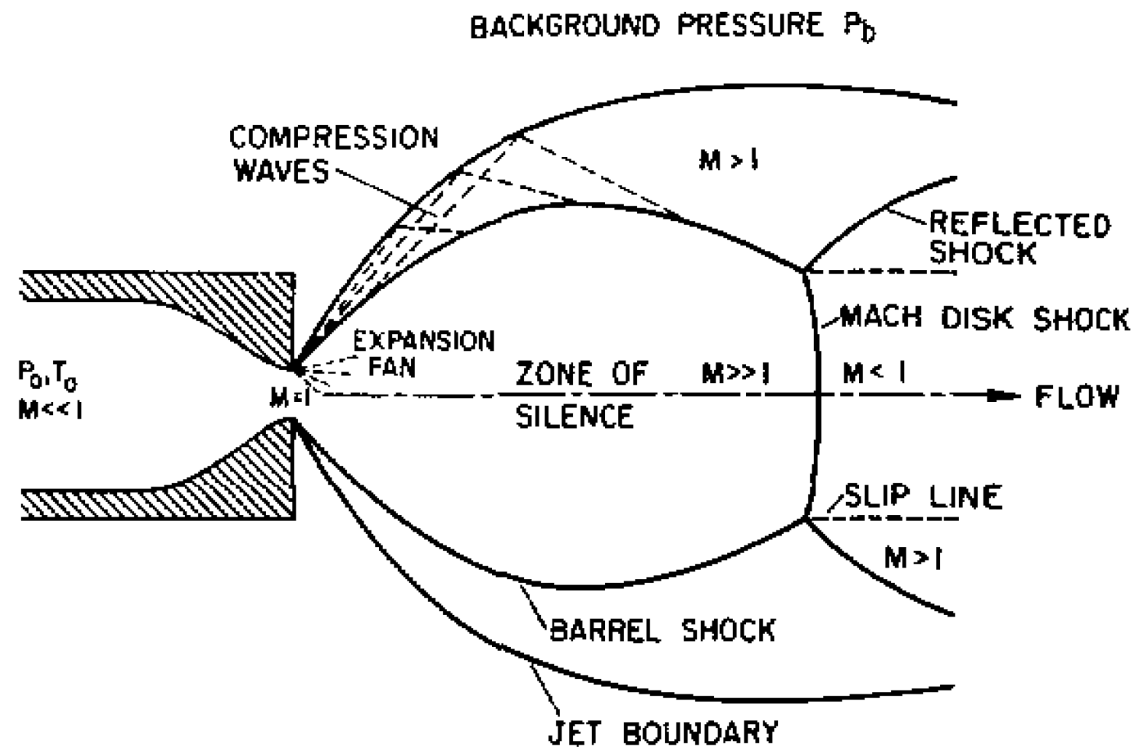


Supersonic expansions



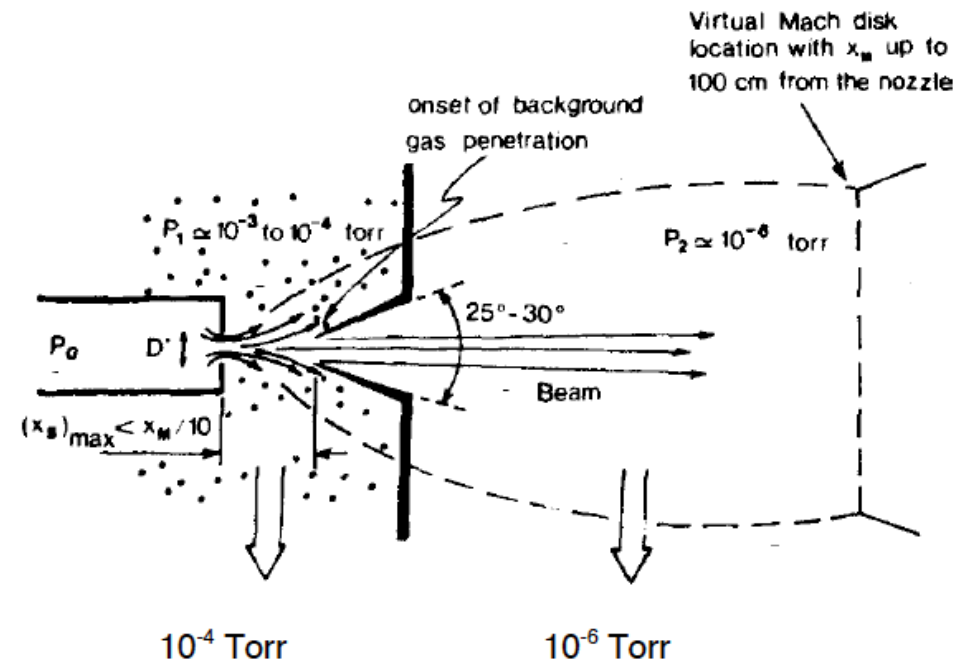
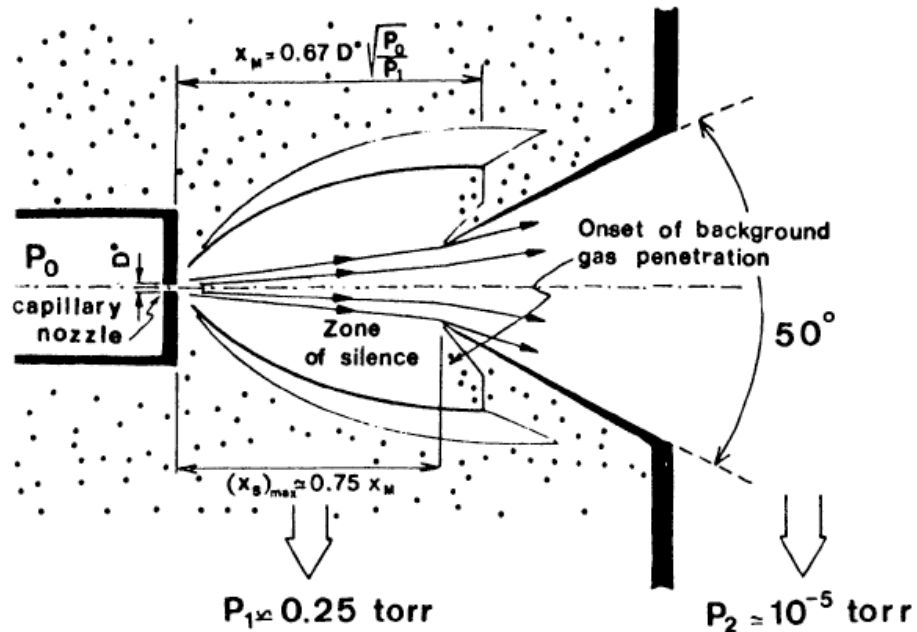
Background pressure

In reality there is background gas...



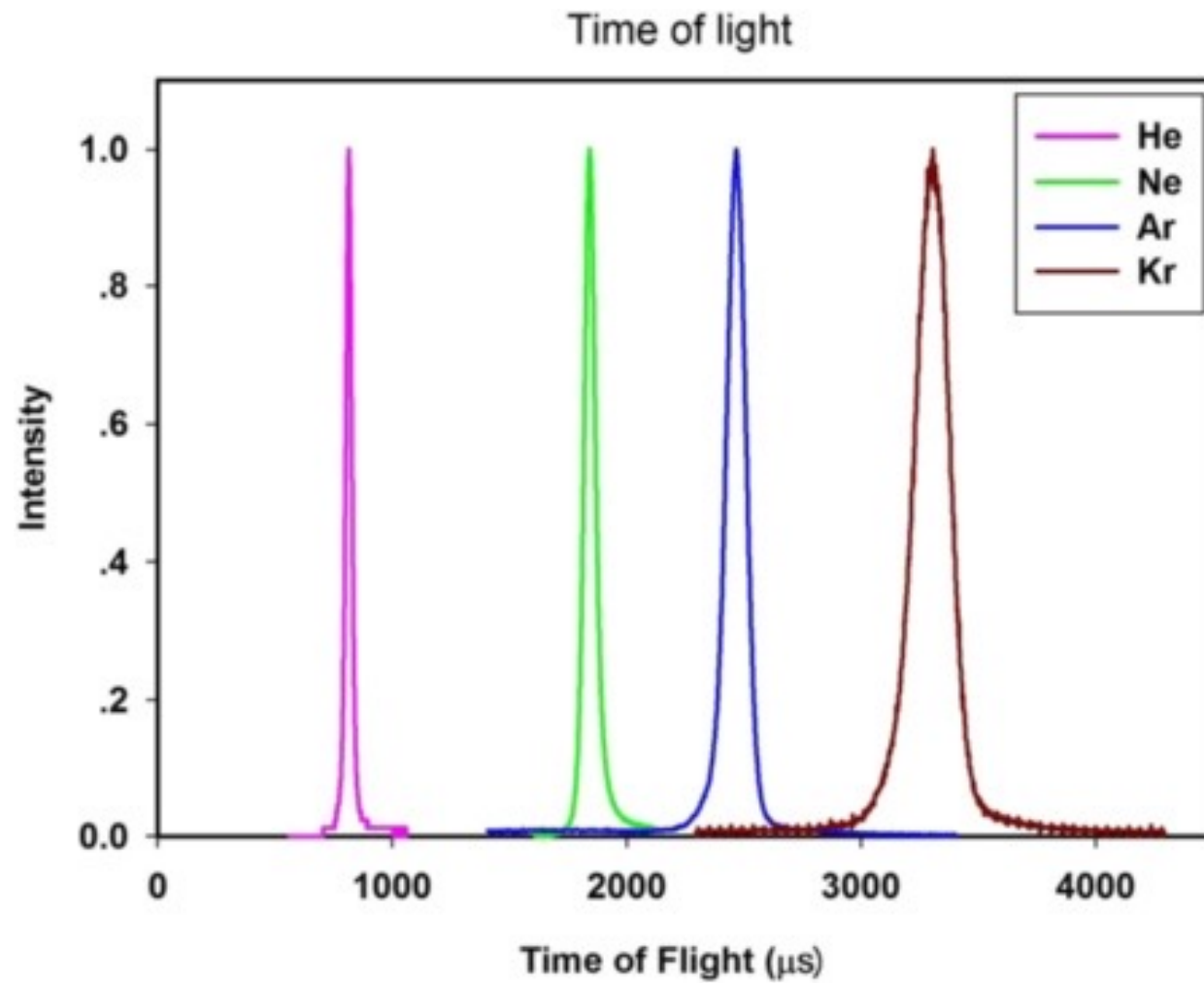
$$\left(\frac{x}{d}\right)_{Mach} \cong 0.67 \left(\frac{p_0}{p_{background}}\right)^{1/2}$$

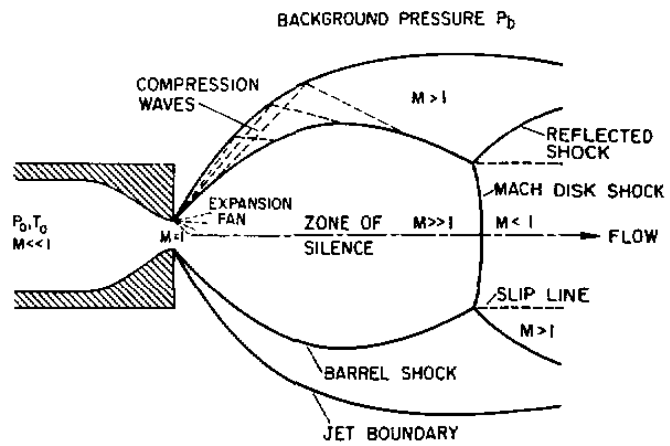
Background pressure



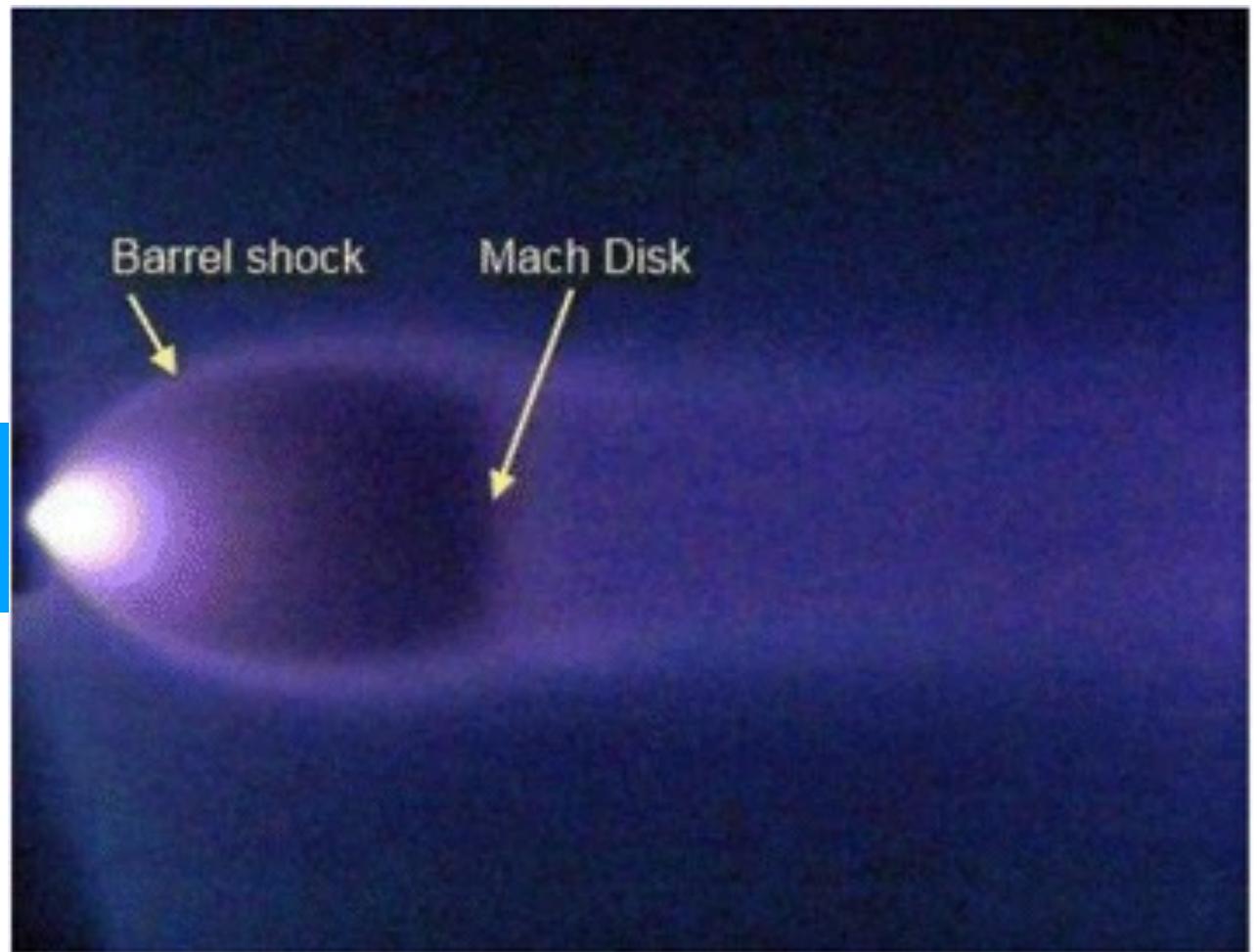
Example

mass (amu)	40
mass conversion	1.66E-27
T0	300.00
P0	2.00
D0	0.01
Cp/R	2.50
Cv/R	1.50
gamma	1.67
k	1.38E-23
M	27.81
Final Velocity	558
Final Temperature	1.16





Valve



Seeded expansions

Supersonic expansions work best with rare gases

Sample gas is seeded in rare gas carrier

$$\bar{m} = \sum_i x_i m_i$$

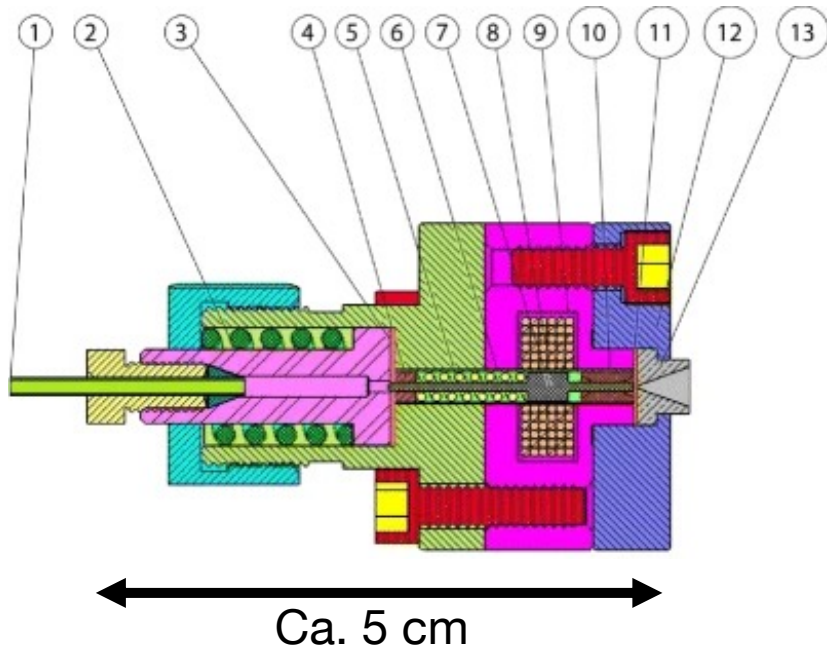
$$\bar{\gamma} = \sum_i x_i \gamma_i$$

$$v_s = \sqrt{\frac{2k}{\bar{m}} \left(\frac{\bar{\gamma}}{\bar{\gamma} - 1} \right) T_0}$$

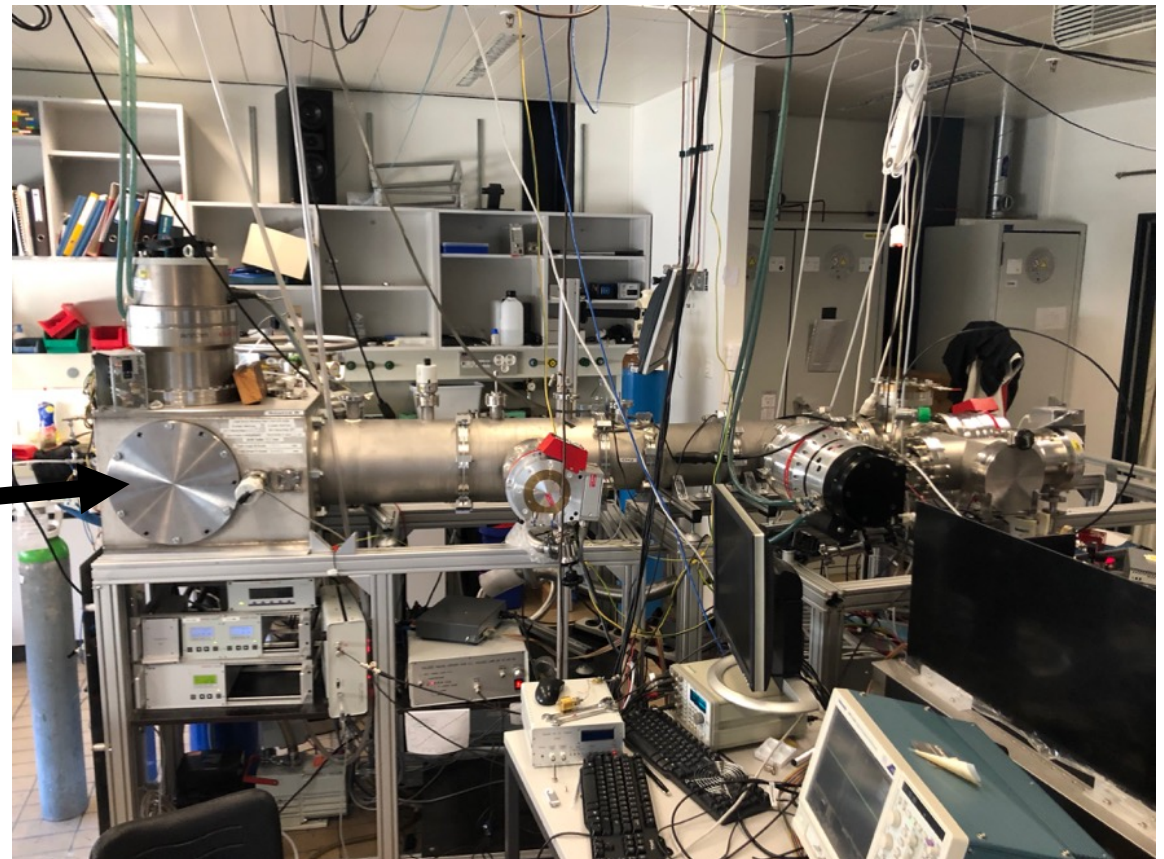
Thus...

- Molecular beams provide gas-phase samples of molecules at low temperatures (translational and rotational). The beams are highly collimated, corresponding to very low transverse velocities. Forward velocities are high, but all within a narrow range.

Technical implementation



Valve is housed inside
a vacuum chamber

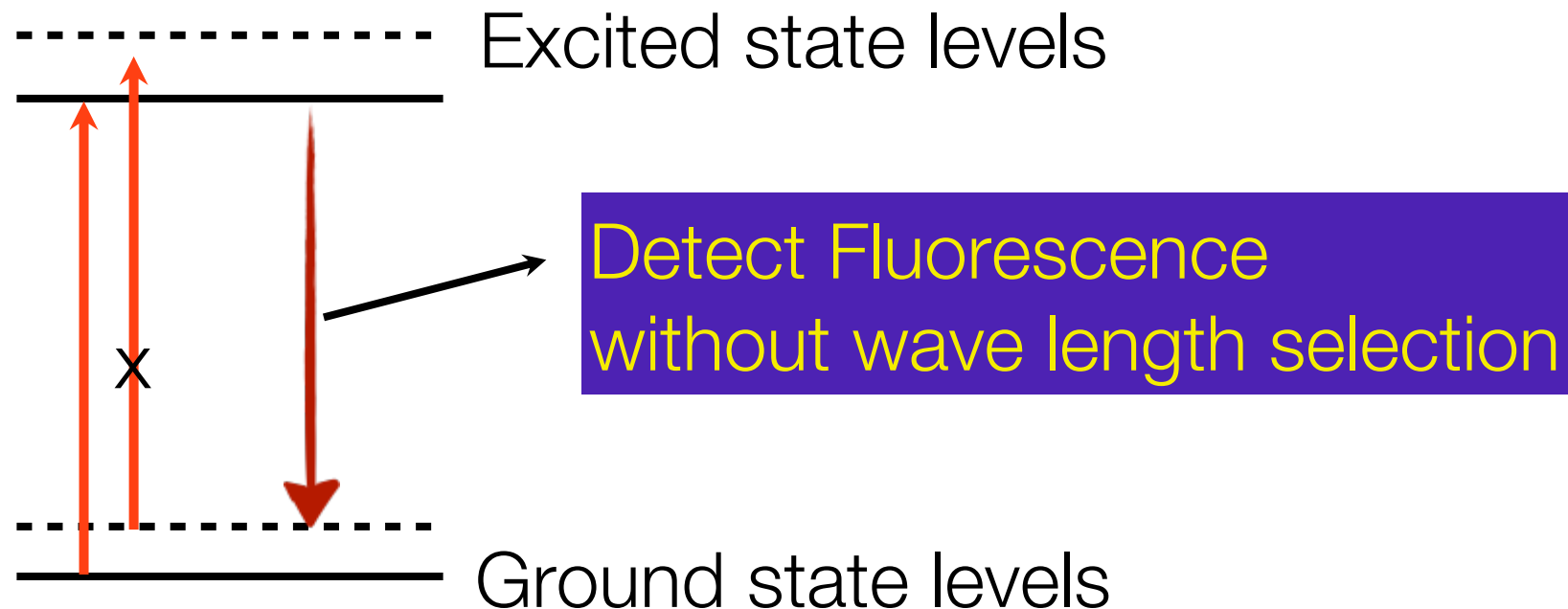


Sensitivity:
Charged-particle or Photon detection

Laser-induced Fluorescence

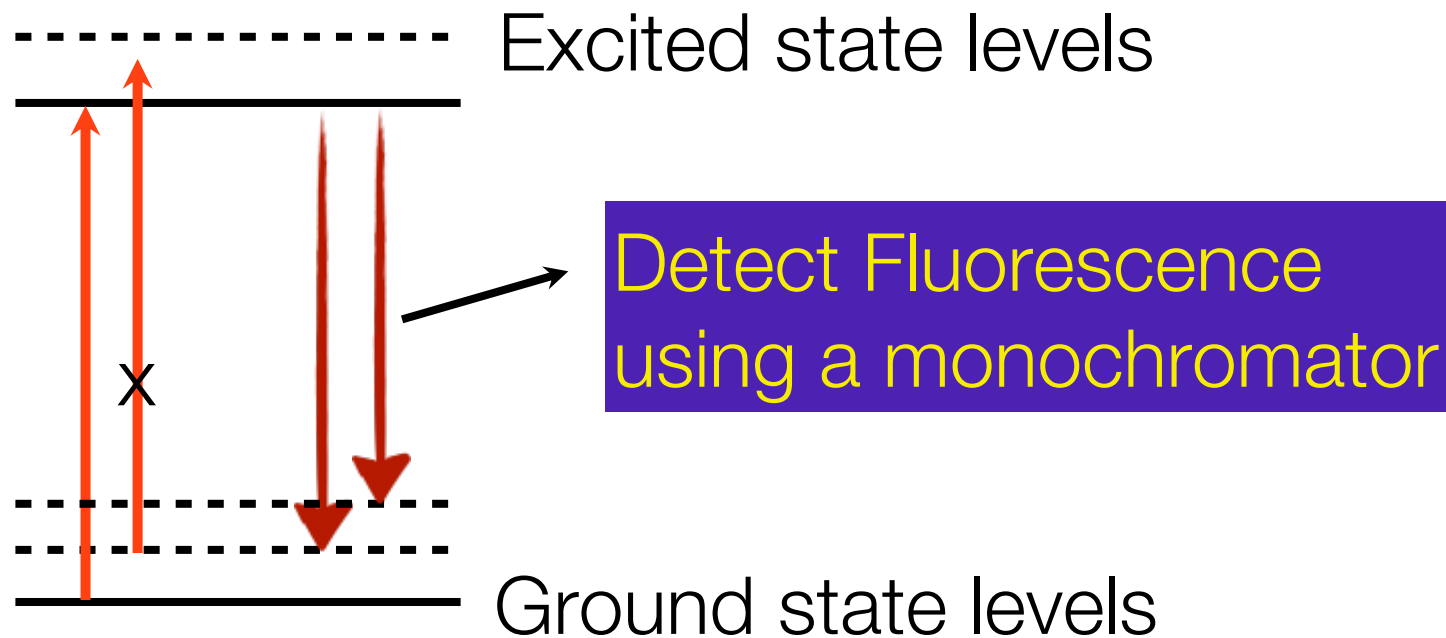
Zare, Annu. Rev. Anal. Chem. 5, 1(2012)

Excite the target molecule to a short-lived fluorescing state and detect the emitted light

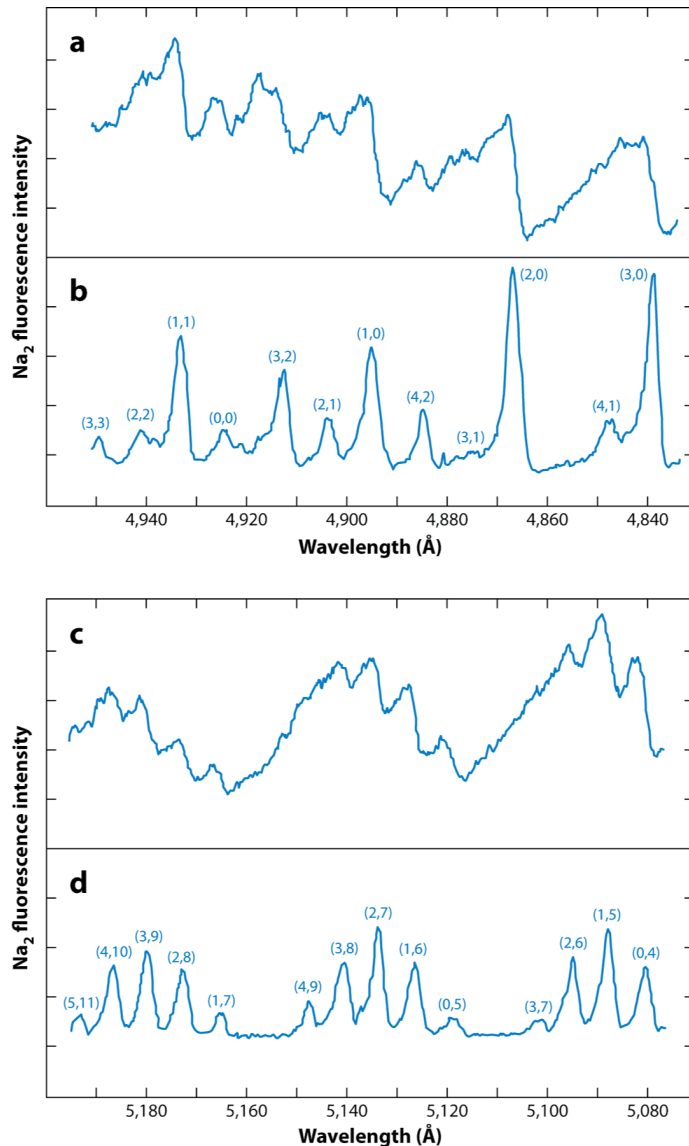


Dispersed Fluorescence

Excite the target molecule to a short-lived fluorescing state and detect the emitted light



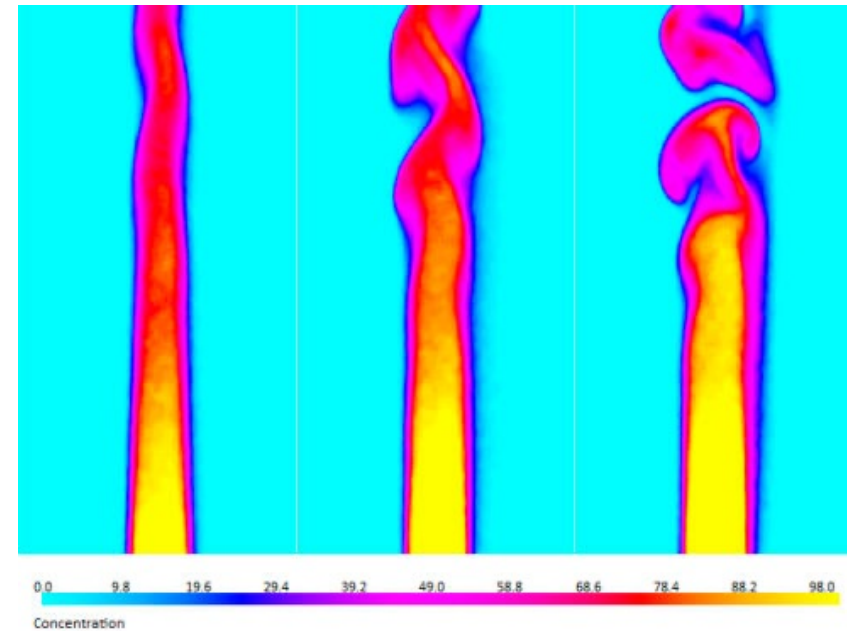
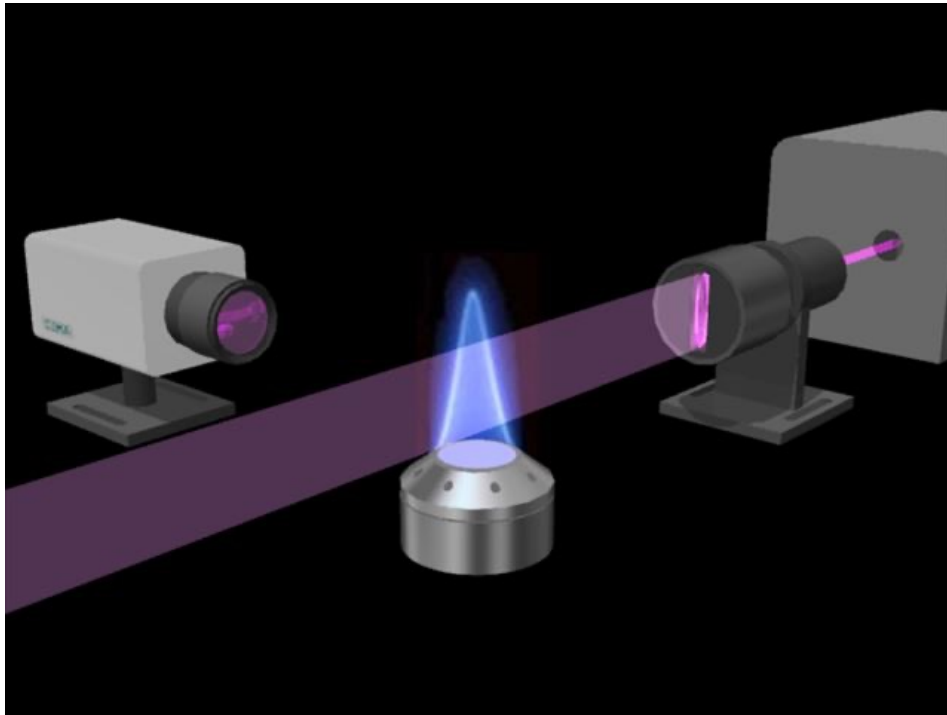
Fluorescence spectrum; example



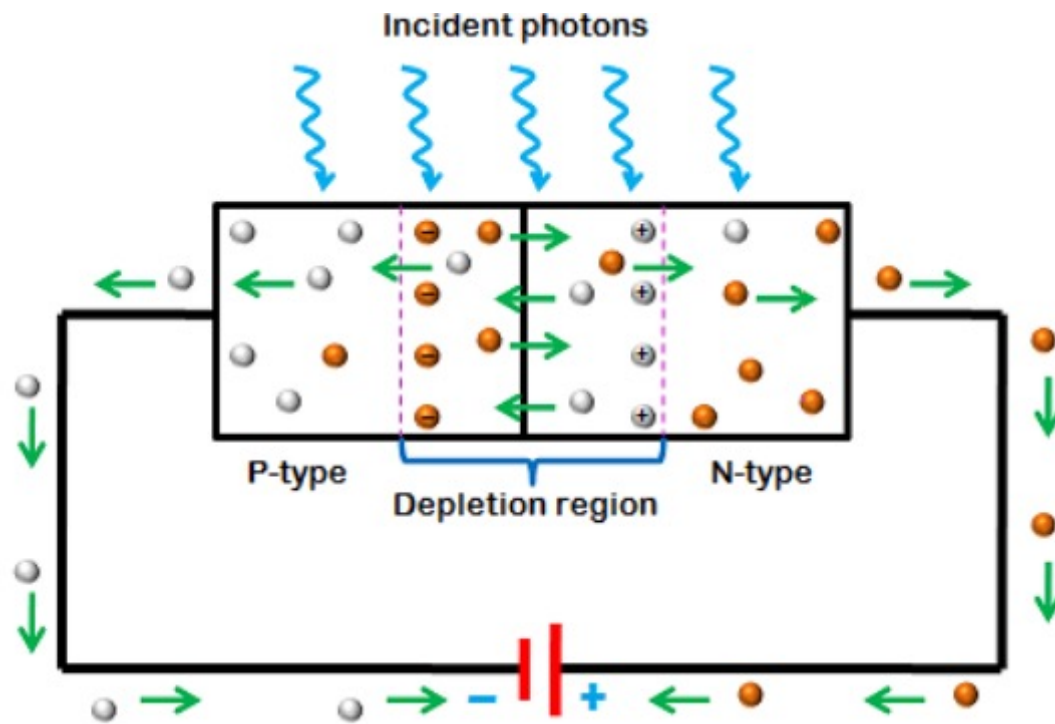
Na₂ fluorescence spectrum excited by white light (a,c) in a cell at 590 K and (b,d) in a nozzle beam with an oven chamber temperature of 920 K and a nozzle chamber temperature of 970 K. The vibrational bands are identified by (v',v'').

Sinha MP, Schultz A, Zare RN. 1973. The internal state distribution of alkali dimers in supersonic nozzle beams. *J. Chem. Phys.* 58,549(1973)

LIF spectrum; application

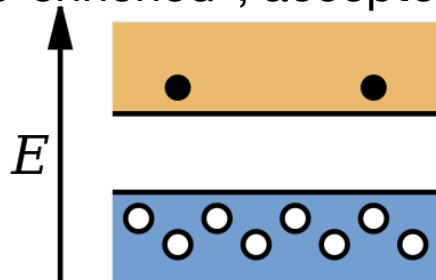


Photodiodes



Current flow requires electrons to be transferred to the conduction band.

p-type semiconductor
("hole-enriched"; acceptor-doped)



n-type semiconductor
("electron-enriched"; donor-doped)

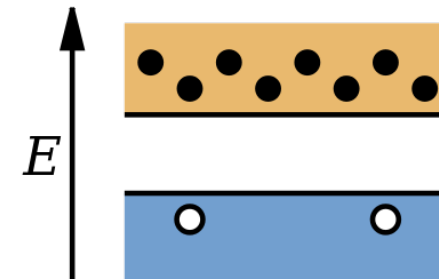
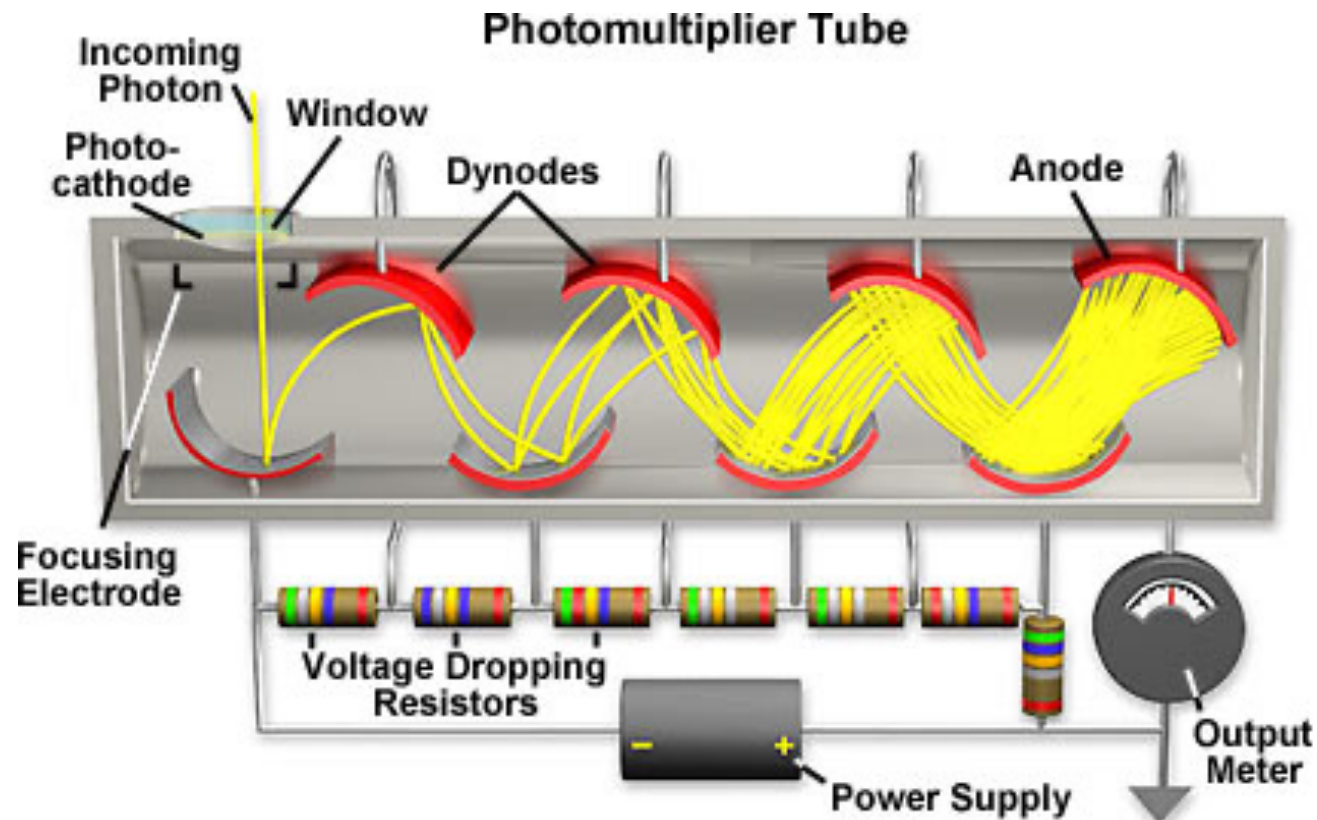


Photo-multiplier tubes

Requirement:

The work-function of the material needs to be lower than the photon energy.

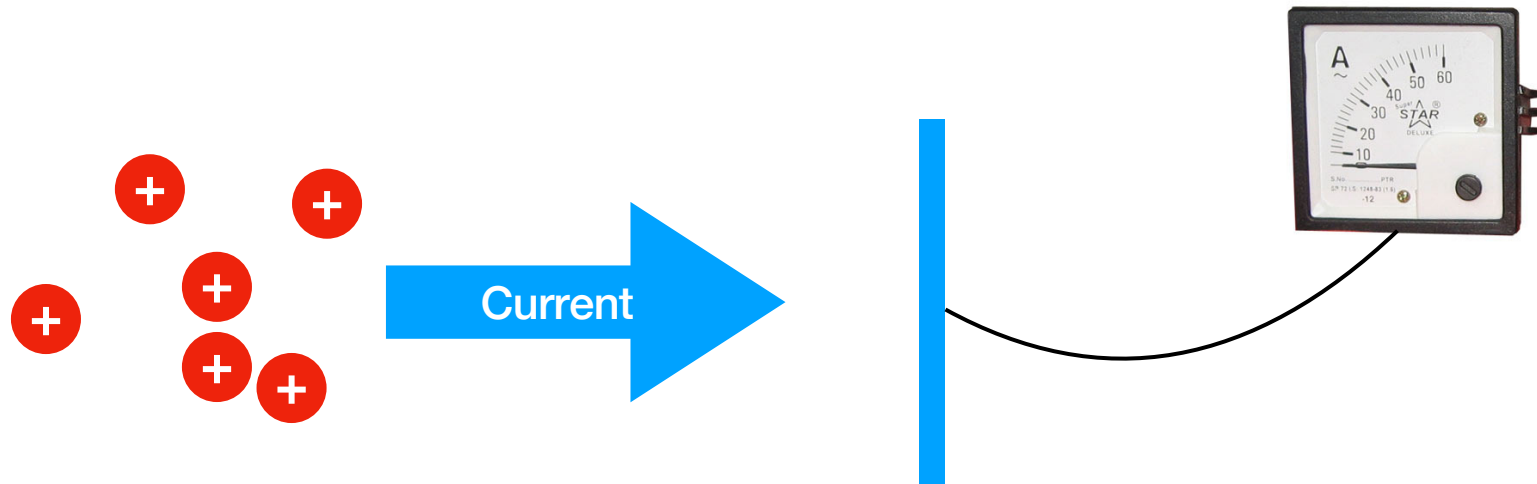


Ionization

- Photoionization
- Multiphoton ionization
- Resonance-enhanced MPI

Charged-particle detection

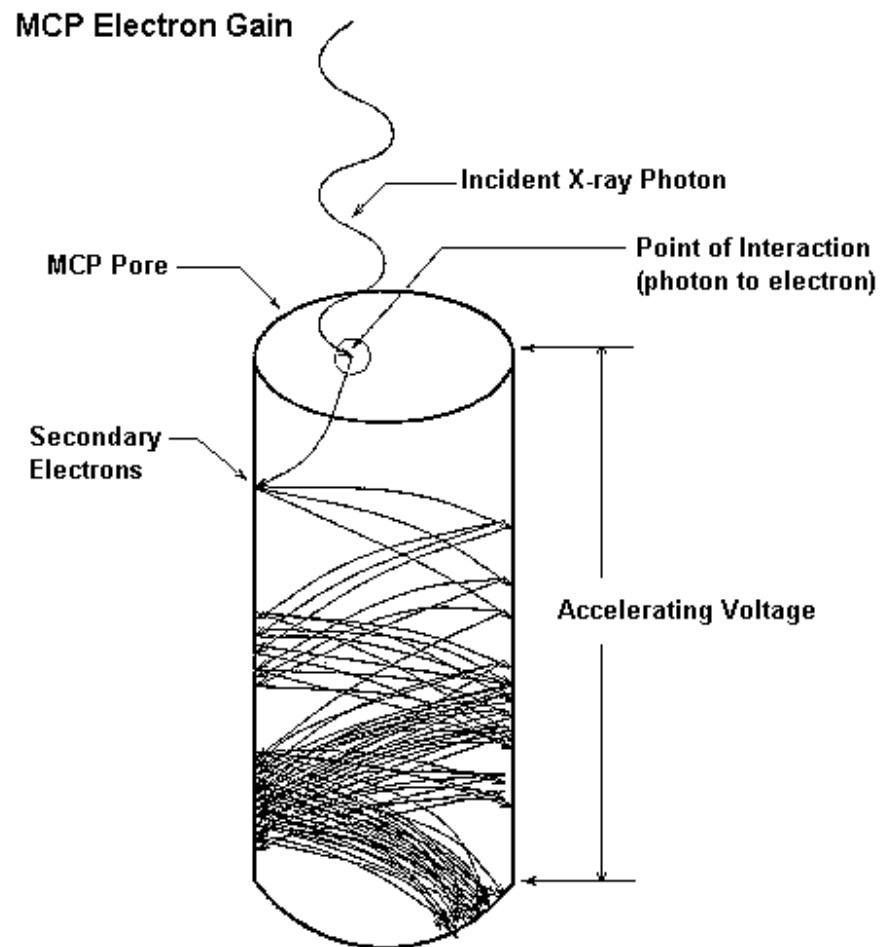
A metal plate



Normally not sufficiently sensitive - we need amplification.

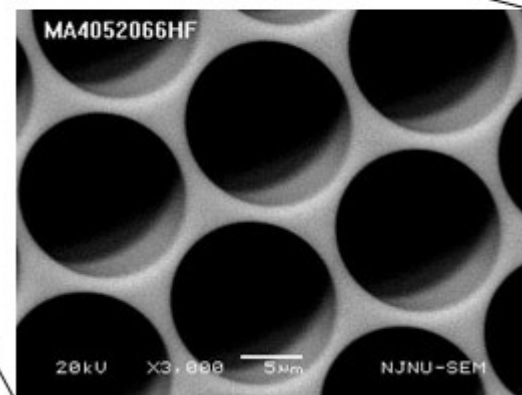
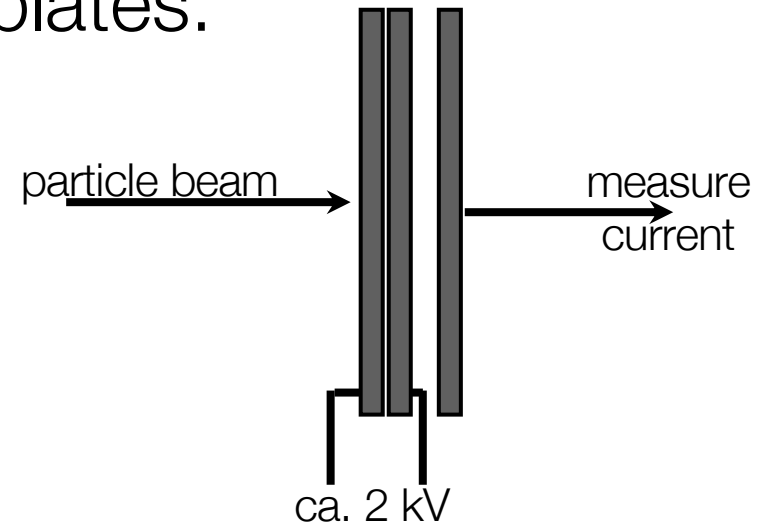
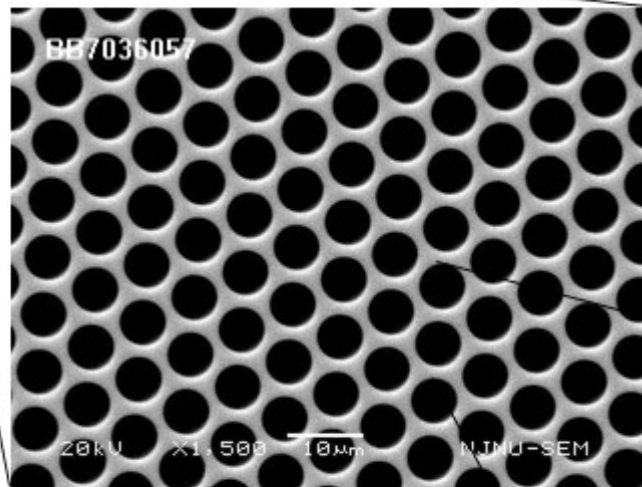
Charged-particle detection

Microchannel plates:



Charged-particle detection

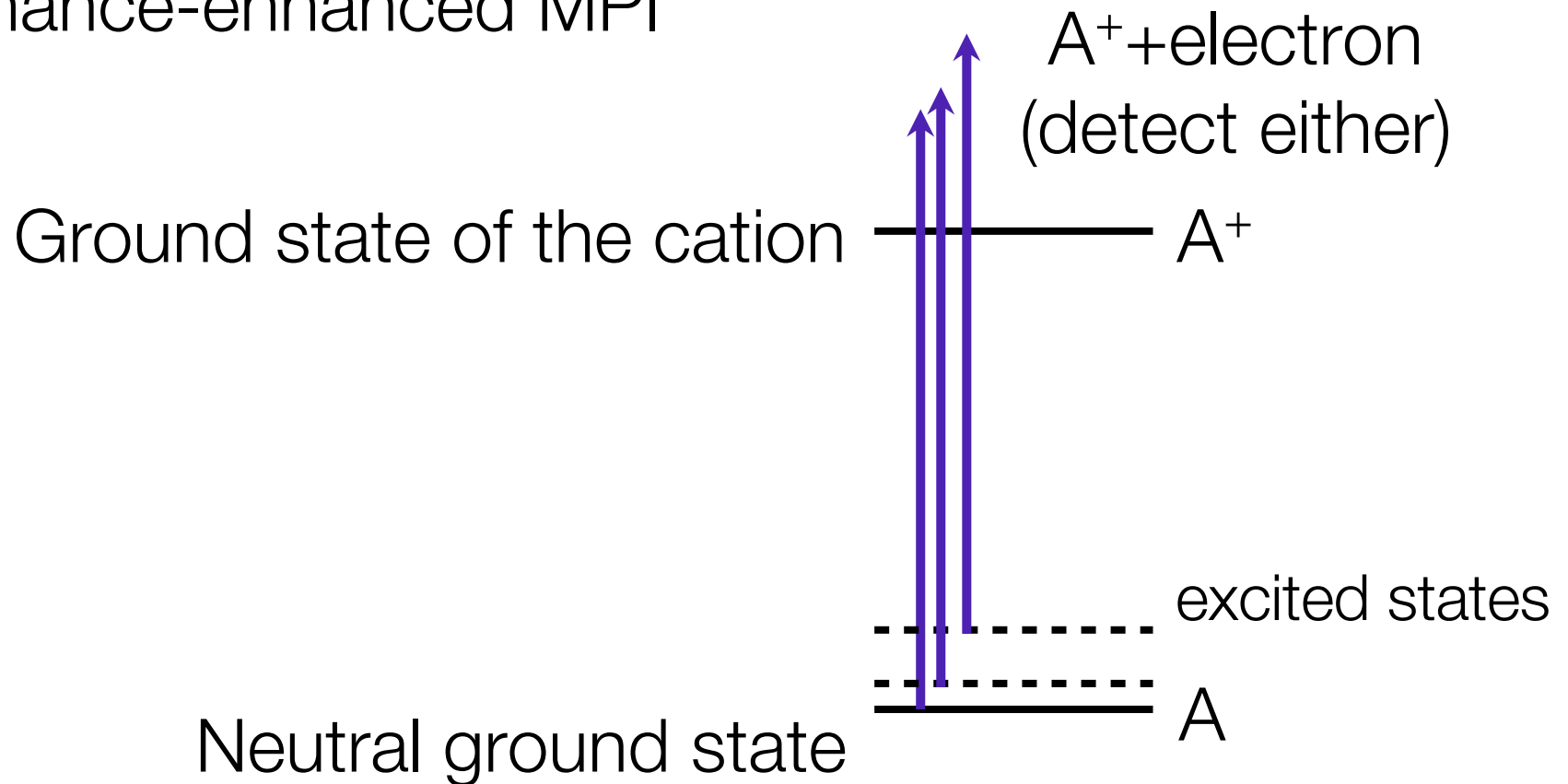
Microchannel plates:



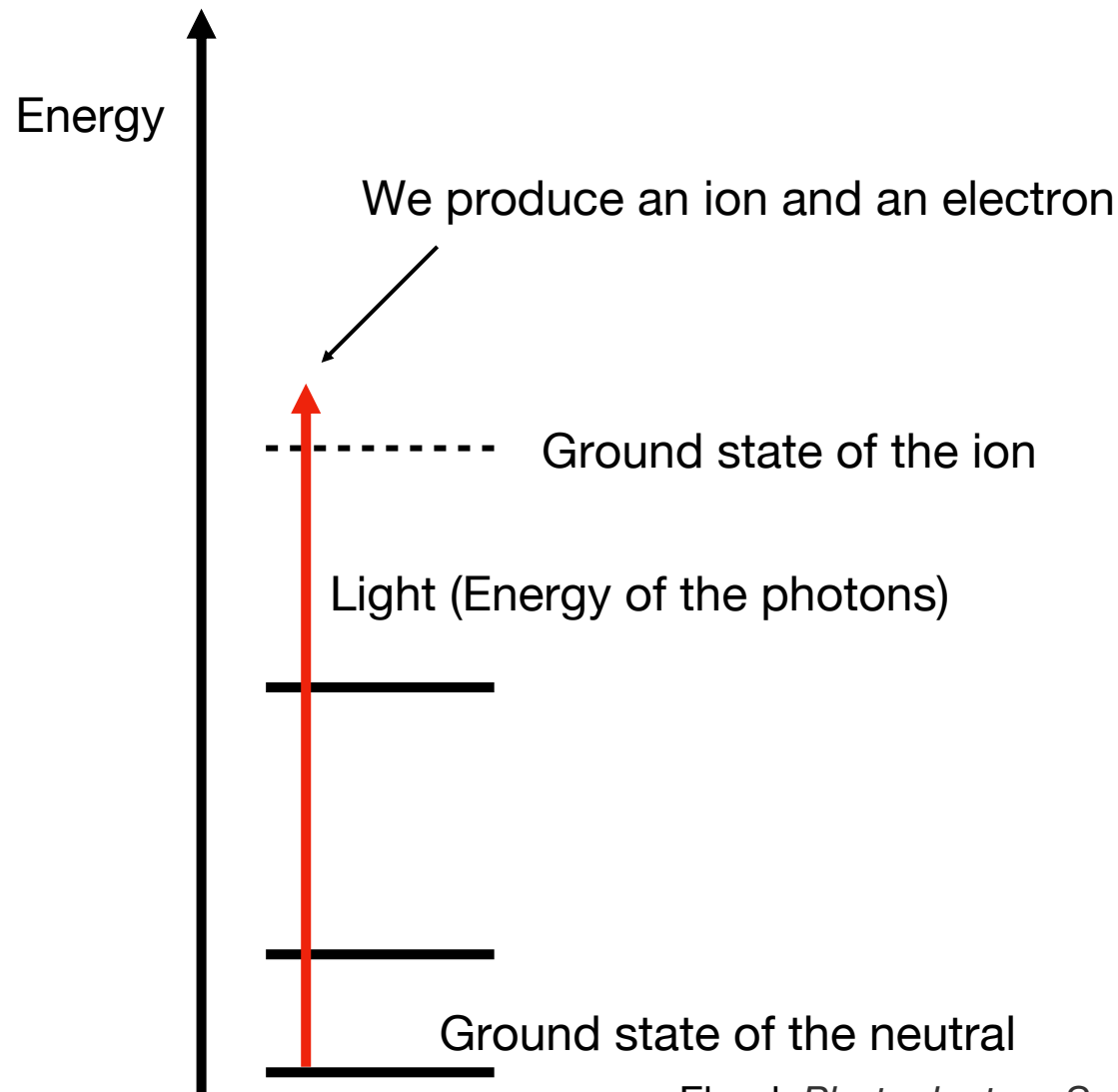
Ionization

- Photoionization

- Multiphoton ionization
- Resonance-enhanced MPI

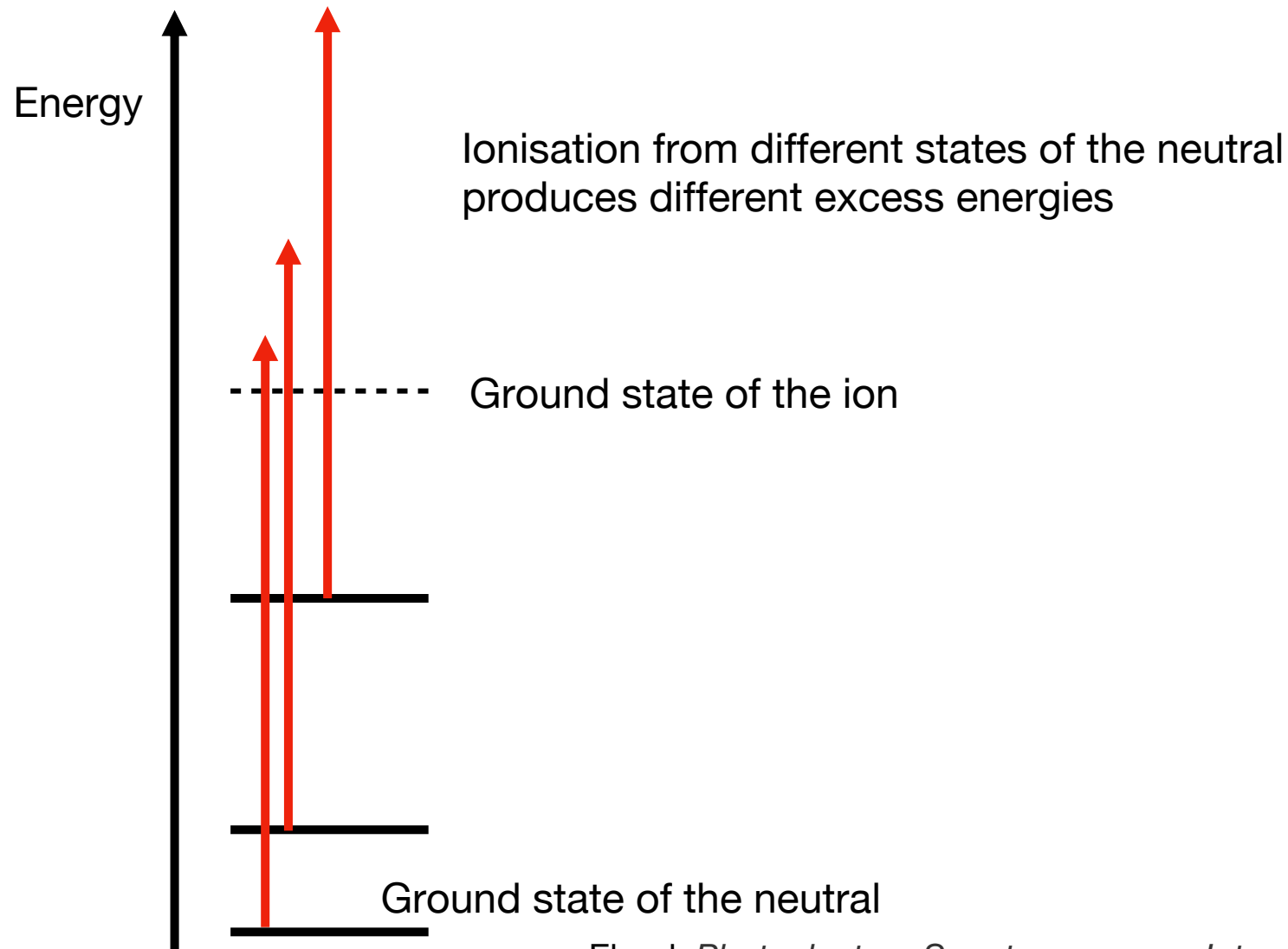


Photoelectron Spectroscopy



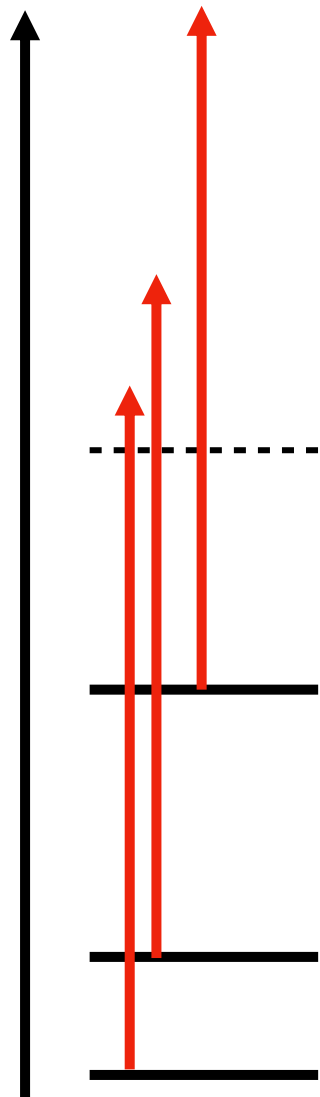
Eland, *Photoelectron Spectroscopy; an Introduction to UV Photoelectron Spectroscopy in the Gas Phase* (2nd edn.), Butterworths, London (1983)

Photoelectron Spectroscopy



Eland, *Photoelectron Spectroscopy; an Introduction to UV Photoelectron Spectroscopy in the Gas Phase* (2nd edn.), Butterworths, London (1983)

Photoelectron Spectroscopy



Energy conservation

$$\begin{aligned}
 E_{total} &= E_{kin} + E_{int} \\
 &= E_{kin,ion} + E_{kin,electron} + E_{int,ion} \\
 &= E_{int,neutral} + h\nu - E_{ionisation}
 \end{aligned}$$

Momentum conservation

$$\begin{aligned}
 p_{total} &= 0 \\
 &= \vec{p}_{electron} + \vec{p}_{ion} \\
 &= |\vec{p}_{electron}| - |\vec{p}_{ion}|
 \end{aligned}$$

$$m_e/m_i = 1893 \text{ for } i=\text{proton}$$

$$v_i \approx 0; E_{kin,ion} \approx 0$$

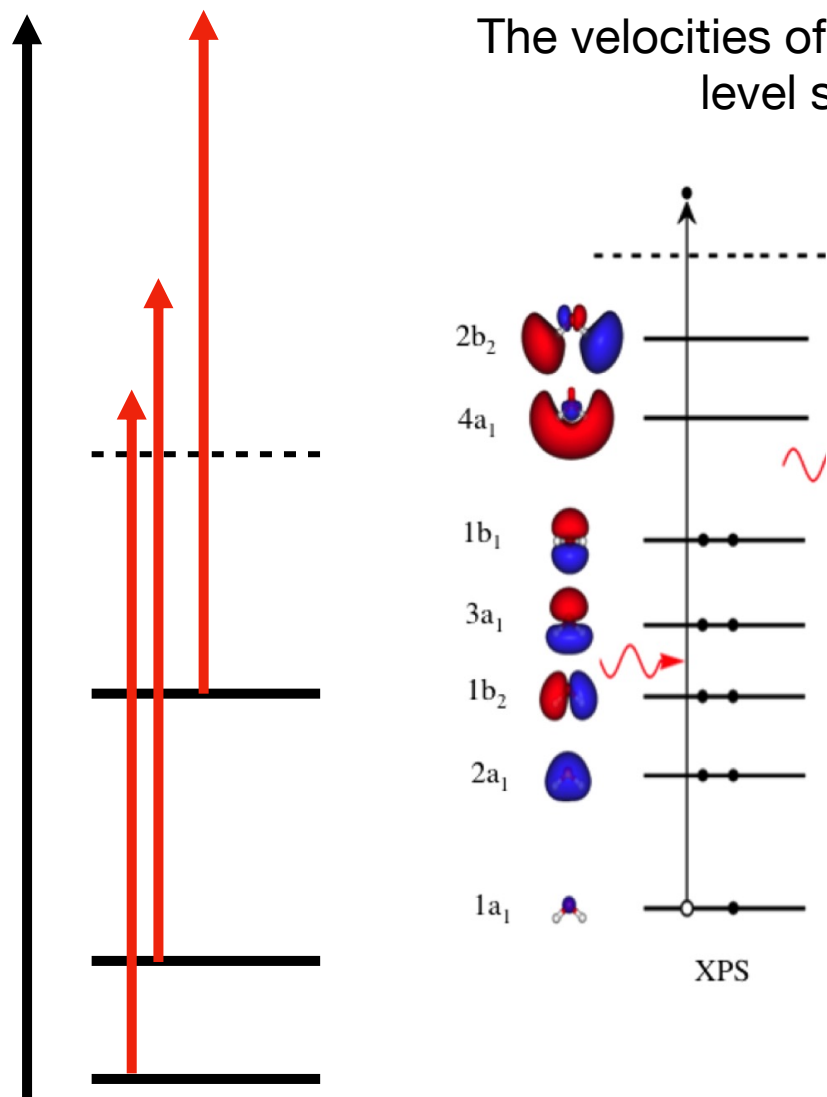
$$m_i v_i = m_e v_e$$

$$v_i = \frac{m_e}{m_i} v_e$$

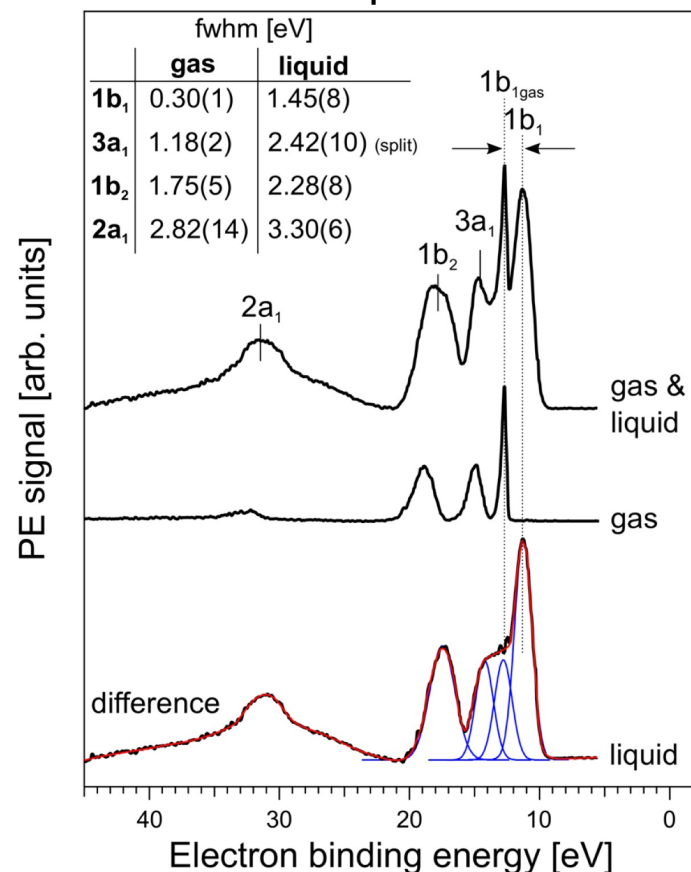
$$\begin{aligned}
 E_{kin,electron} &= E_{int,neutral} + h\nu - E_{ionisation} \\
 &\quad - E_{kin,ion} - E_{int,ion}
 \end{aligned}$$

Photoelectron Spectroscopy

The velocities of the photoelectrons correspond to the energy level structure of the neutral (and the ion)

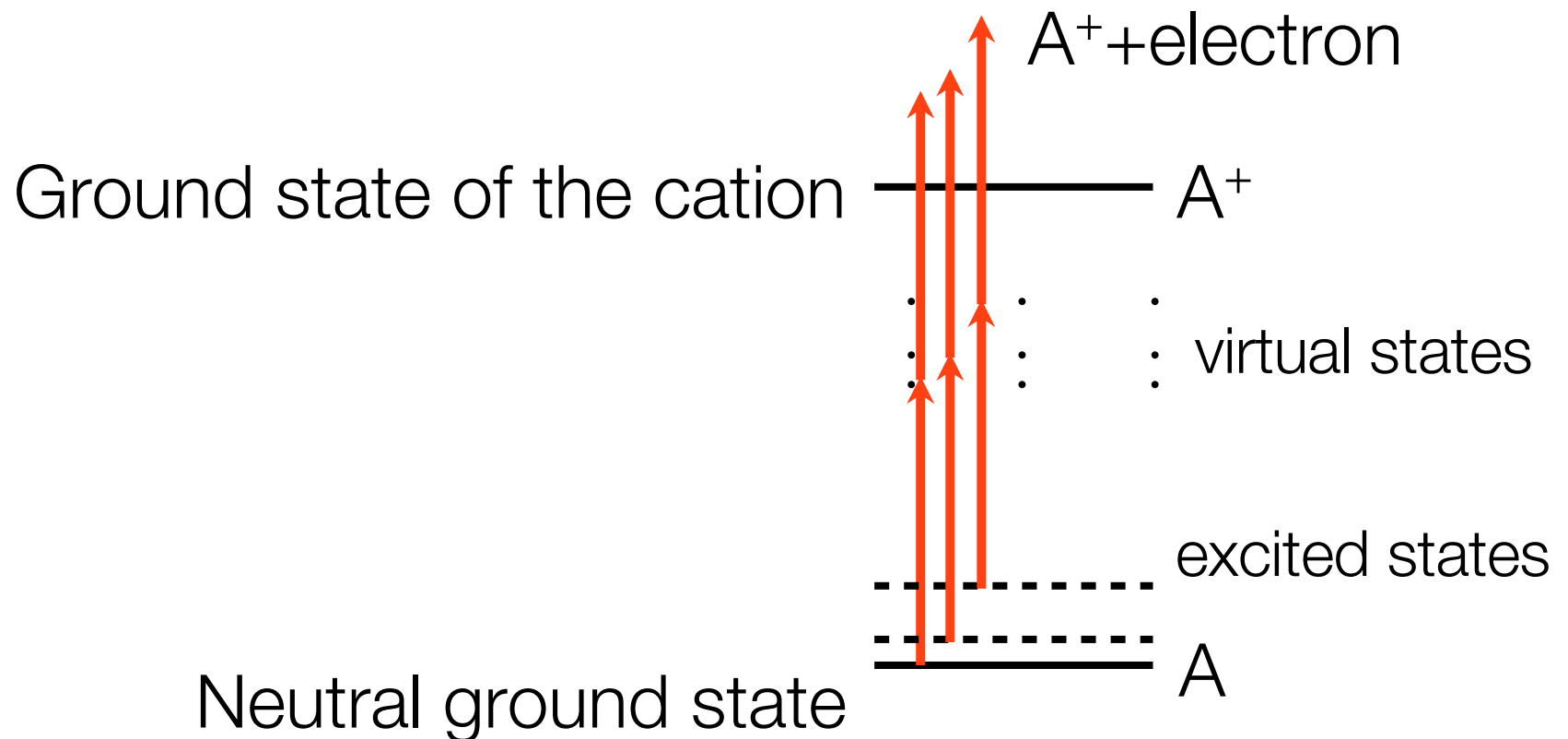


Example: water



Ionization

- Photoionization
- Multiphoton ionization
- Resonance-enhanced MPI



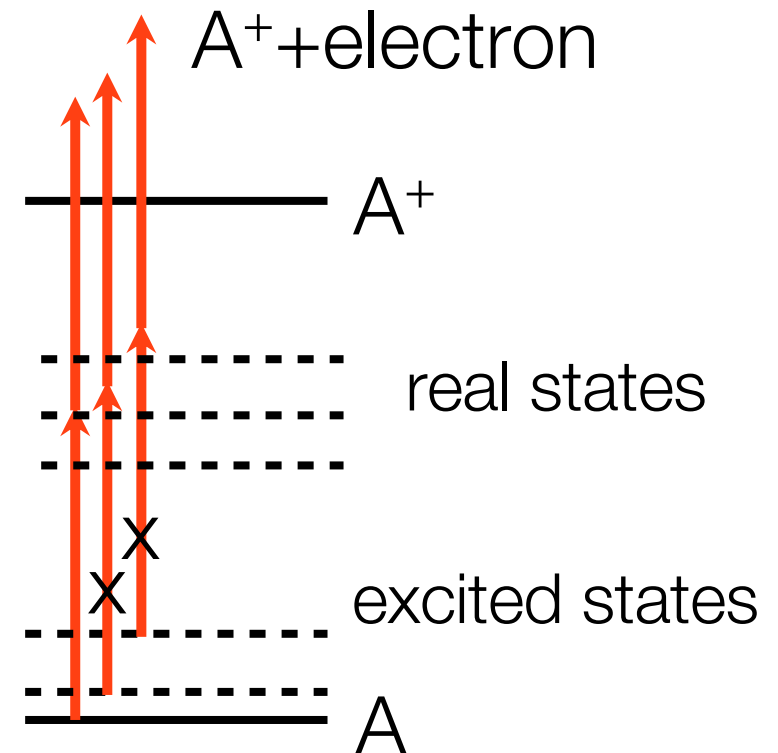
Ionization

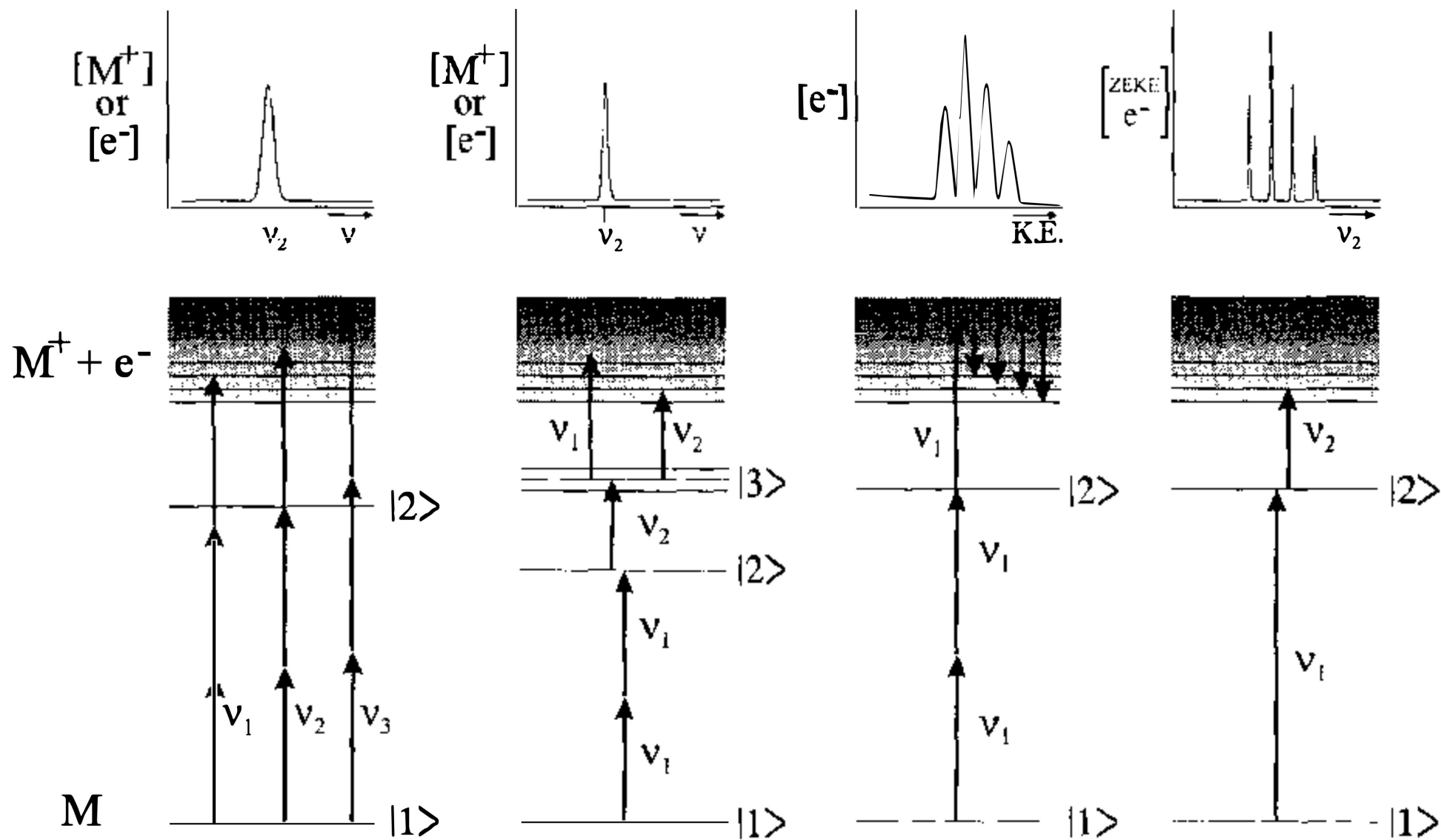
- Photoionization
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Ground state of the cation

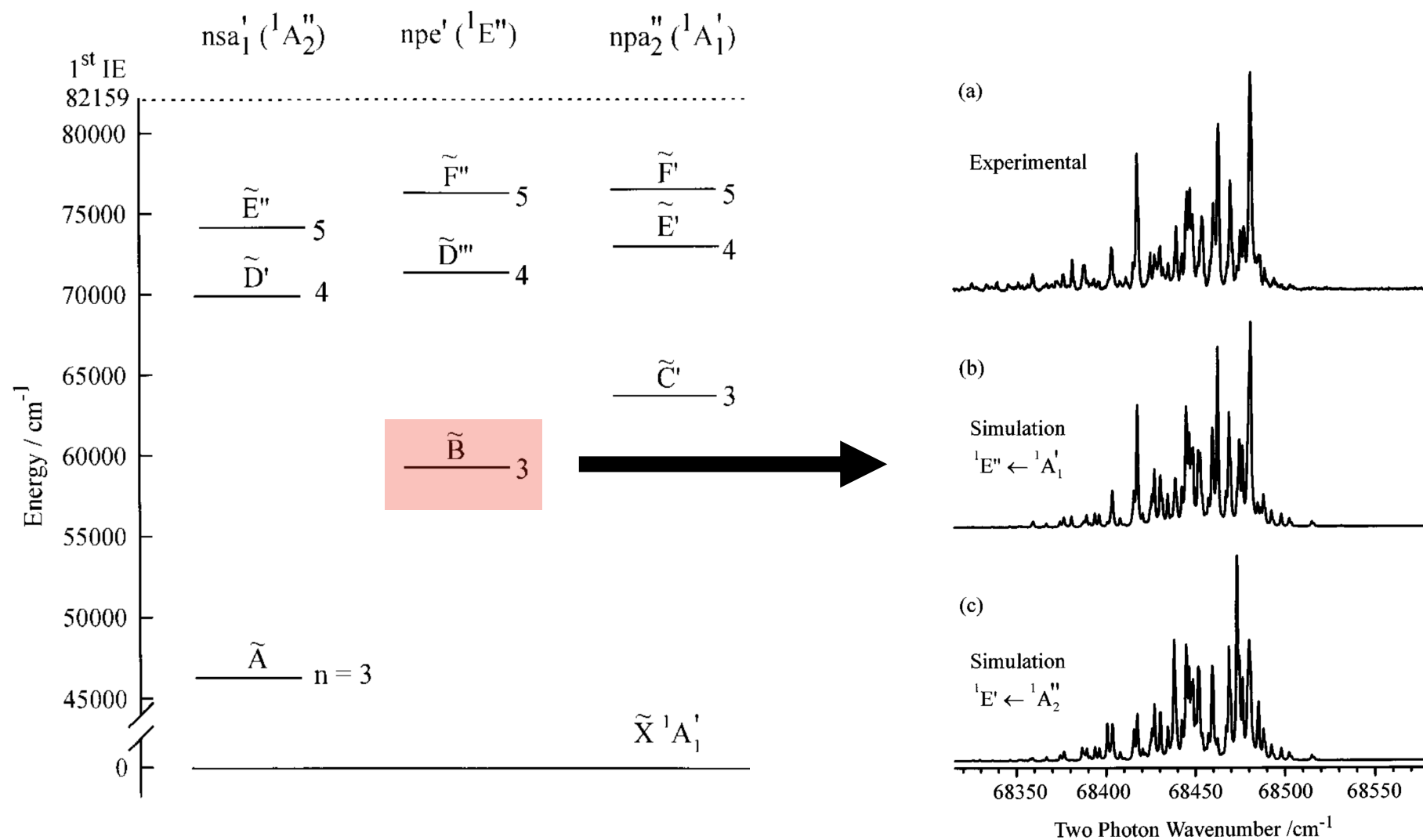
State-selective
detection!

Neutral ground state

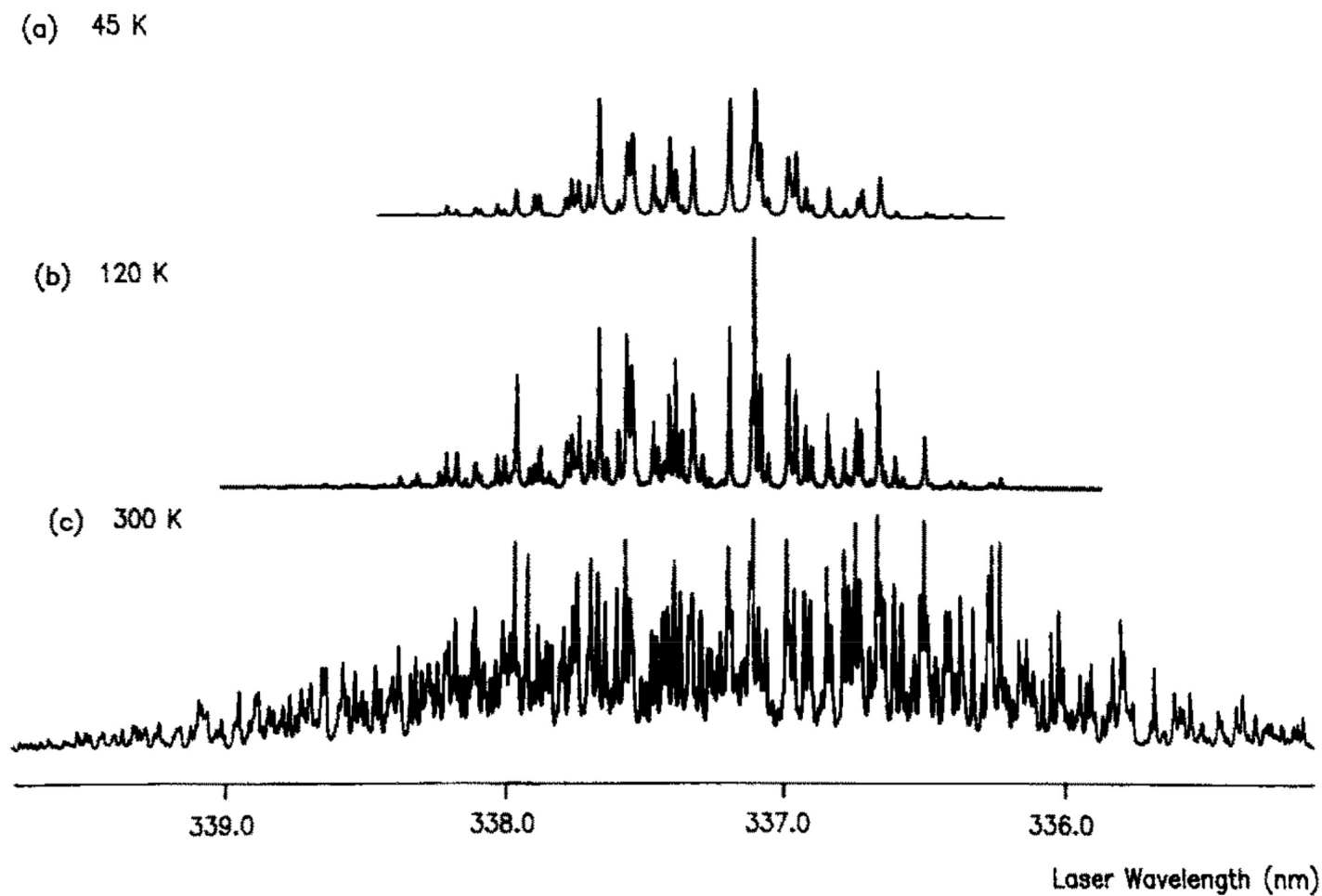




REMPI of ammonia



One vibrational band with individual rovibronic transitions resolved



Anisotropic distributions

Background:

Many processes yield particles with anisotropic angular velocity distributions. These distributions contain information on the underlying process, hence we would like to be able to measure them.

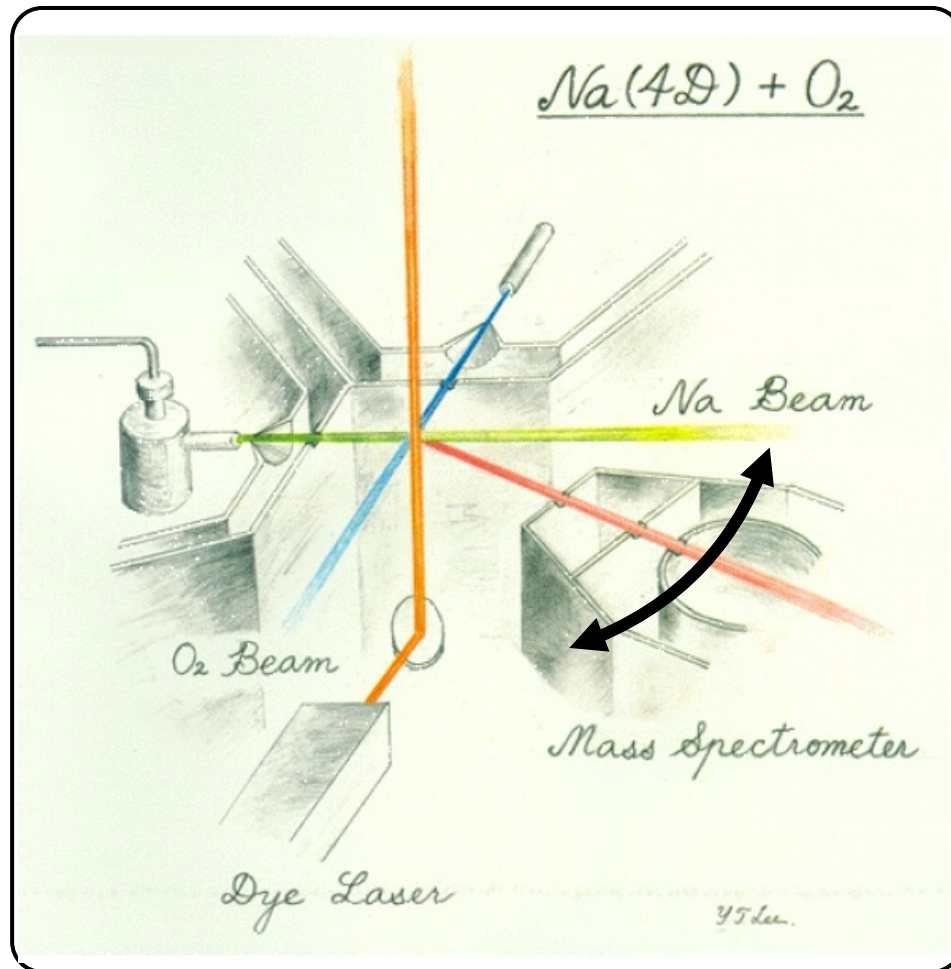
Example

photoionisation produces an electron with an angular momentum of 1 (“p-orbital”) With a quantisation axis given by the laser polarisation the resulting angular distribution will not be isotropic.

(similar effects can take place in chemical reactions)

How can we measure this?

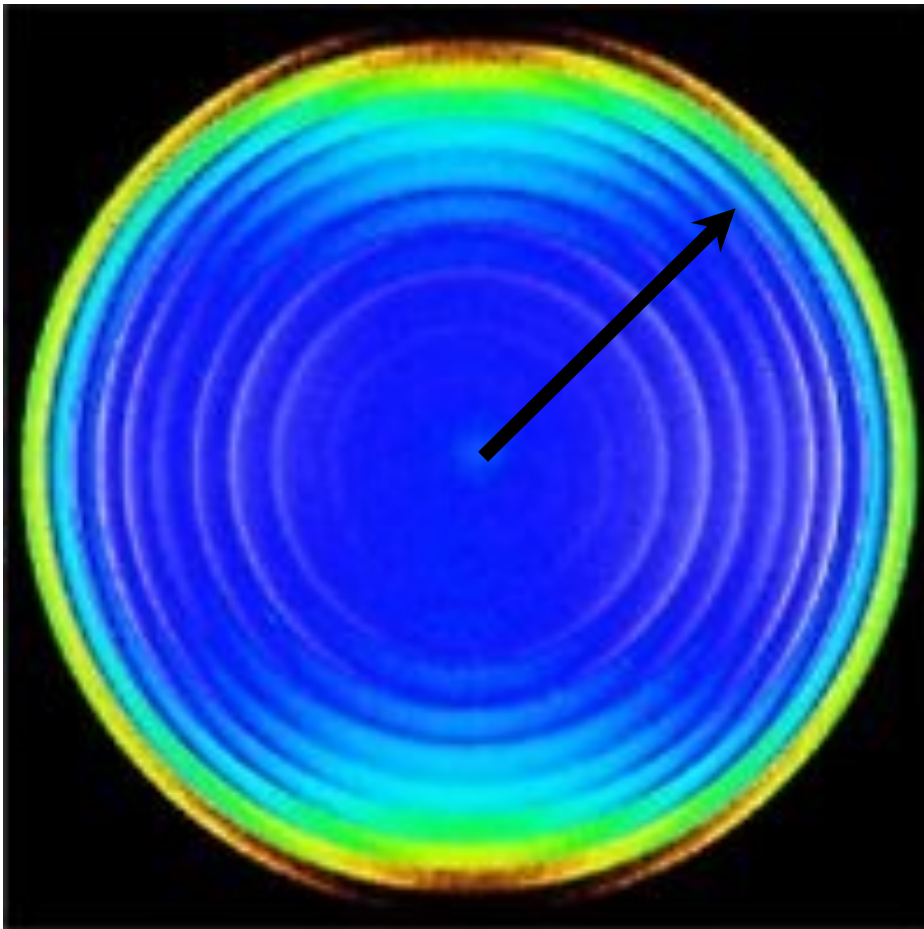
Anisotropic distributions



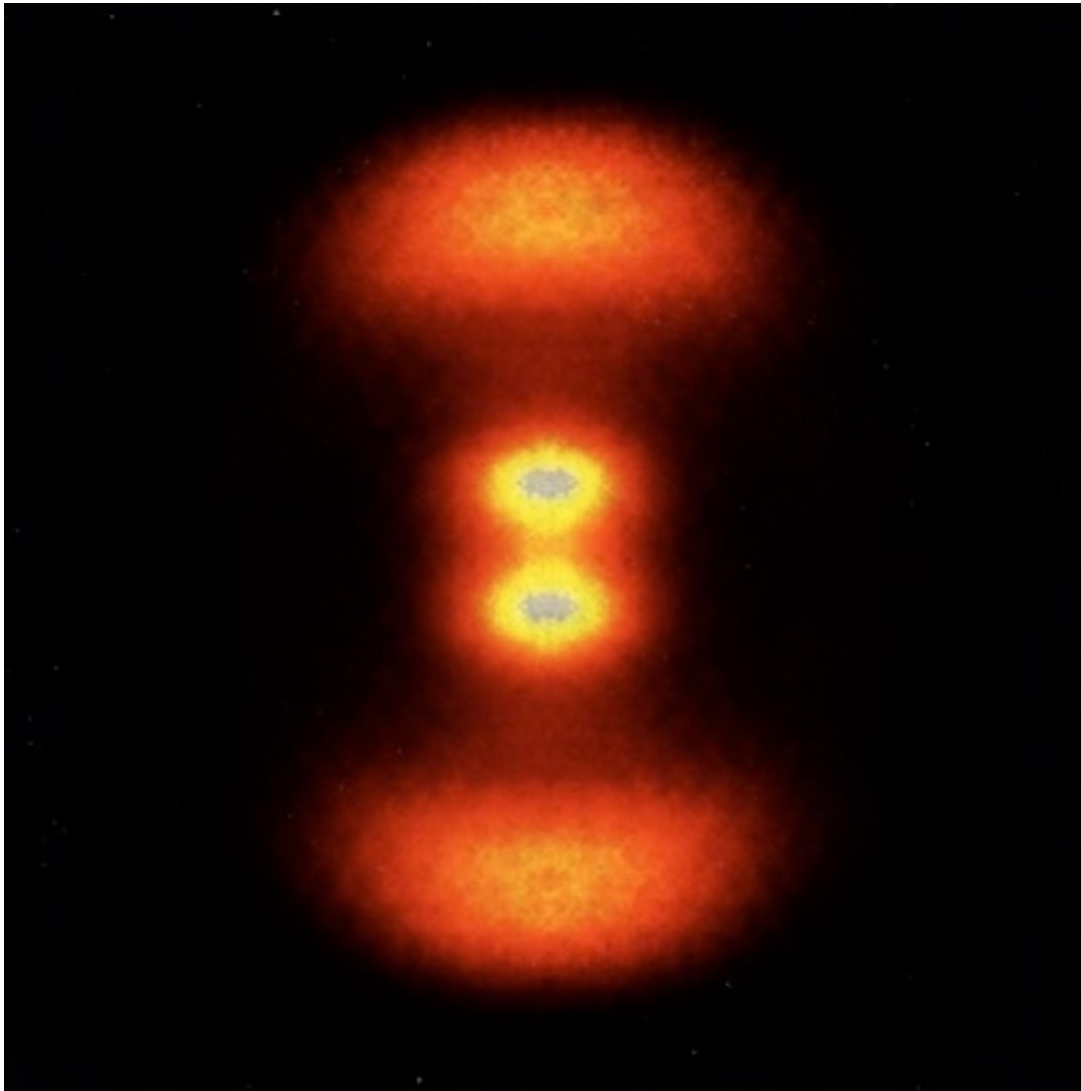
4.3.2022

For example:
Rotatable detector

Imaging



Radial position is
proportional to radial
velocity



REMPI of O atoms
produced in the
photodissociation
of Ozone

Angular distribution:

$$I(\theta) = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta)]$$

β can range from -1 to 2
(since $I(\theta) > 0$), and it tells us
about the symmetry of the
transition

Velocity-map imaging

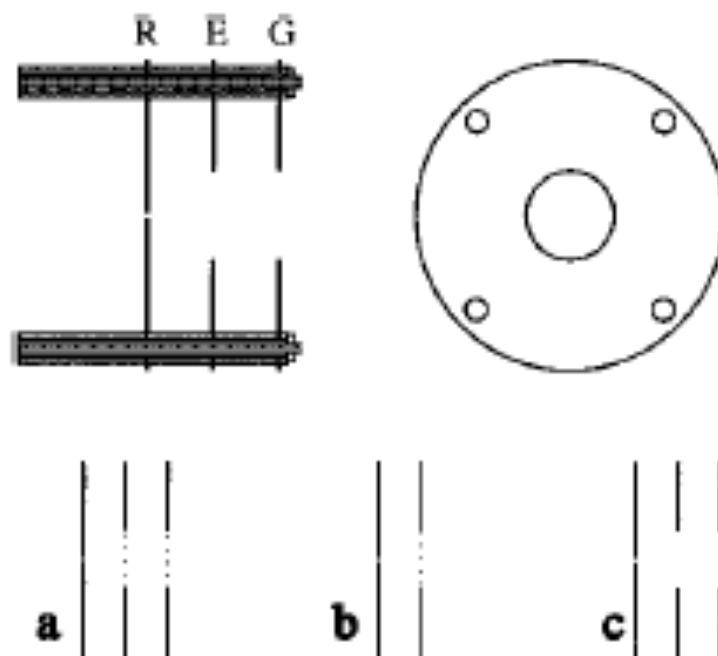
**Velocity map imaging of ions and electrons using electrostatic lenses:
Application in photoelectron and photofragment ion imaging
of molecular oxygen**

André T. J. B. Eppink^{a)} and David H. Parker

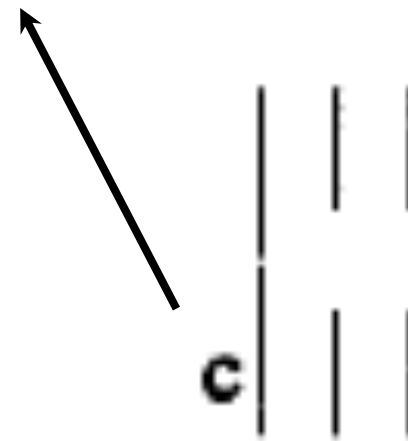
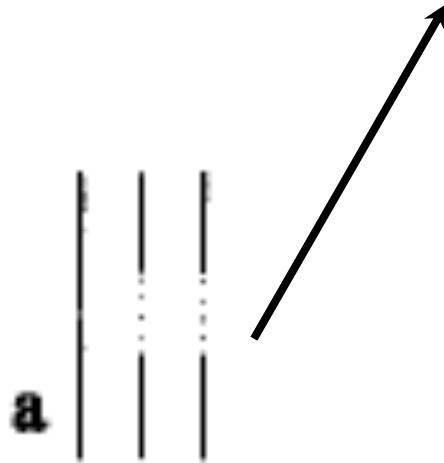
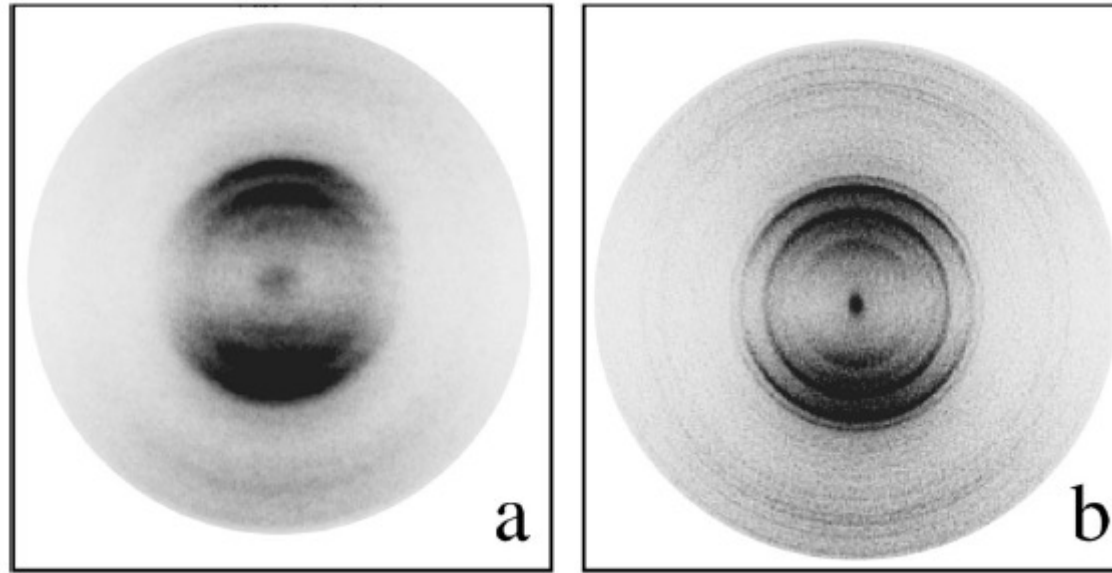
*Department of Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen,
The Netherlands*

(Received 12 March 1997; accepted for publication 30 June 1997)

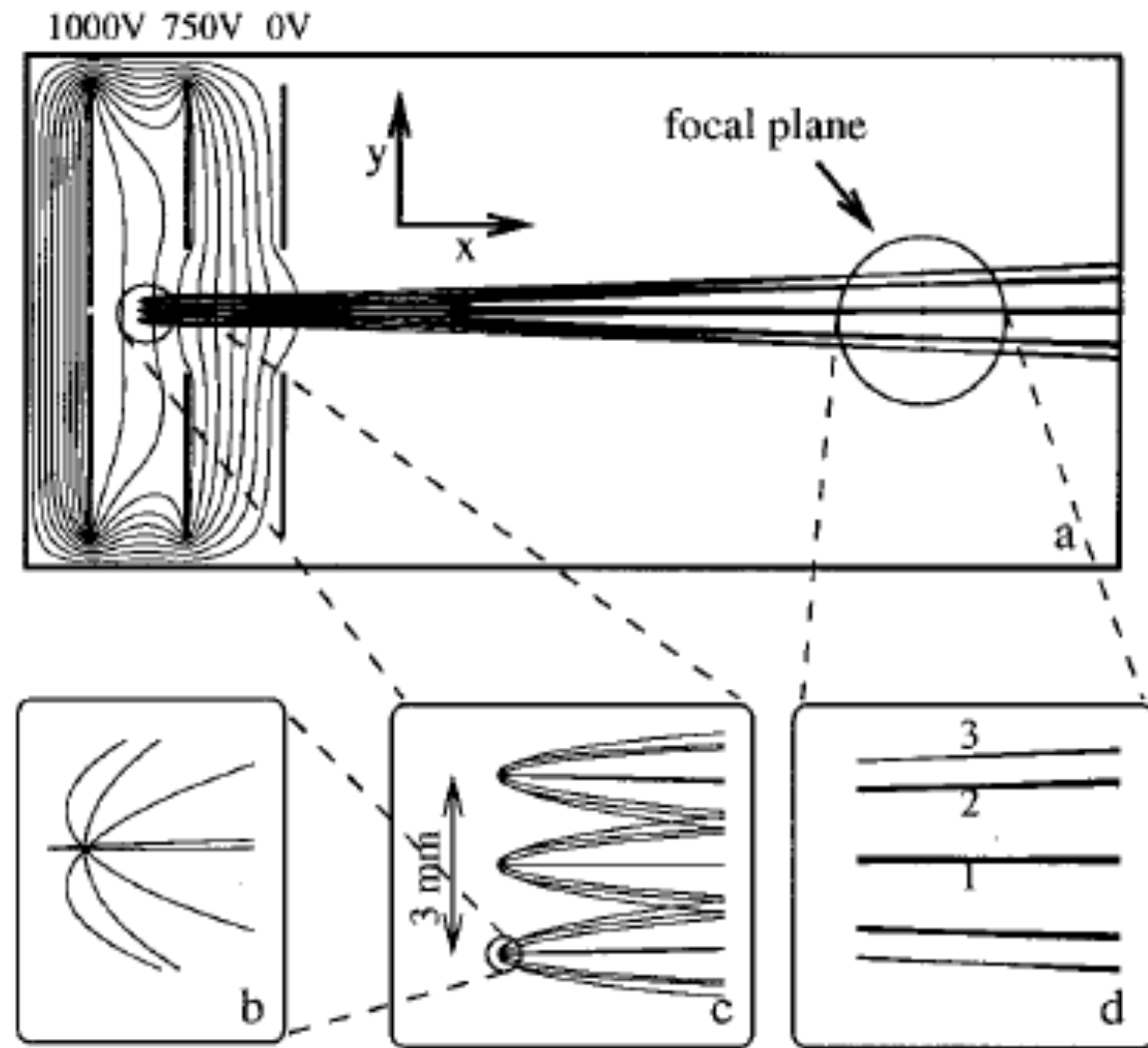
Rev. Sci. Instrum. 68 (9), September 1997

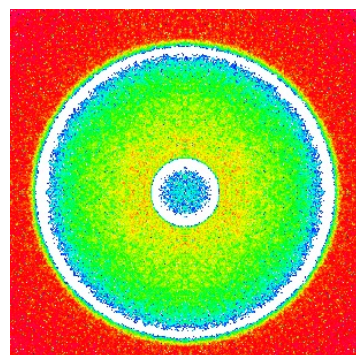
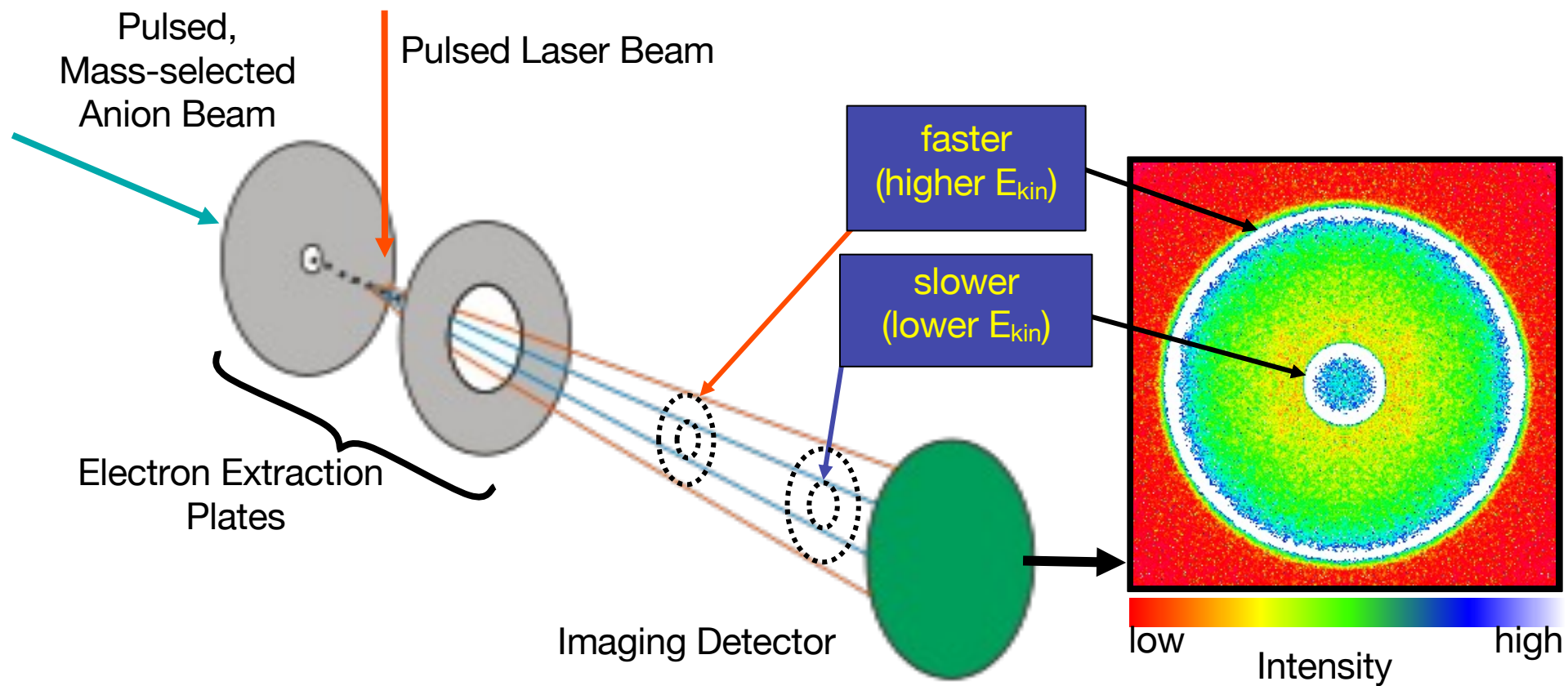


Velocity-map imaging



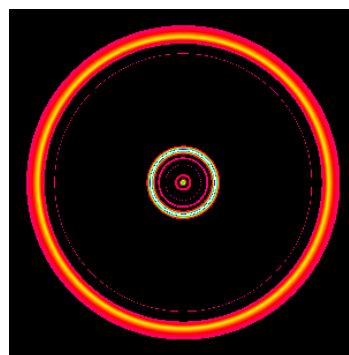
Velocity-map imaging





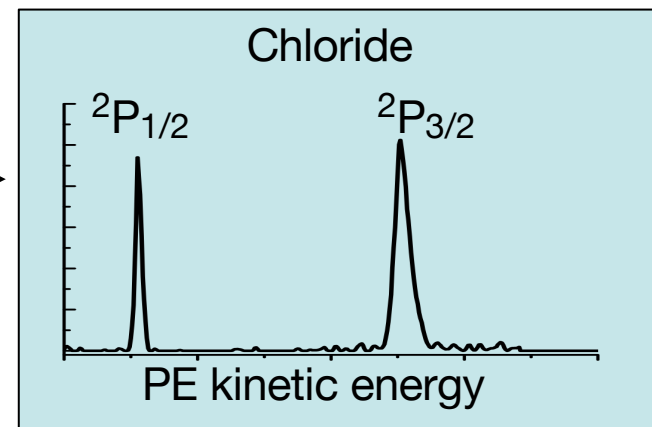
Raw image

Inverse
transform



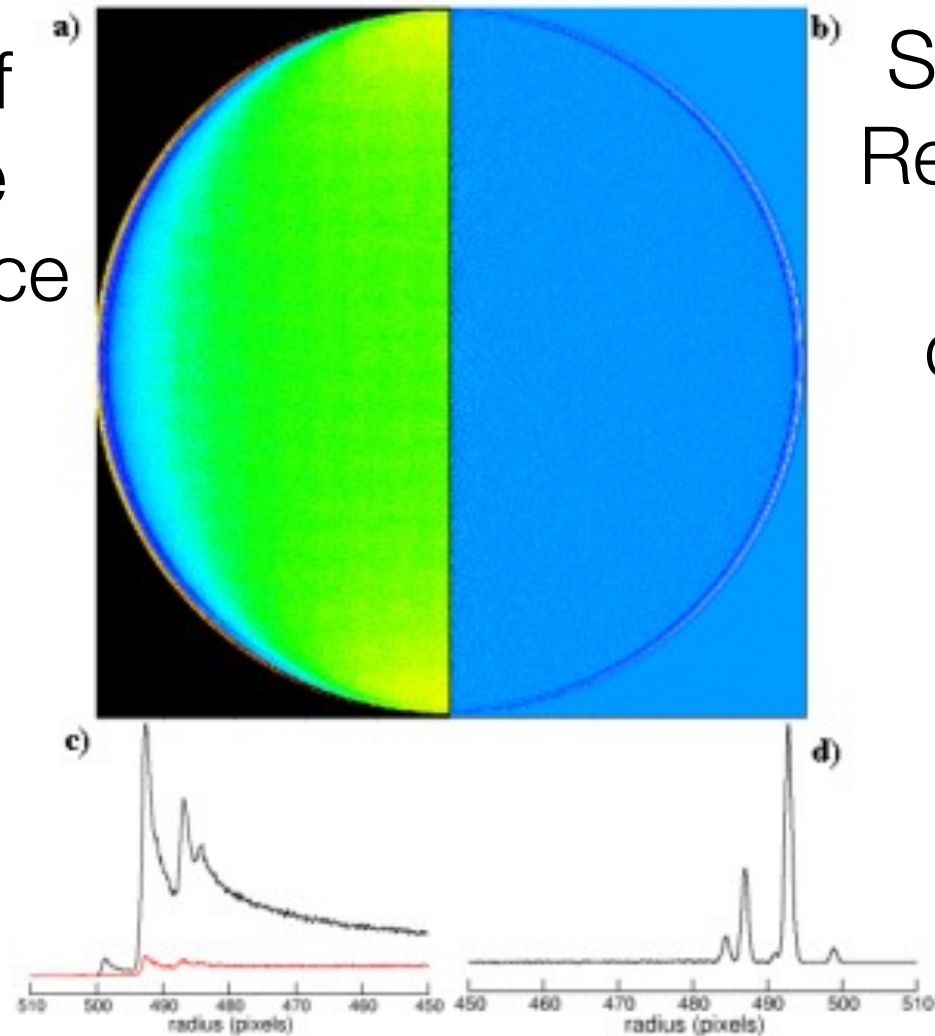
Slice through
original distribution

Angular
integration



Photoelectron Spectrum

Projection of
a 3D sphere
on a 2D surface

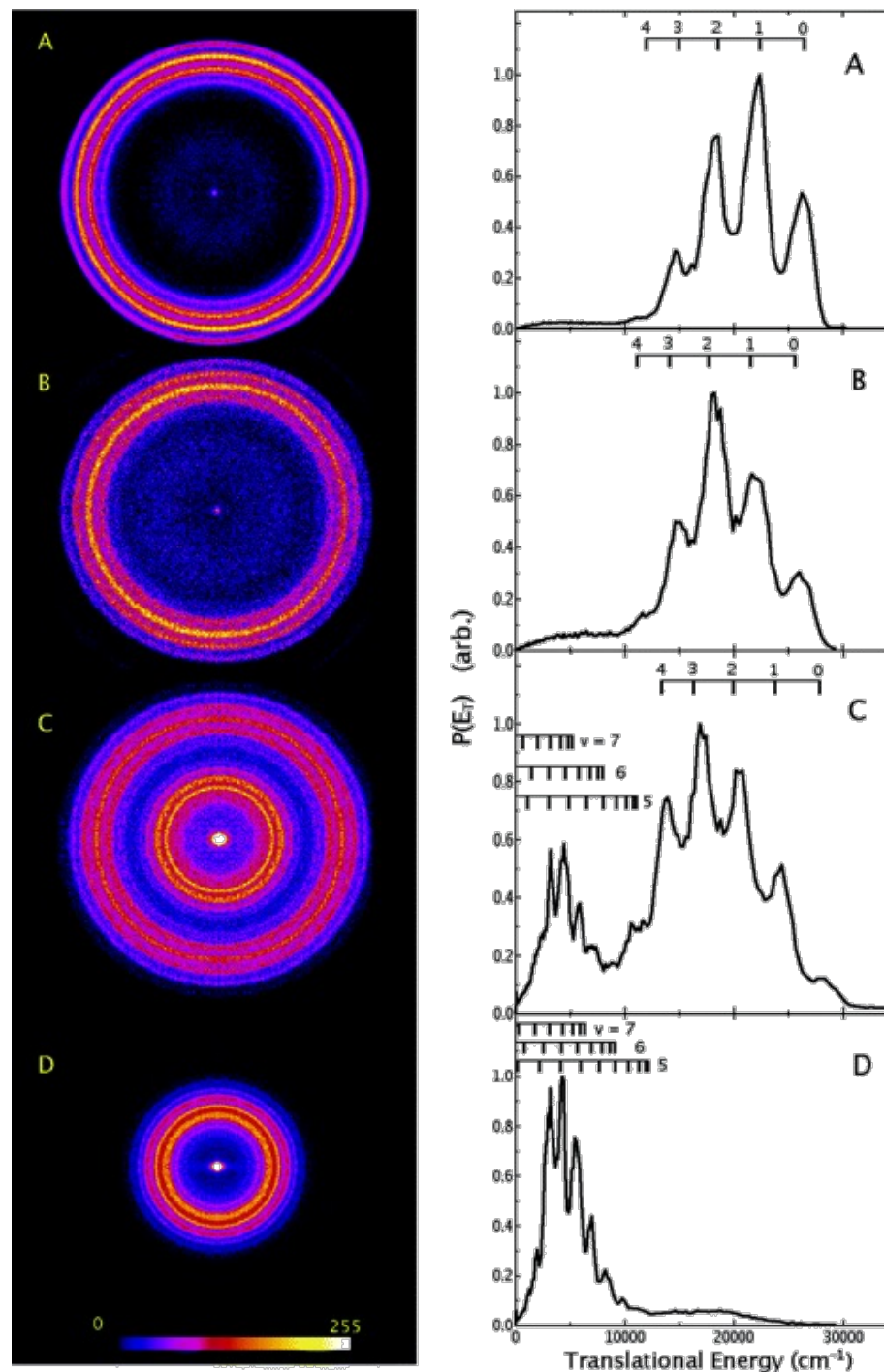


Slice through
Reconstructed
original
distribution

Example application

Sliced images of CO for dissociation of H_2CO on different rovibrational transitions.

Right: Translational energy distributions obtained from the corresponding images at left. Markers indicate correlated H_2 vibrational levels for $j_{\text{H}_2} = 5$ (for $v = 0-4$) or rovibrational levels (for $v = 5-7$).



Experimental techniques

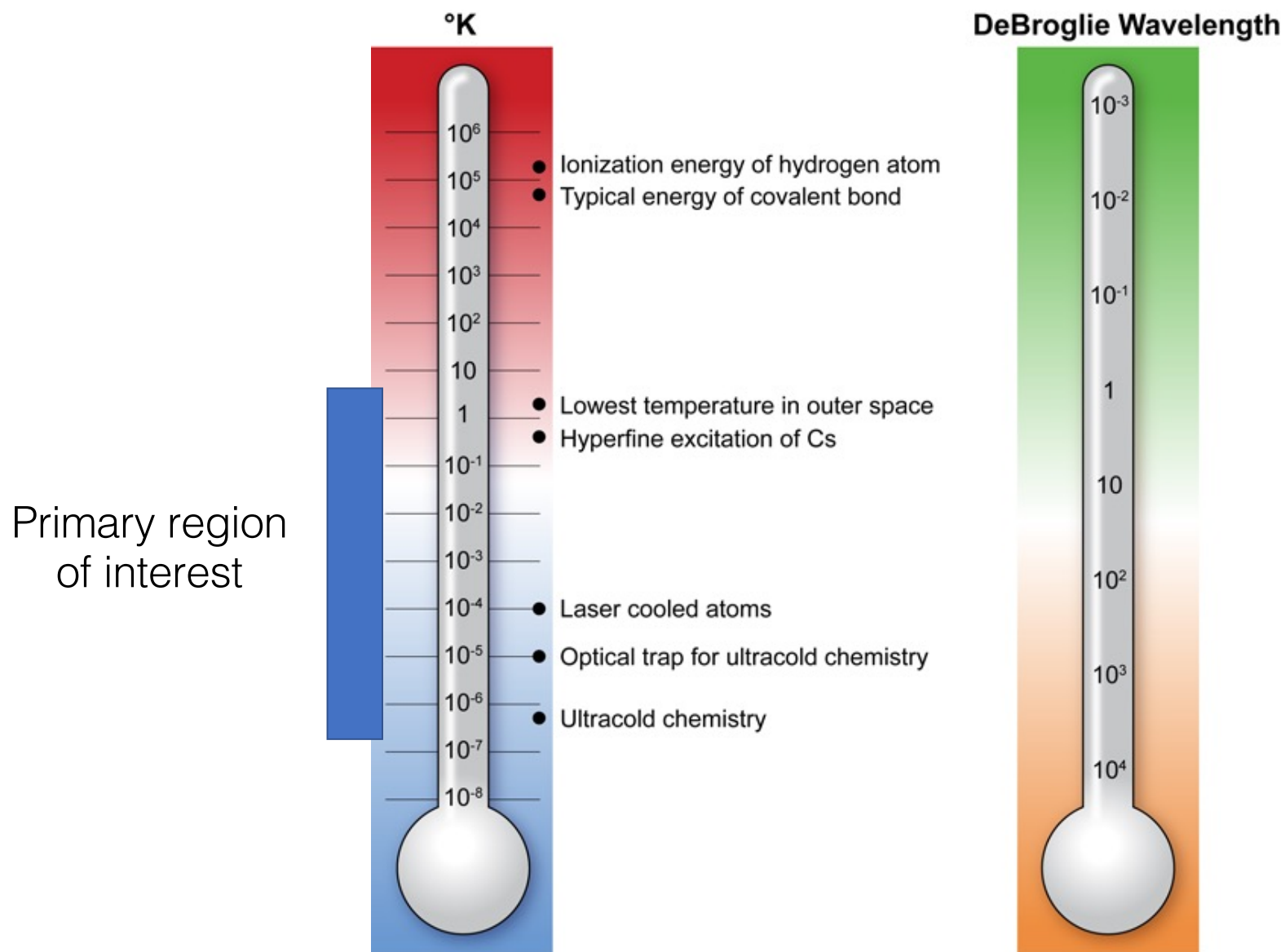
1. Reaction Dynamics

Experimental Aspects of (Cold and Controlled) Reaction Dynamics

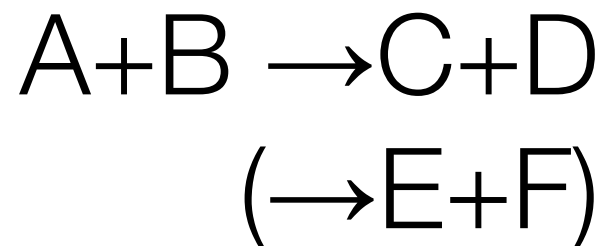
What are we talking about?

? What does cold mean
What does control mean ?
What is interesting
How are we tackling this

Cold Chemistry

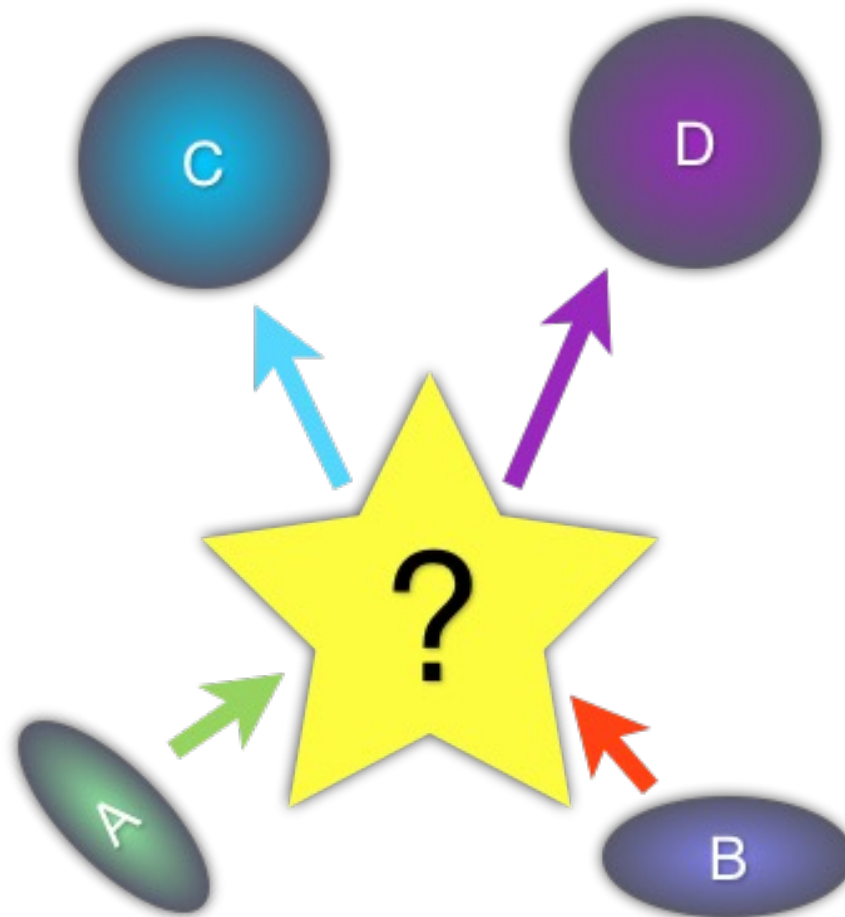


Control?



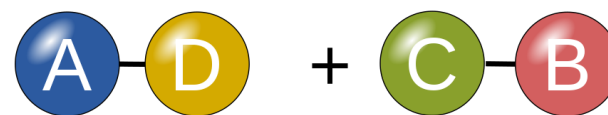
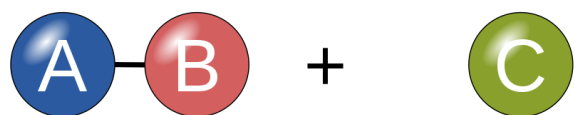
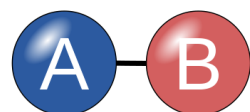
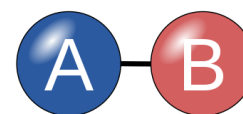
Questions:

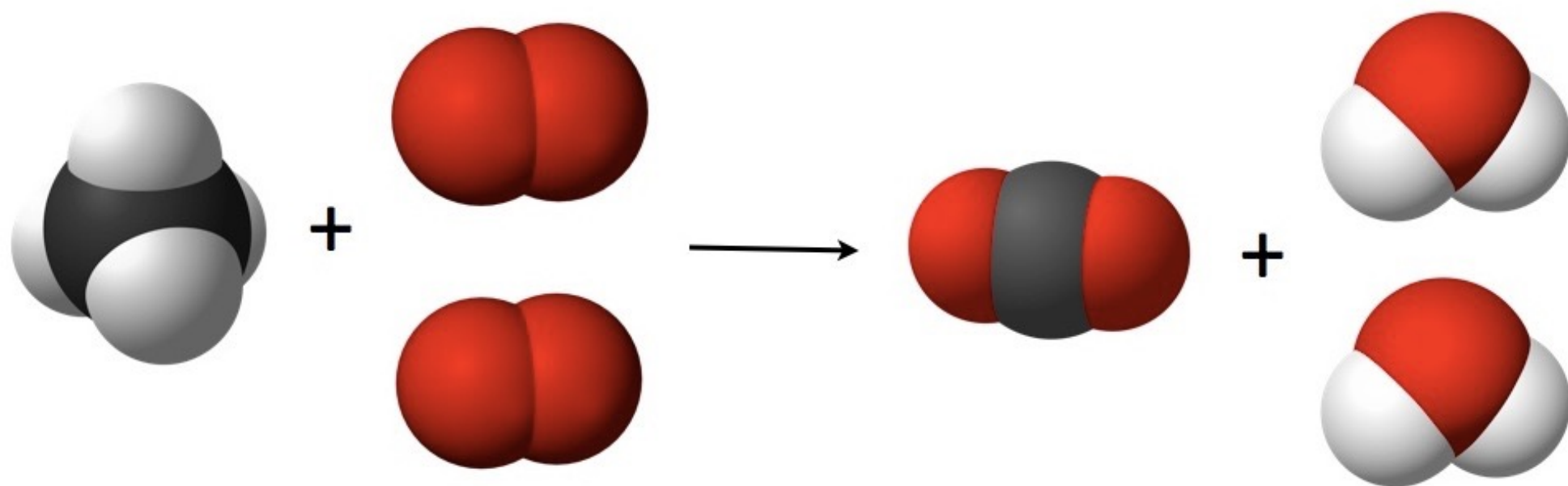
- Alignment/Orientation?
- Internal Energy?
- Kinetic Energy?
- Branching ratios?



Cold and Controlled?

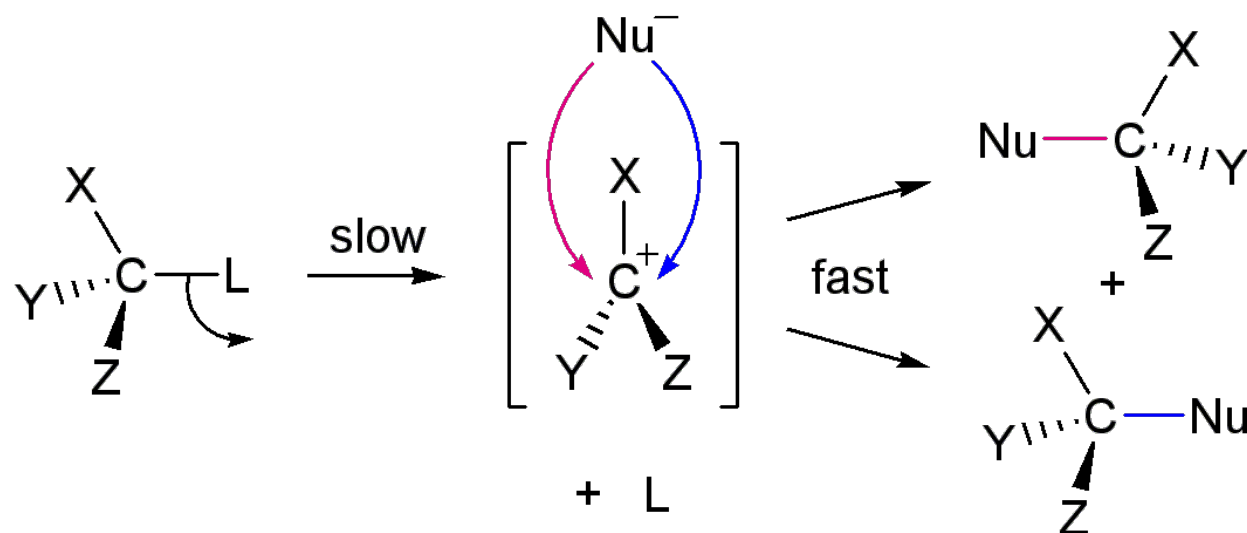
- Wave character of atoms/molecules?
- Long time scales
- Few partial waves
- Selected (low) amounts of internal and translational energy
- Quantum mechanical effects in Chemistry
- Effects of electric/magnetic fields



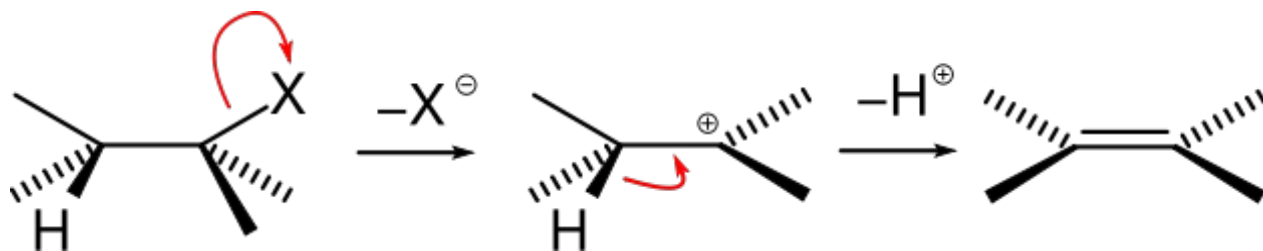


Nucleophilic substitution, Elim

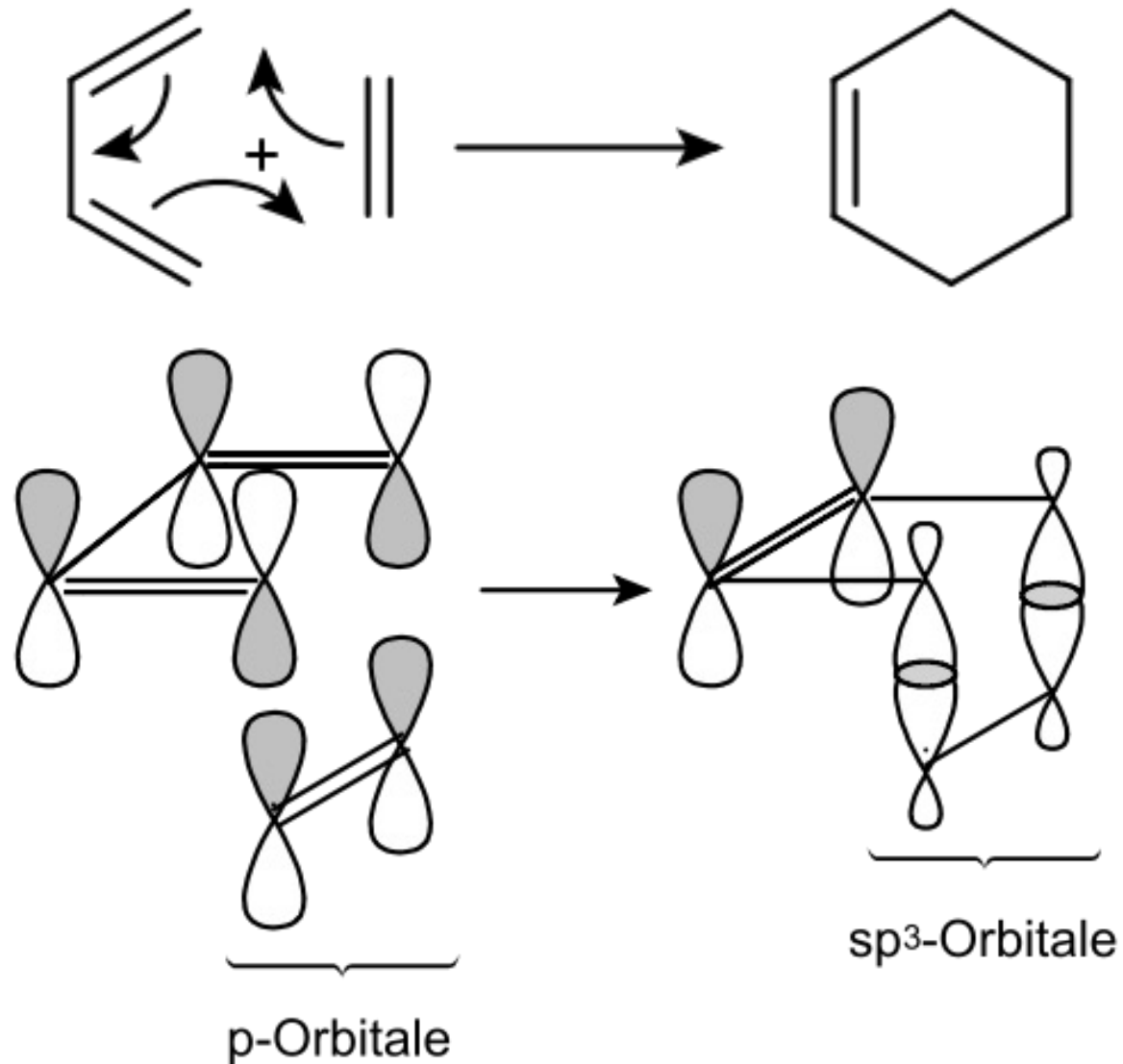
SN₁



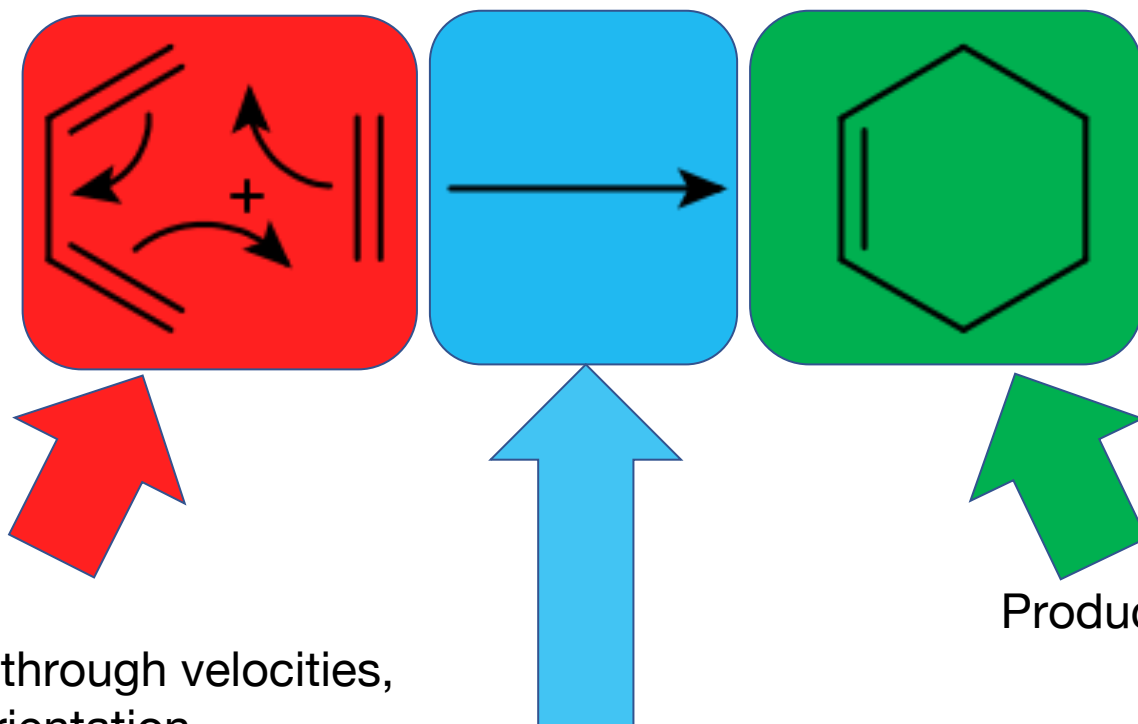
E₁



Diels-Alder Cycloaddition



What does “Control” mean?



Reactants

Control possible through velocities,
internal states, orientation, ...

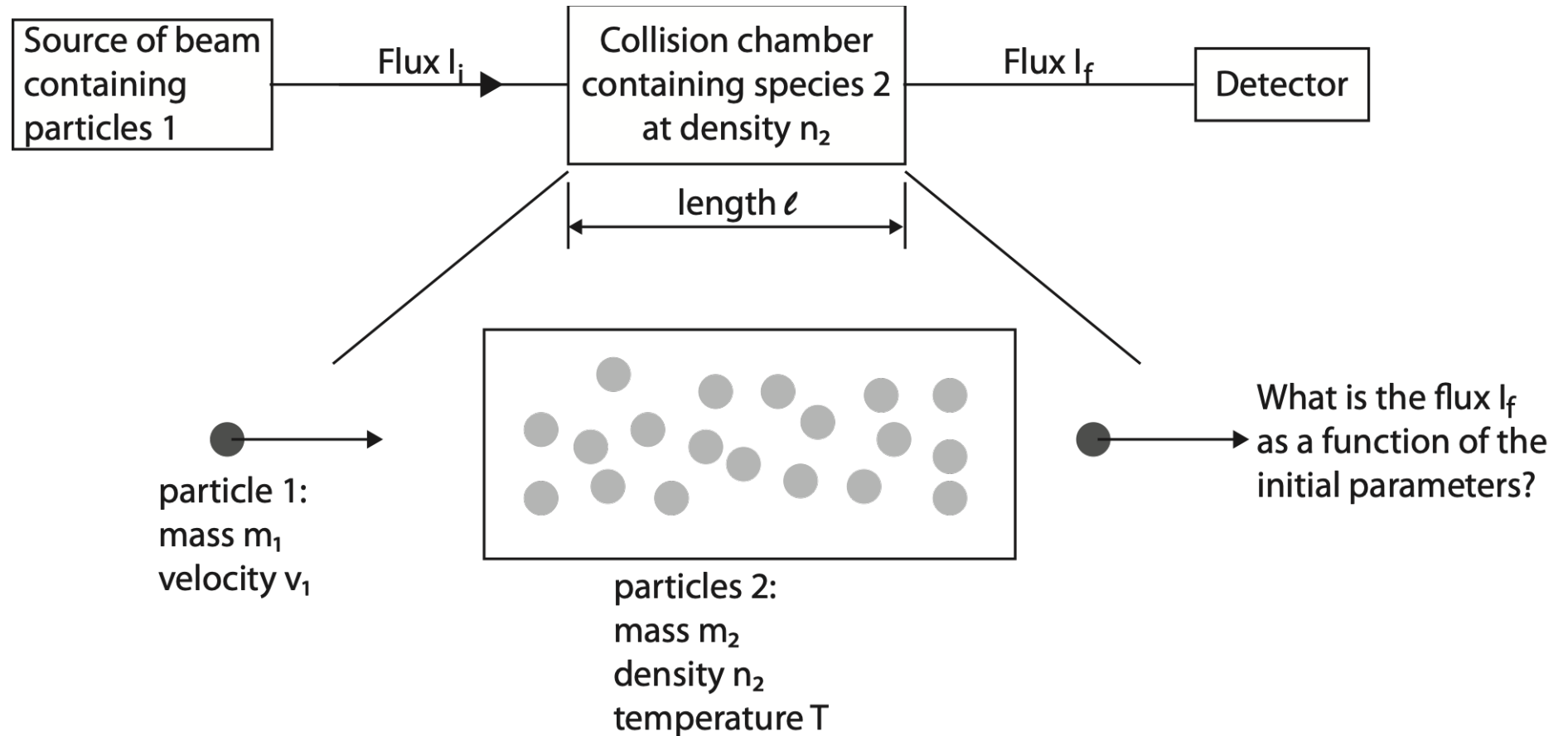
Products...

Chemistry

Given by intermolecular PES

Control?

Reaction Dynamics



Reaction dynamics vs Kinetics

Collisions between single molecules
Single-collision conditions

Reaction Cross sections
Control at the molecular level

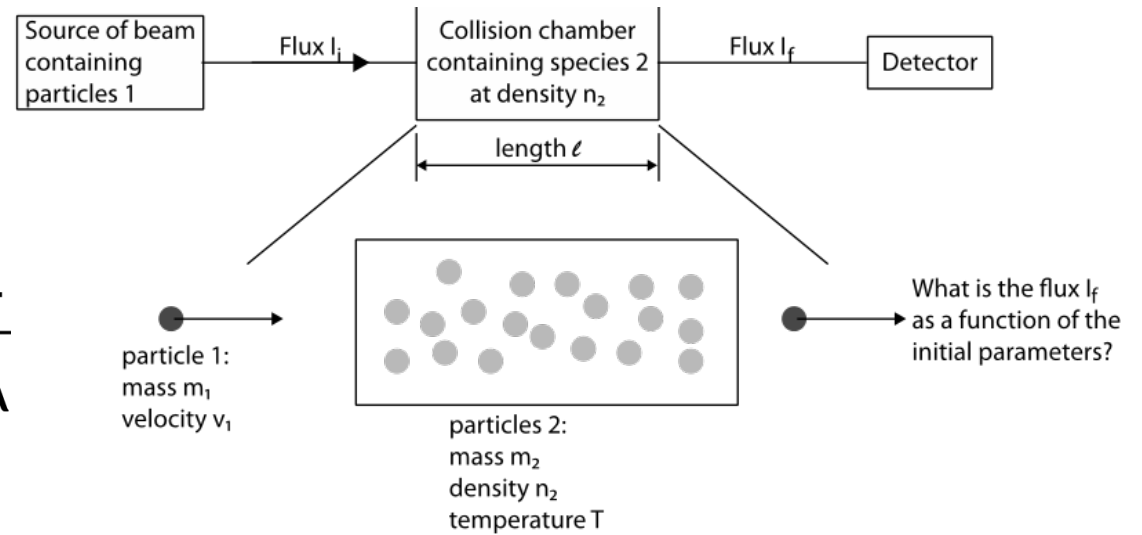
Collision energy
Rovibronic states

Bulk reactivity
Many collisions required

Rate Coefficients
Control is difficult...

Temperature
Population distributions

$$-\frac{\frac{\Delta I}{I}}{\frac{dI/dx}{I}} = -\frac{\frac{\Delta x}{\lambda}}{\frac{d \ln I}{dx}} = \frac{1}{\lambda}$$



$$\begin{aligned} \langle \text{free path} \rangle &= \int_0^\infty x q(x) dx = \int_0^\infty x p(x) dx / \lambda \\ &= \int_0^\infty x \exp(-x/\lambda) (dx/\lambda) = \lambda, \end{aligned}$$

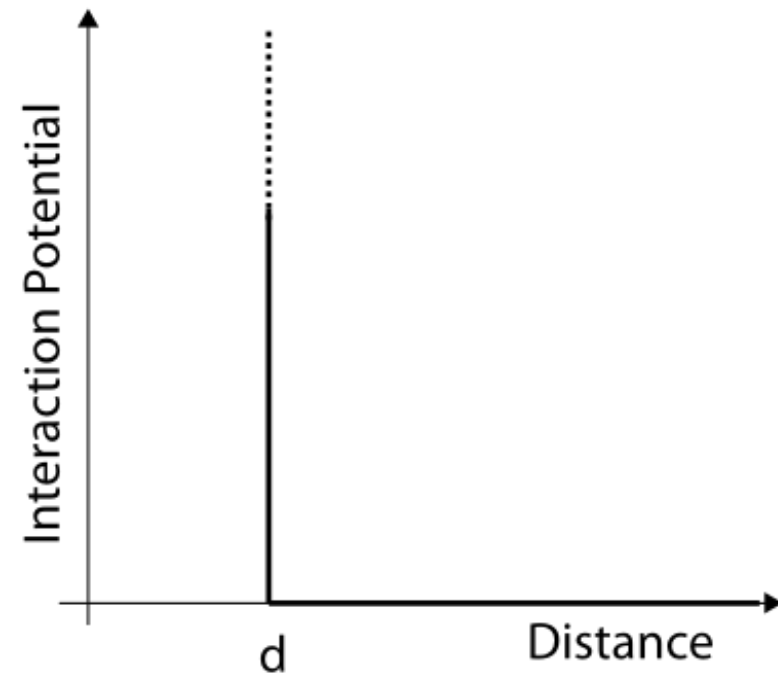
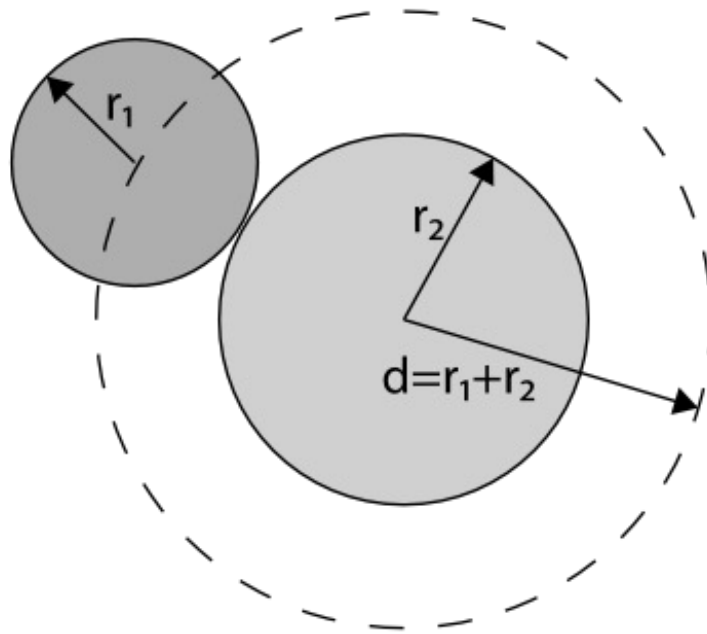
Mean Free Path and Cross Section

$$\lambda \propto \frac{1}{p}$$

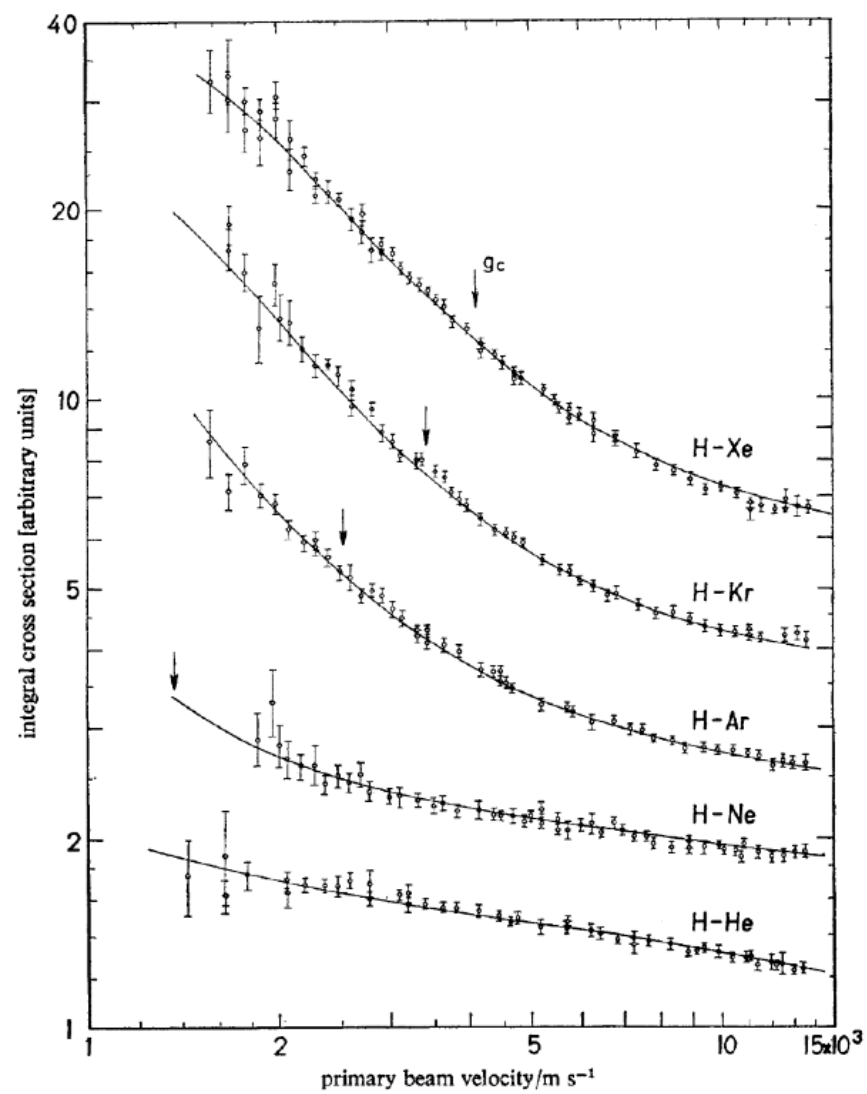
$$\lambda = \frac{1}{\sigma n}$$

$$\sigma = \pi(r_1 + r_2)^2 = \pi d^2$$

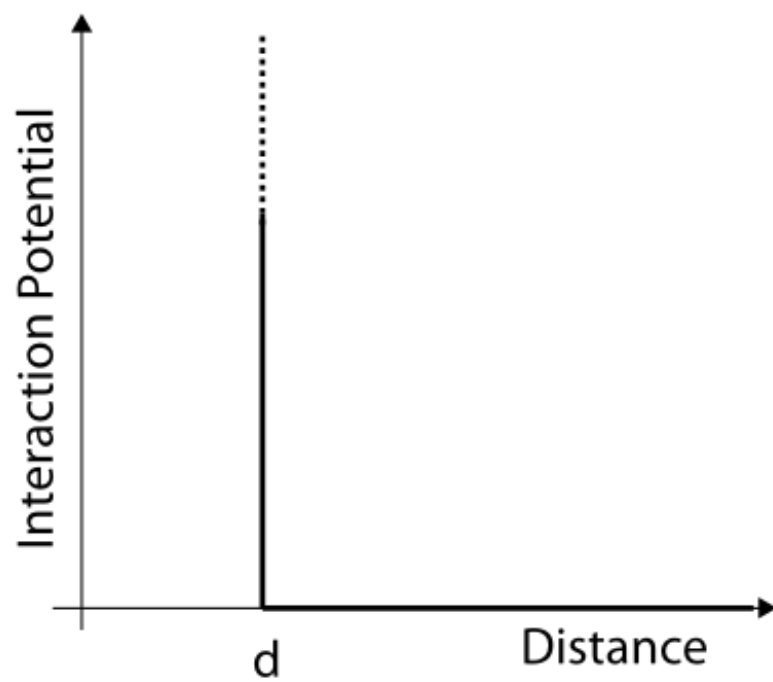
Cross Section; Hard spheres



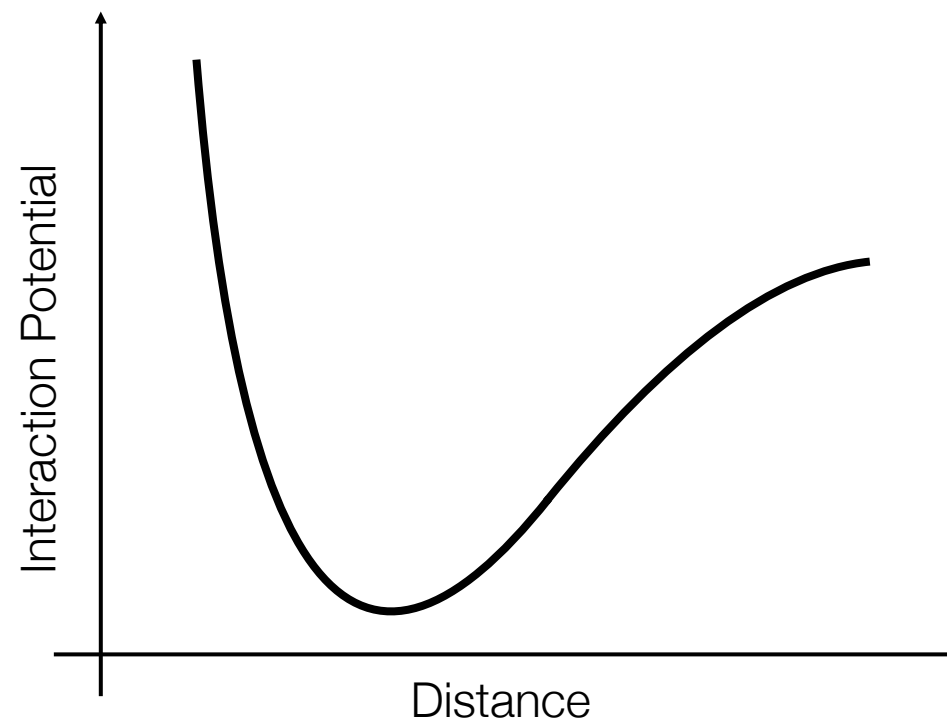
Most real systems...

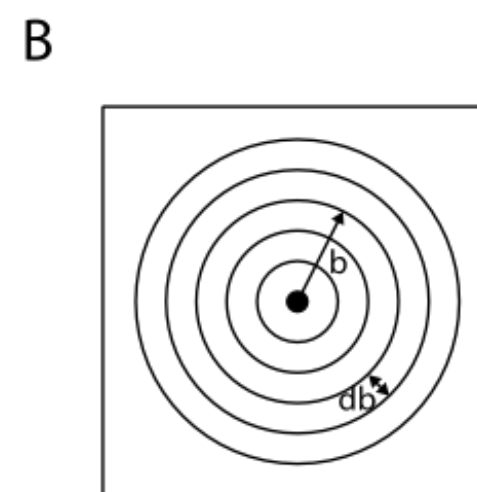
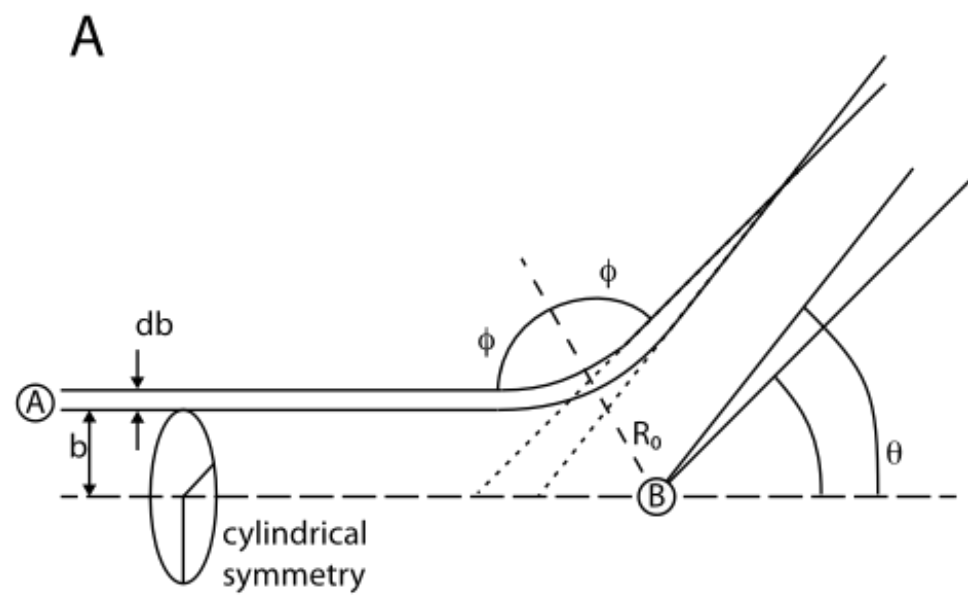


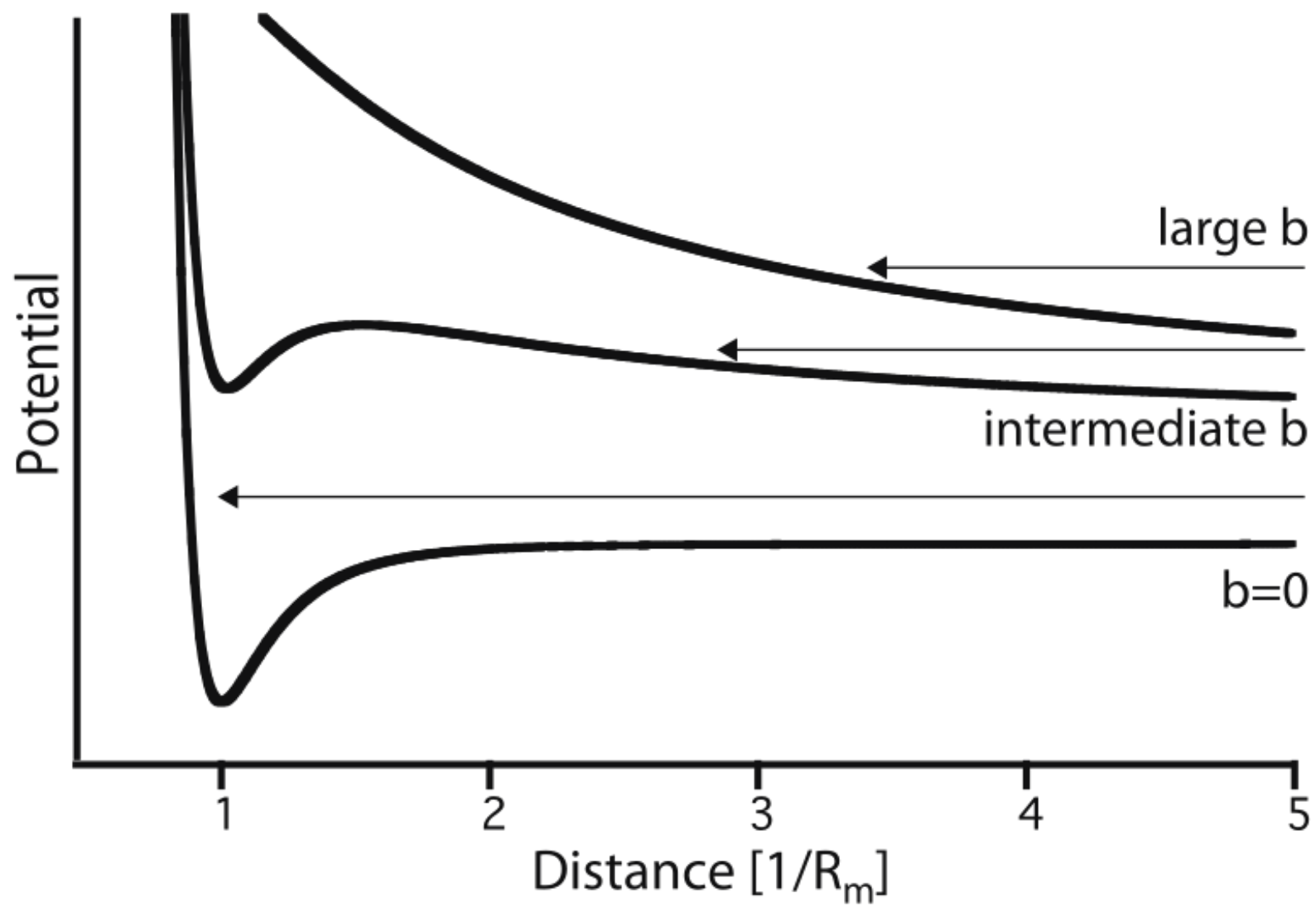
Hard Sphere

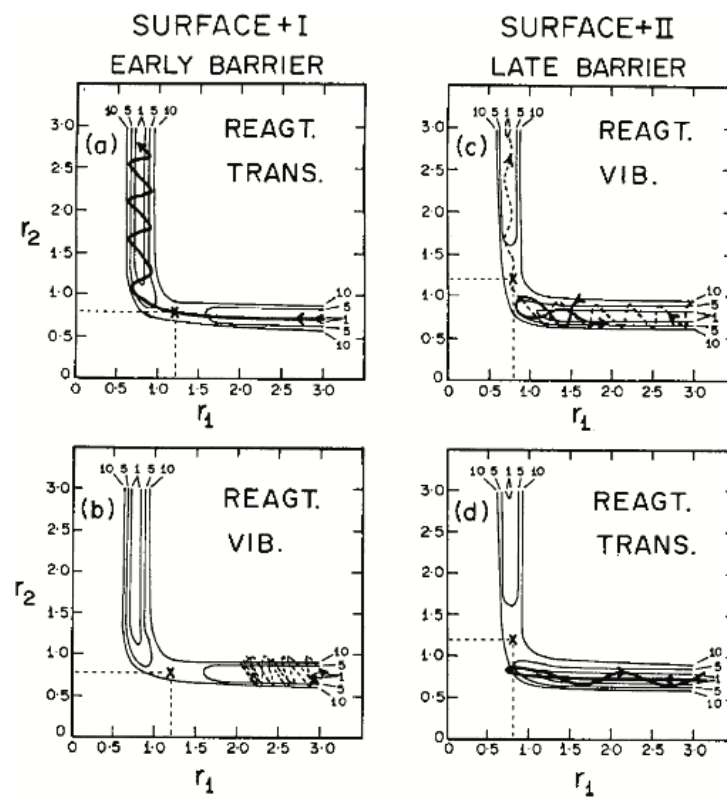


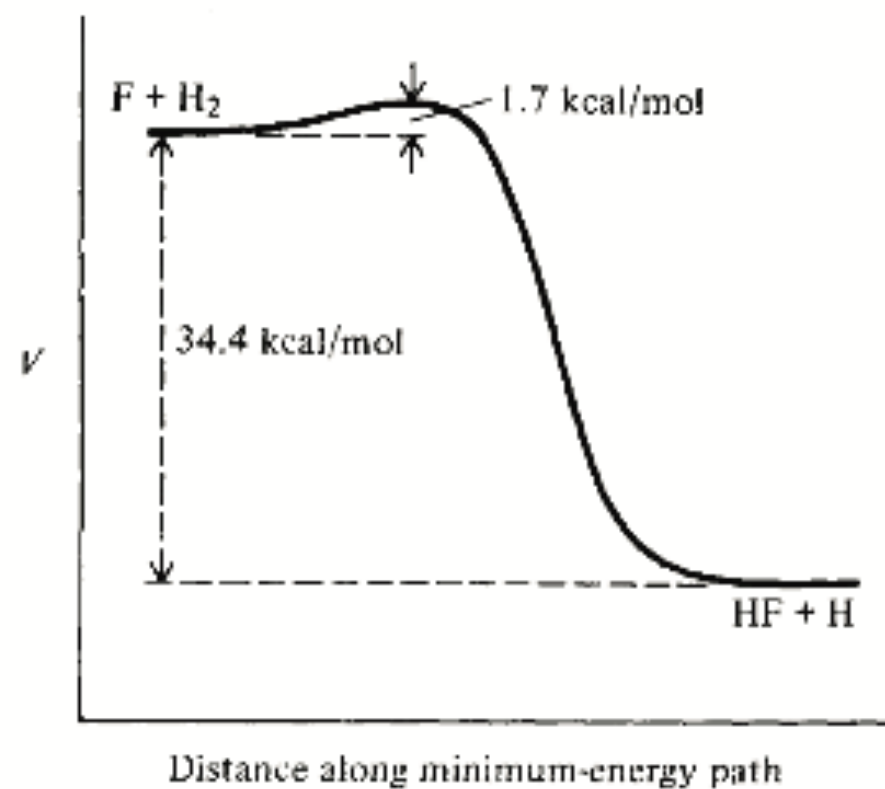
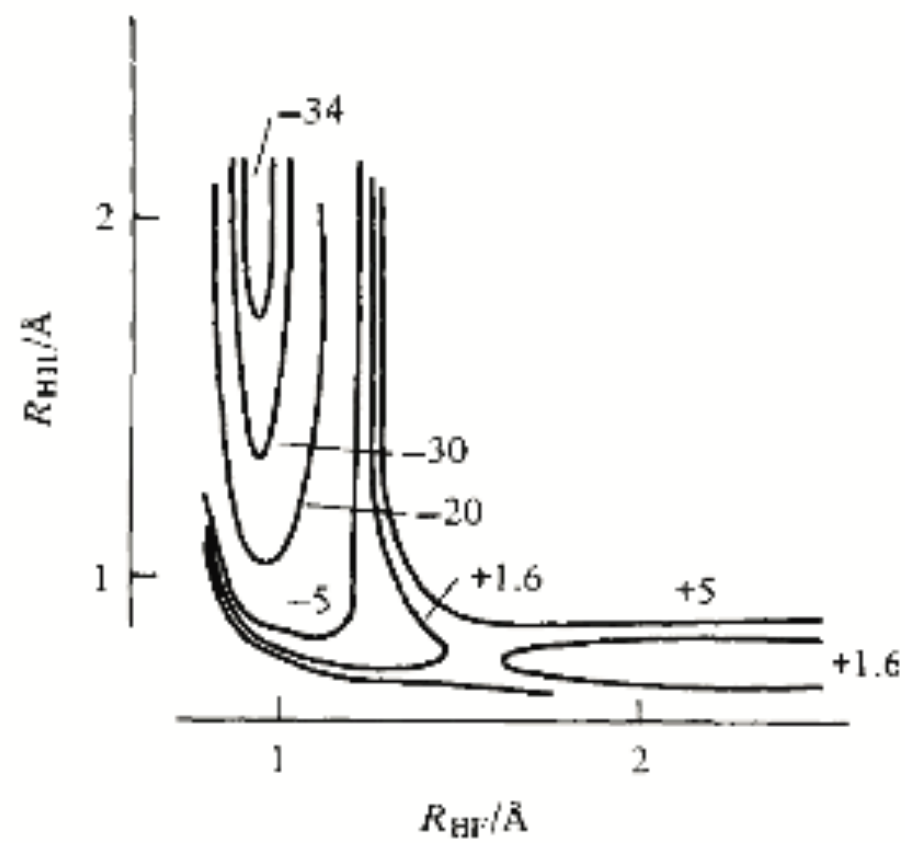
Real Atoms/Molecules

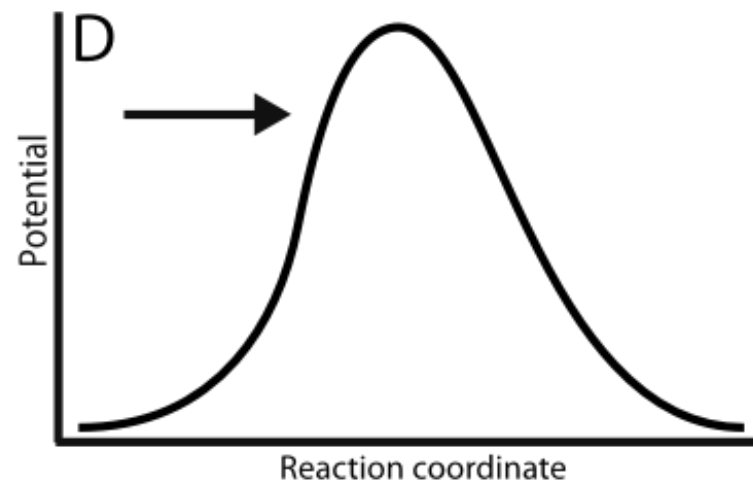
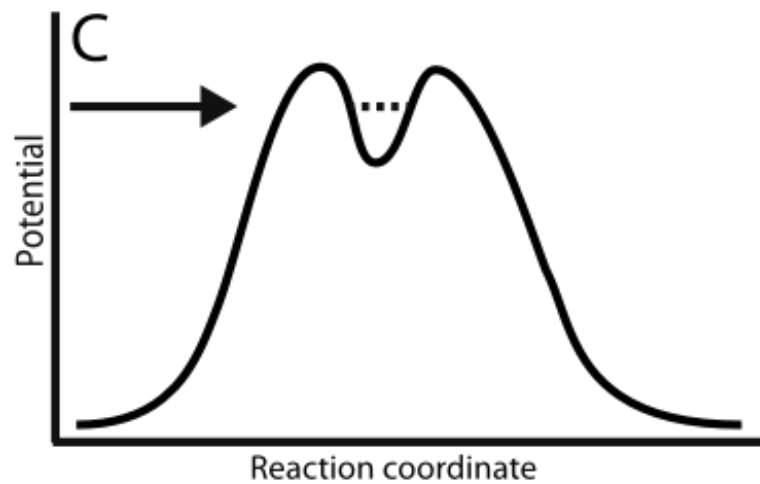
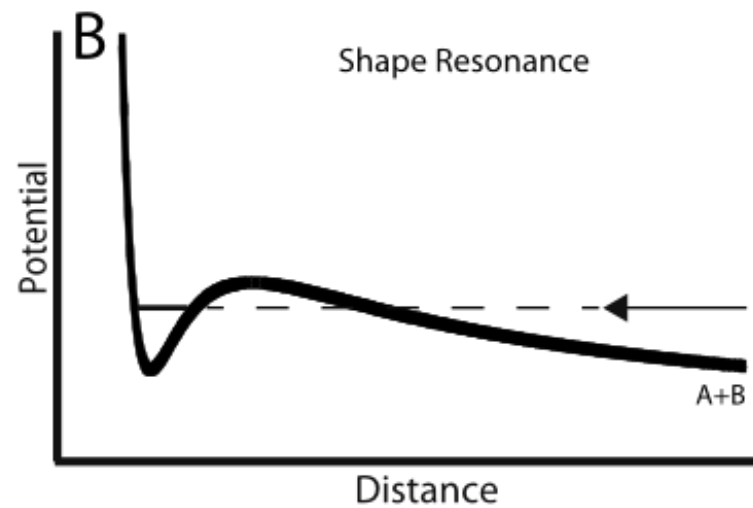
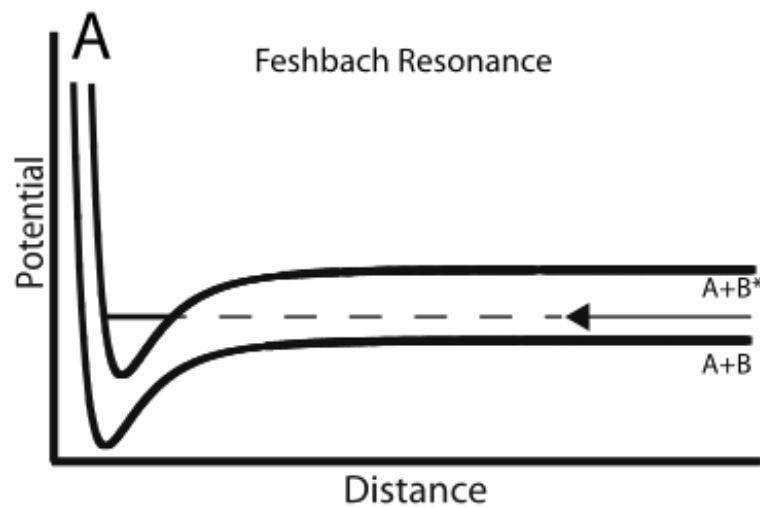




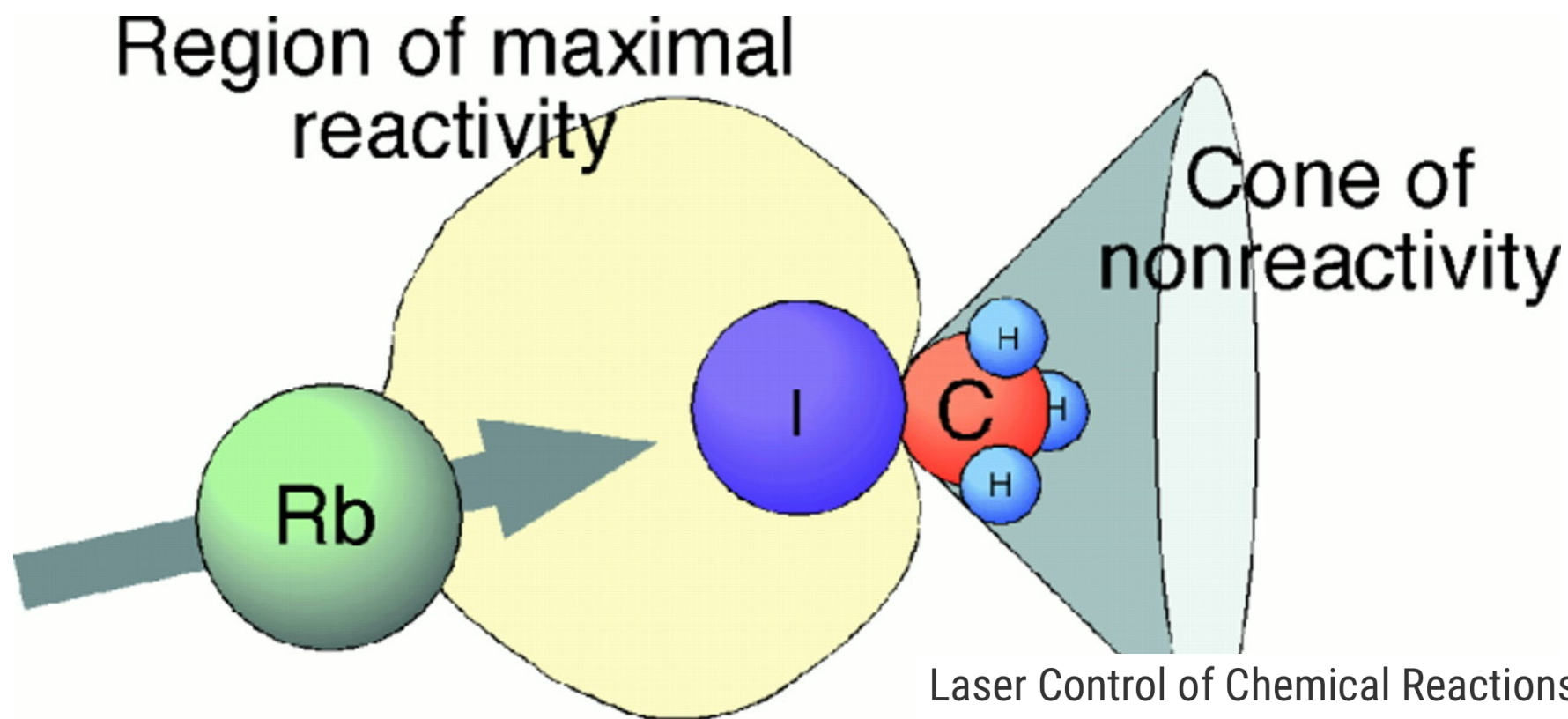








Effects of Orientation: Stereodynamics

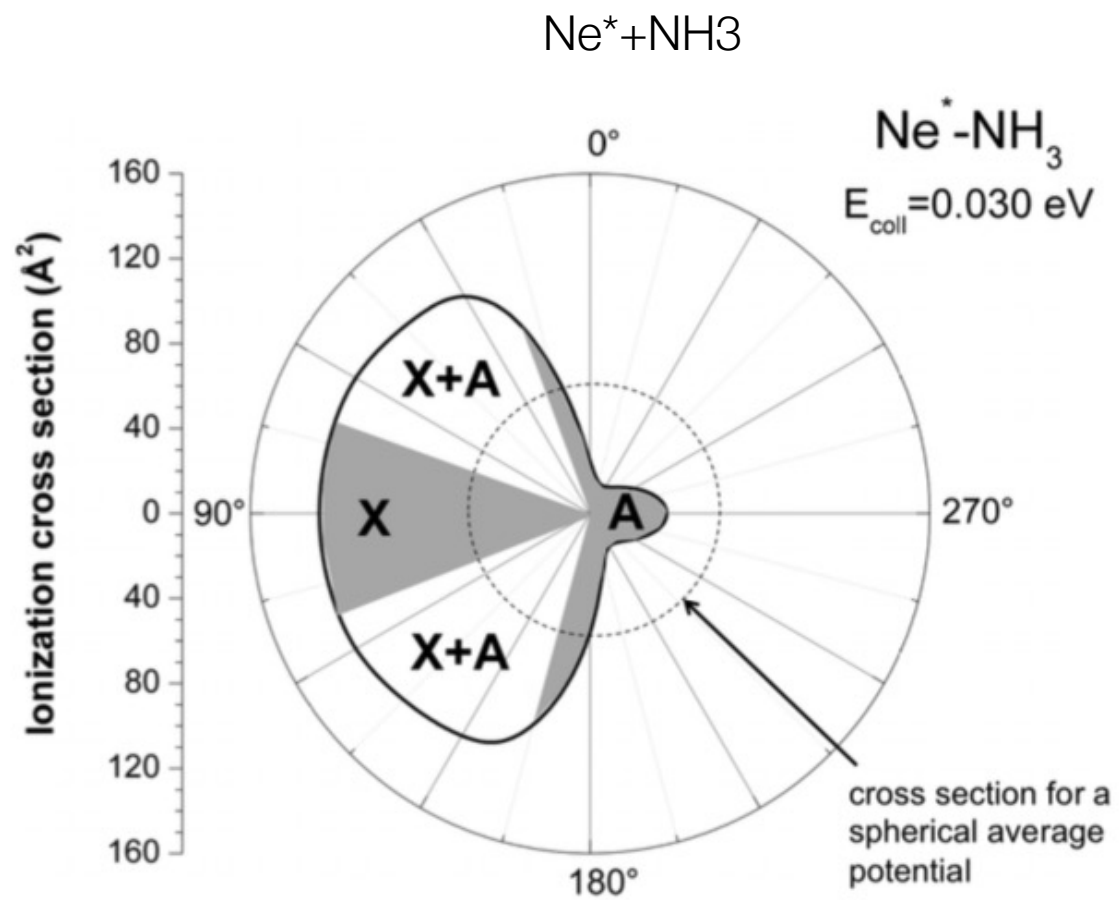


Richard N. Zare

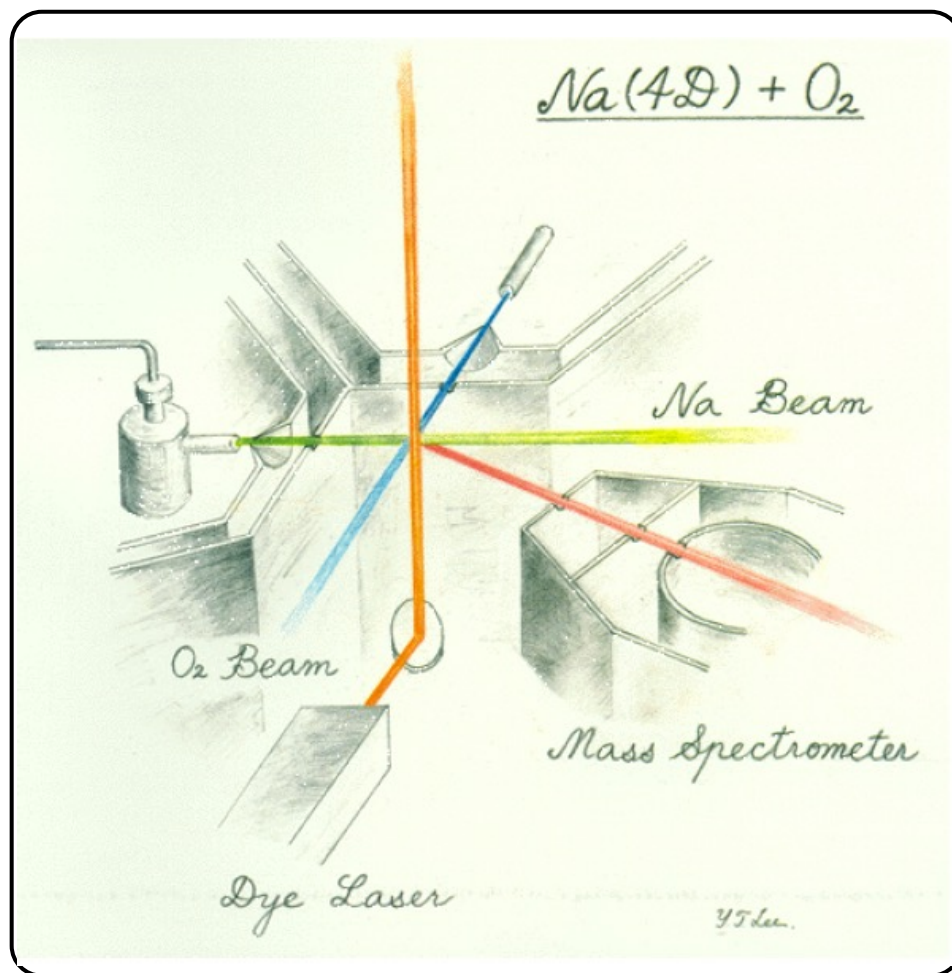
+ See all authors and affiliations

Science 20 Mar 1998:
Vol. 279, Issue 5358, pp. 1875-1879
DOI: 10.1126/science.279.5358.1875

Effects of Orientation: Stereodynamics



Crossed Molecular Beams



Chemistry Nobel Prize 1986:
Herschbach, Lee, Polanyi

Experiments: Criteria

Sensitivity

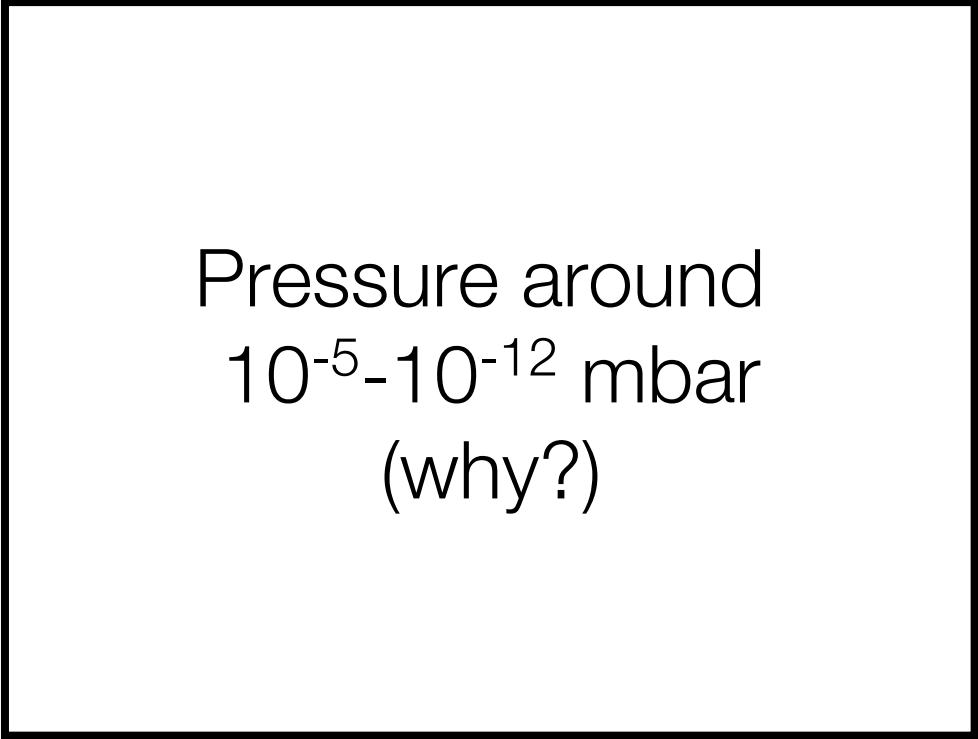
Selectivity

Energy resolution

Time resolution

practical considerations

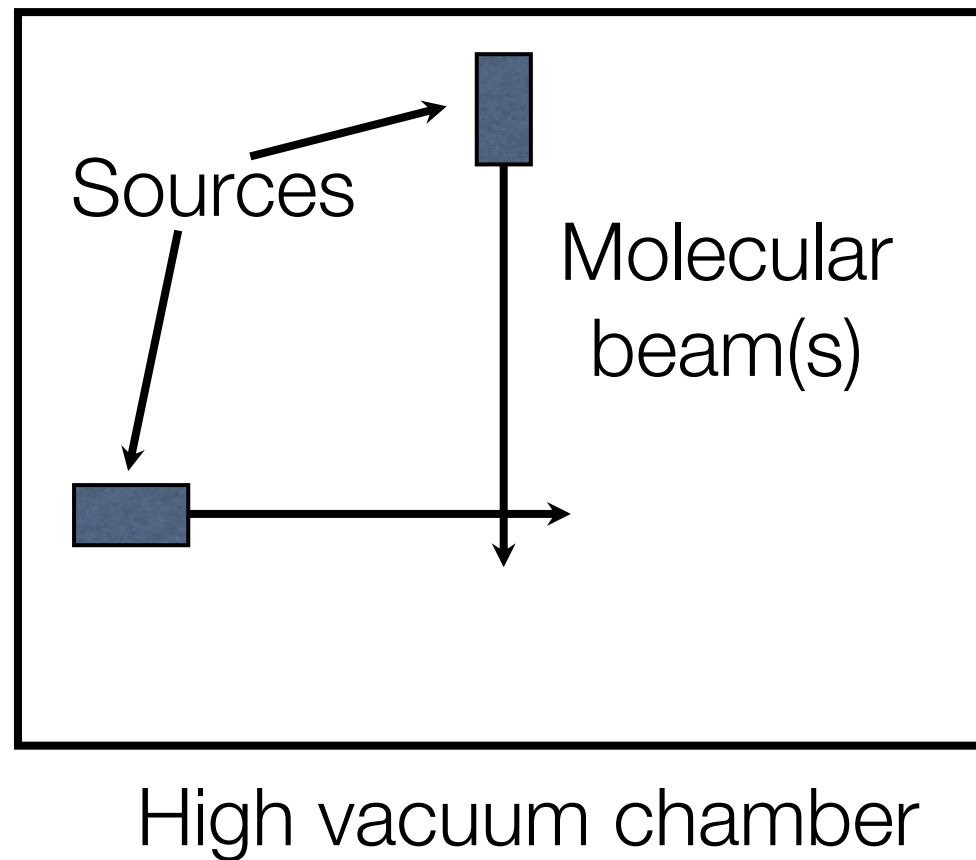
The generic setup



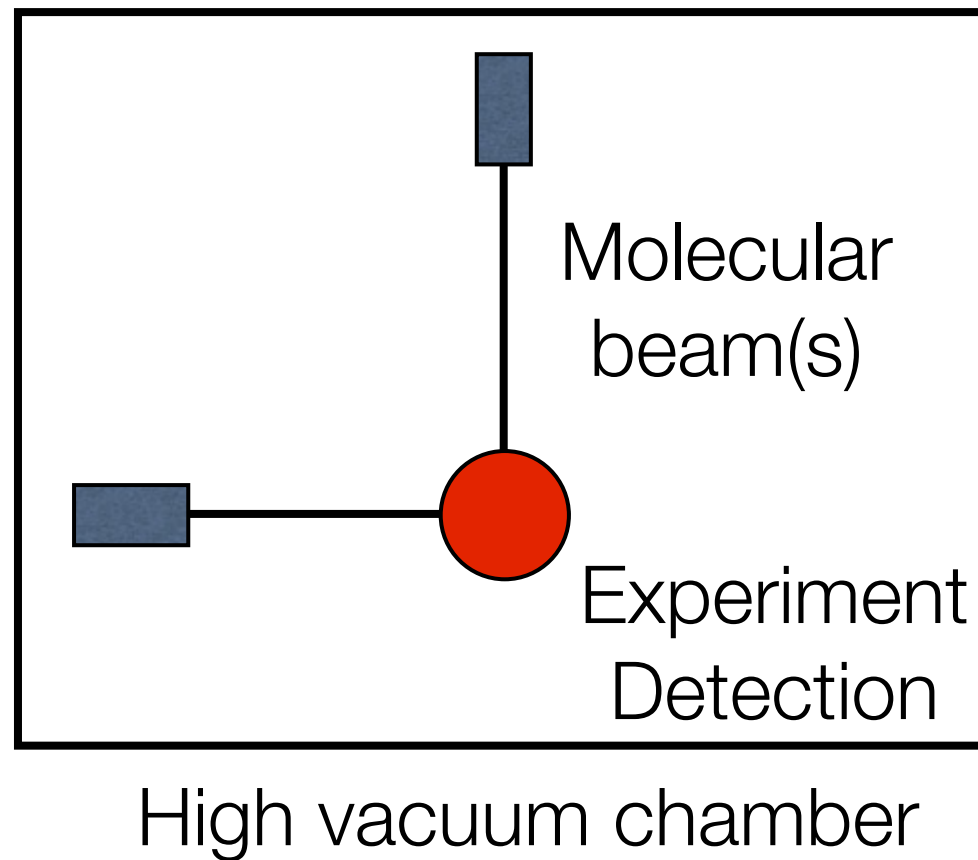
Pressure around
 10^{-5} - 10^{-12} mbar
(why?)

High vacuum chamber

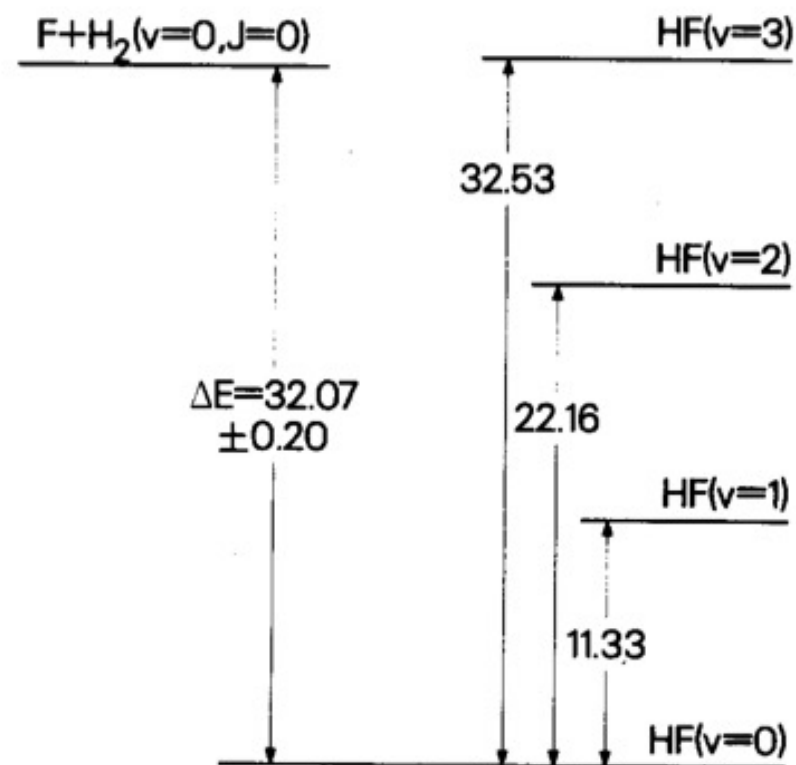
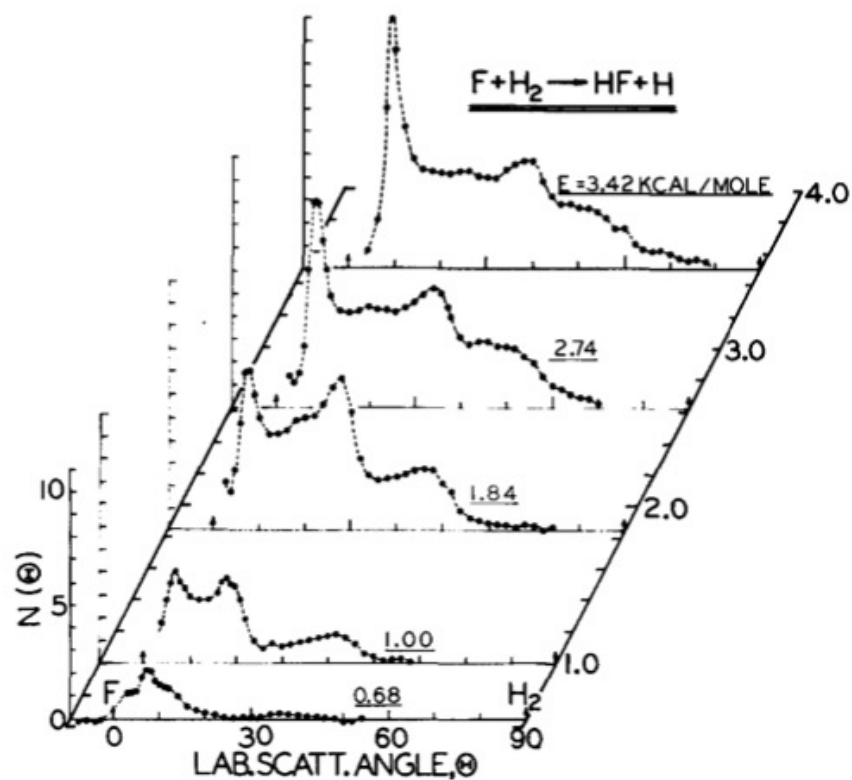
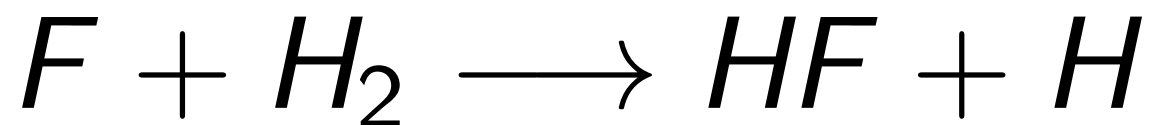
The generic setup



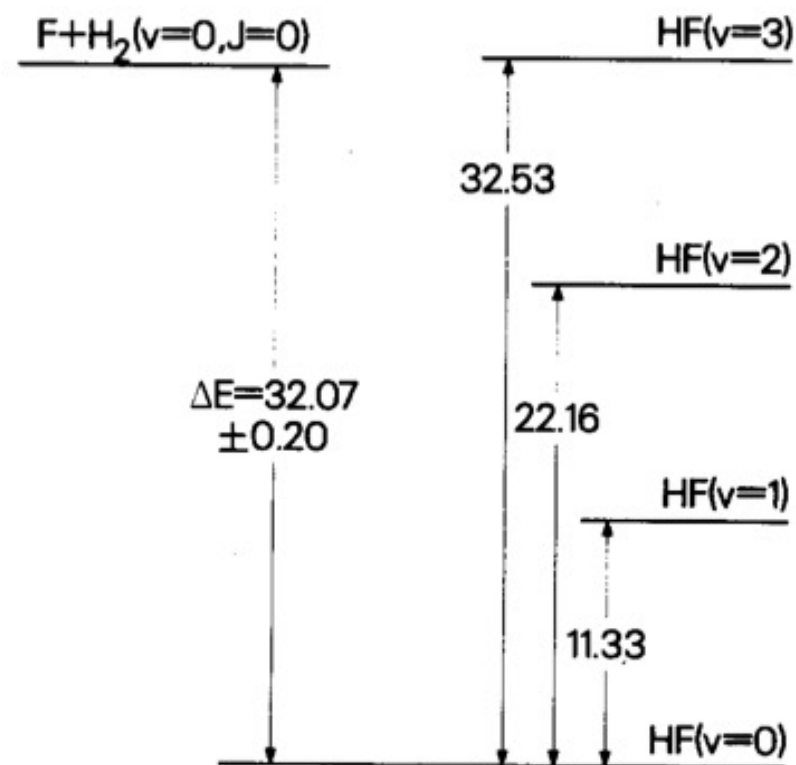
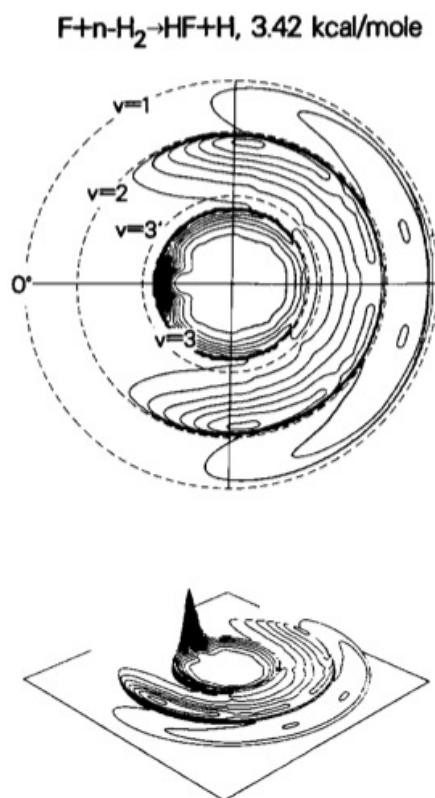
The generic setup



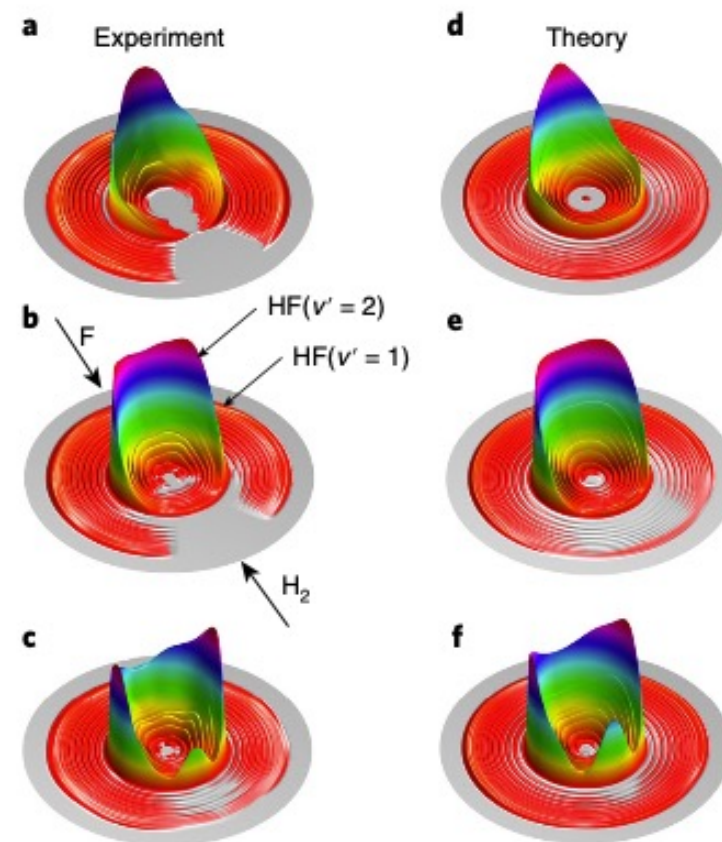
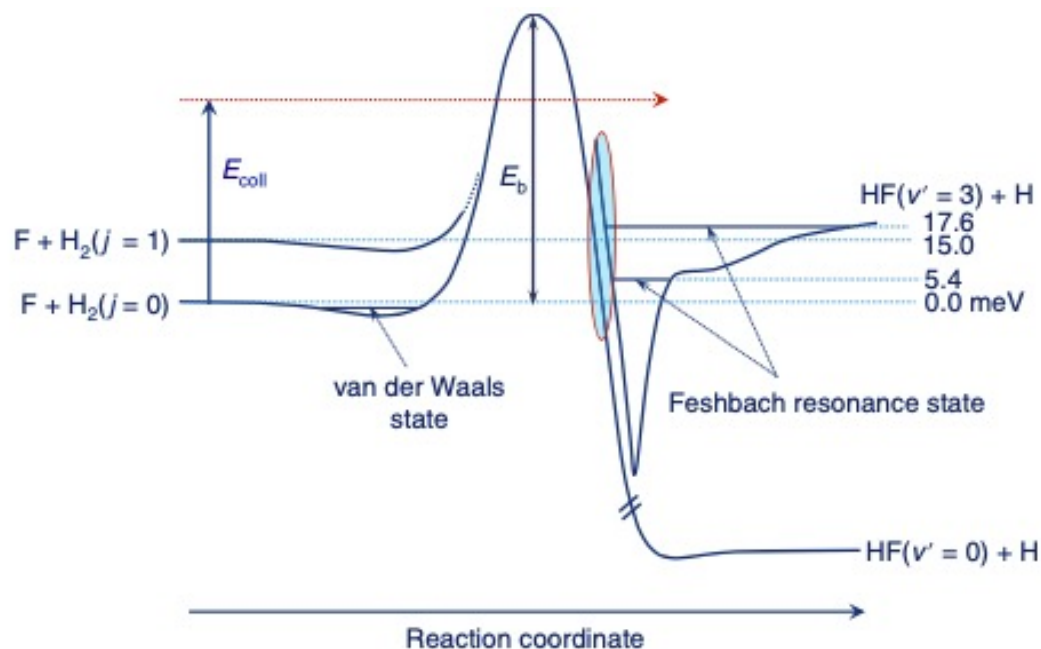
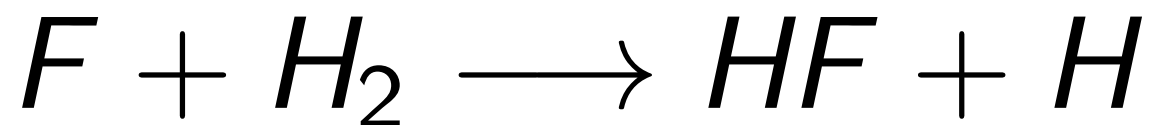
Examples



Examples

$$F + H_2 \longrightarrow HF + H$$


Examples



Yang, Huang, Xiao, Chen, Wang, Dai, Lique, Alexander, Sun, Zhang, Yang, and Neumark, *Nature Chem.* **11**, 744 (2019).

Control of neutral molecules in the gas phase

Control all degrees of freedom

Expansions provide cold samples, but only limited control

- Control internal degrees of freedom
- Control translational degrees of freedom

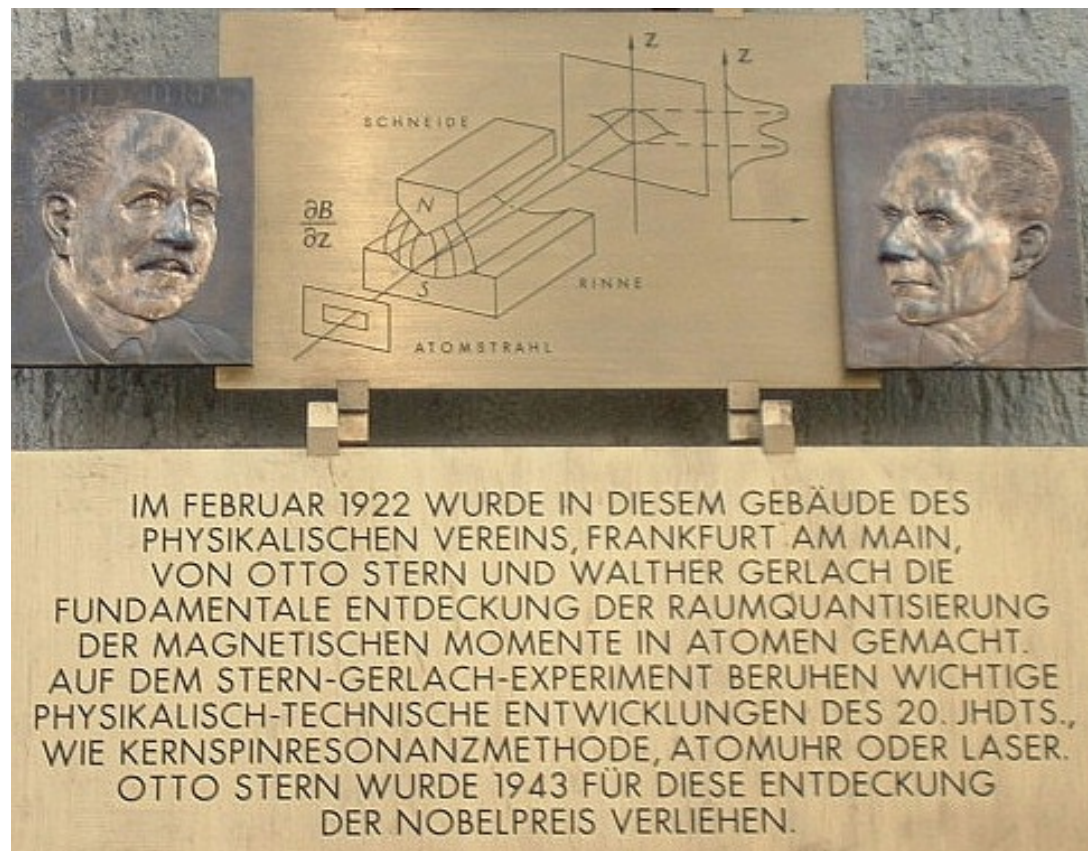
Internal

- Controlled excitation
- Complete population transfer using lasers

External

Use of, for example, electric fields to modify the trajectories of polar molecules

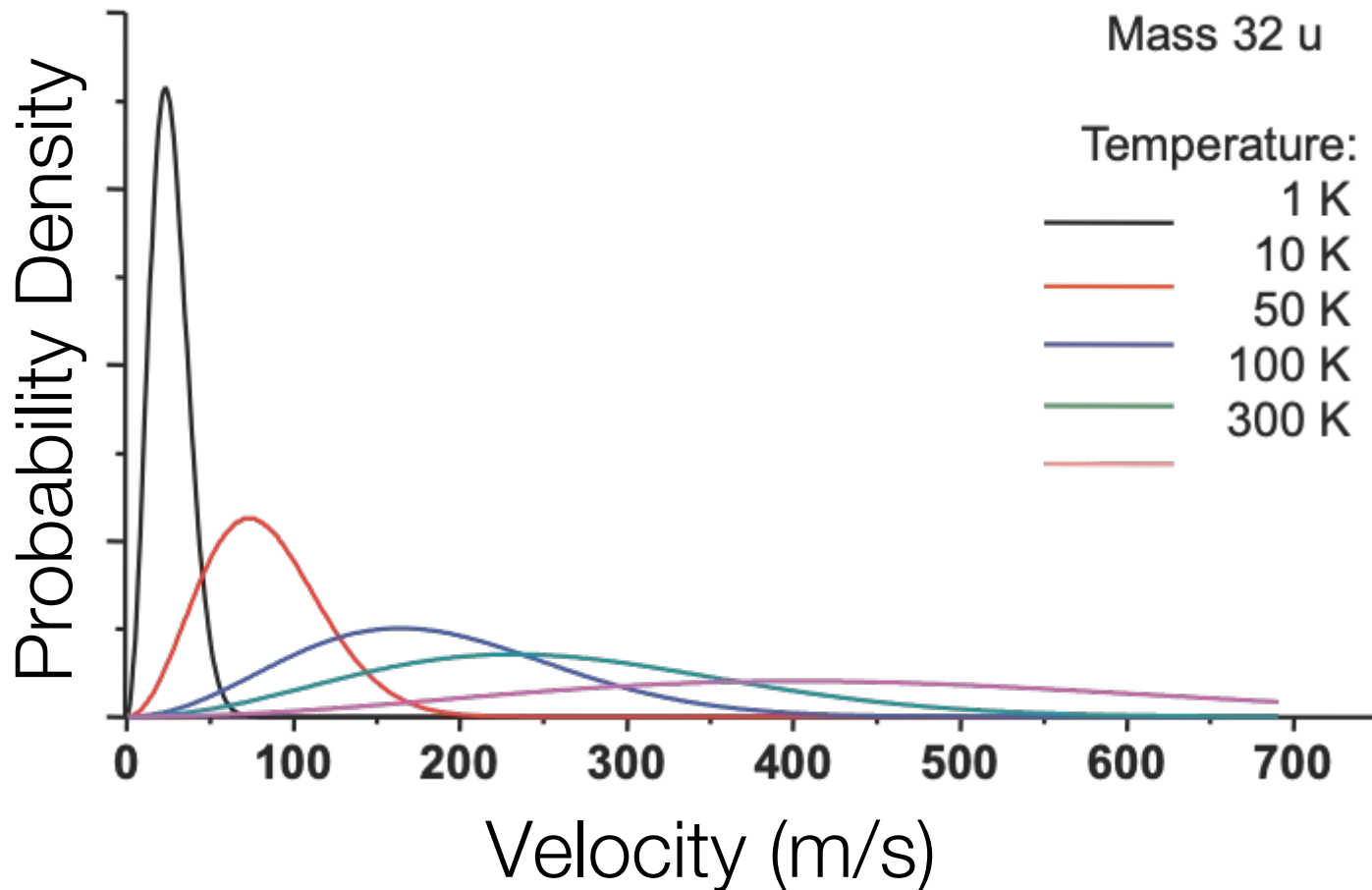
Remember Stern-Gerlach Experiment:



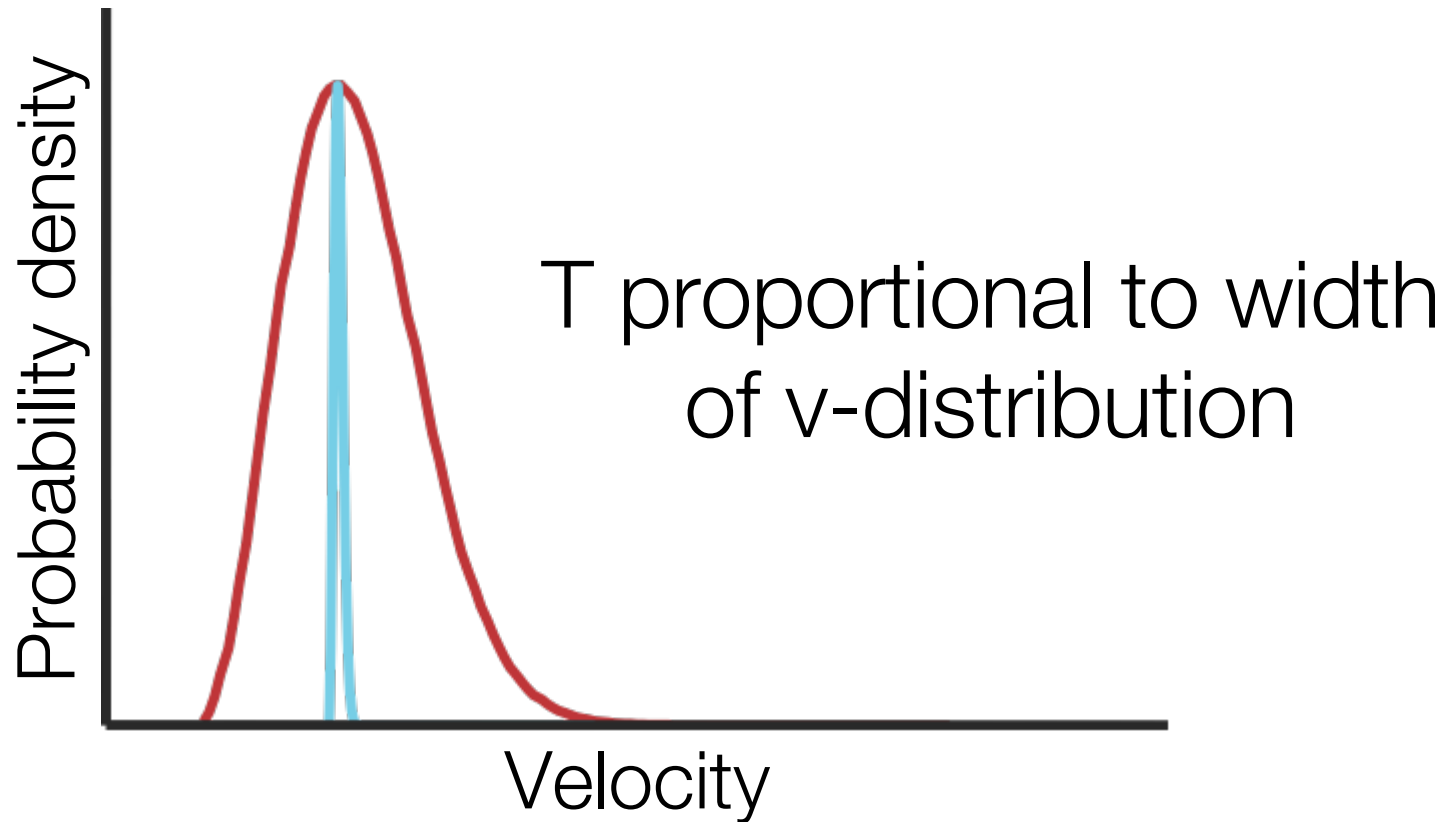
Temperature

Internal vs. external
degrees of freedom

Translationally cold

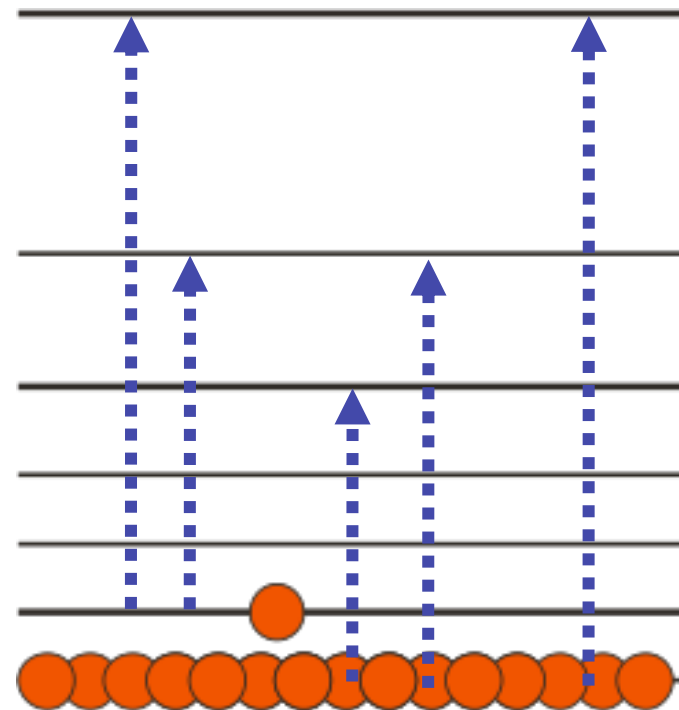
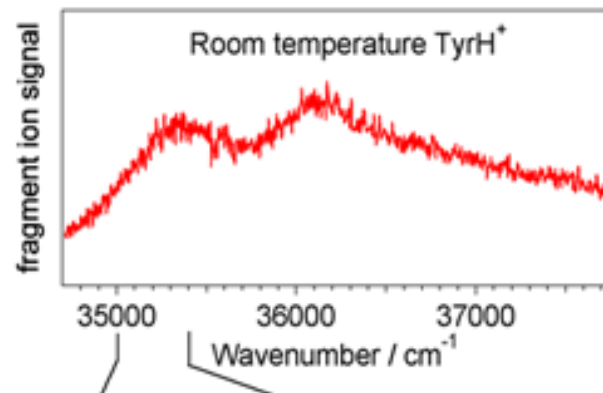


Translationally cold



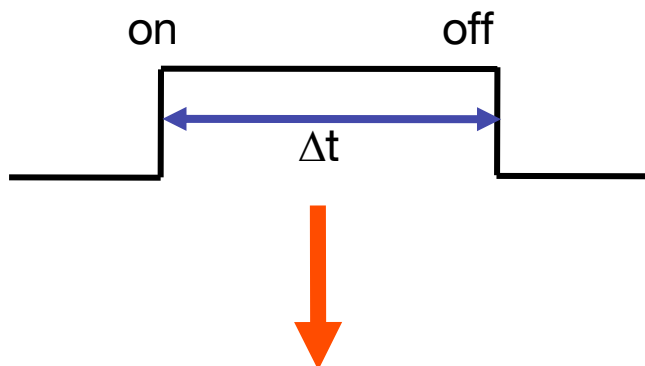
Why?

Spectroscopy
Collision Dynamics / Cold Chemistry
Quantum Information
Molecular BEC



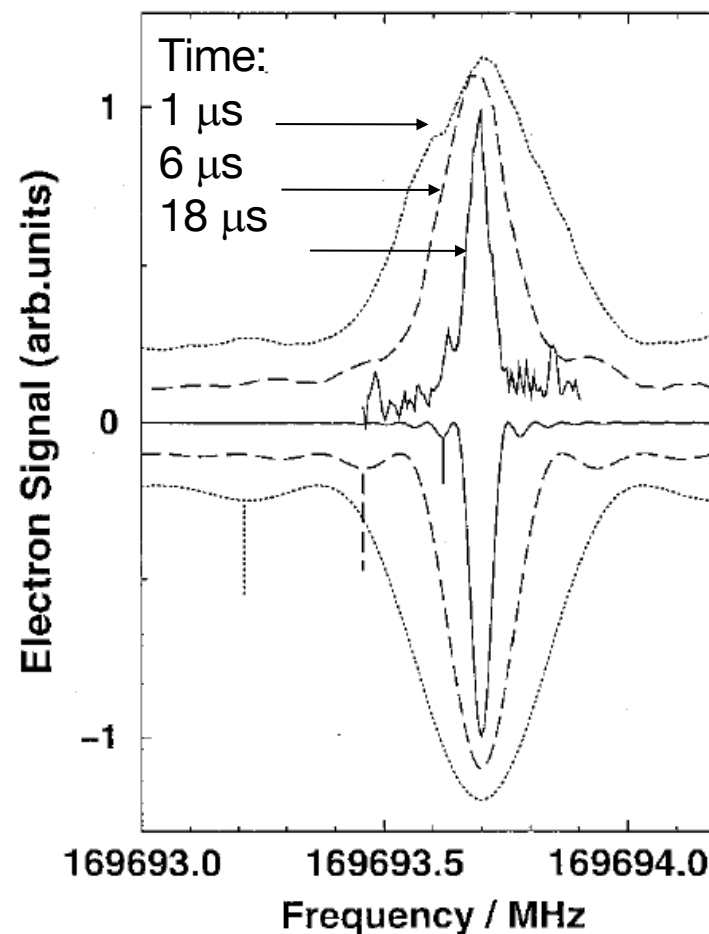
Low Temperature →
Fewer states populated;
Fewer transitions possible

Maximum spectral resolution is inversely proportional to the measurement time.



Spectrum is a sinc^2 function:

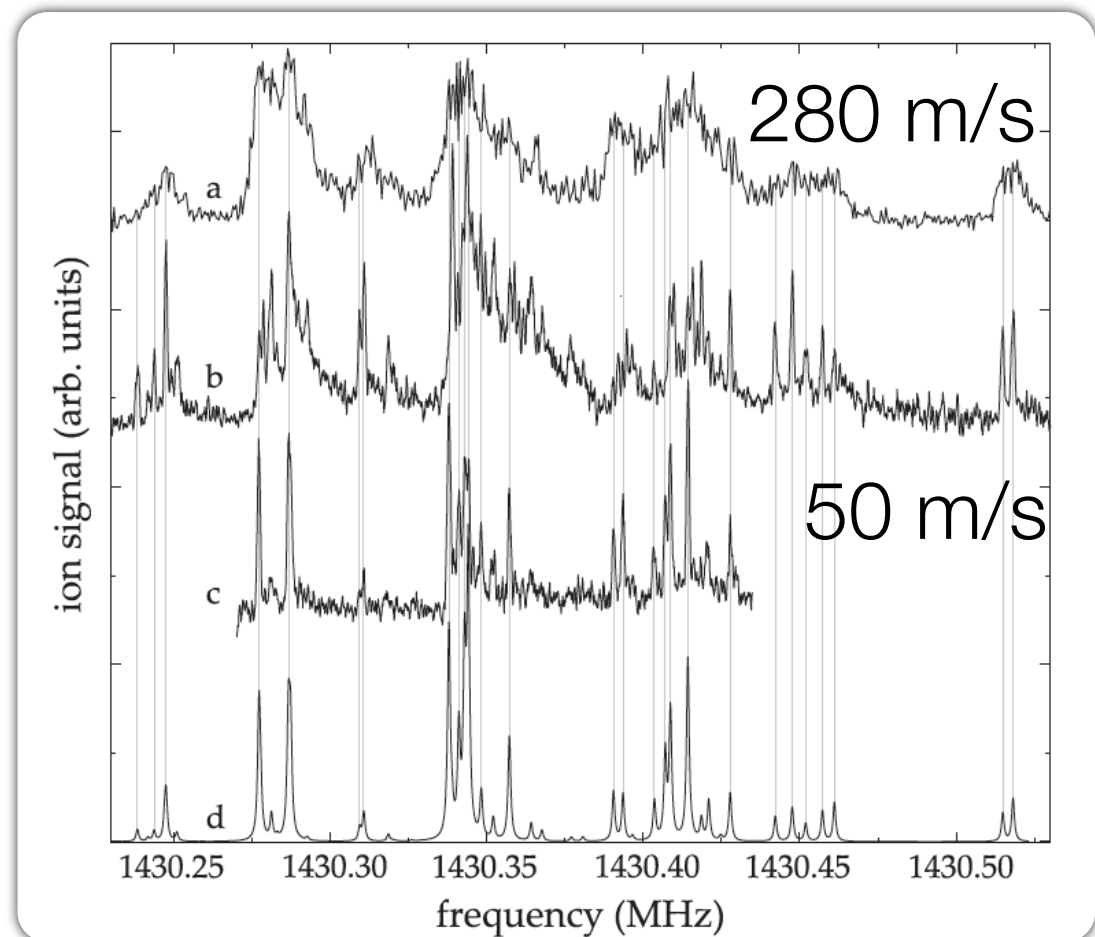
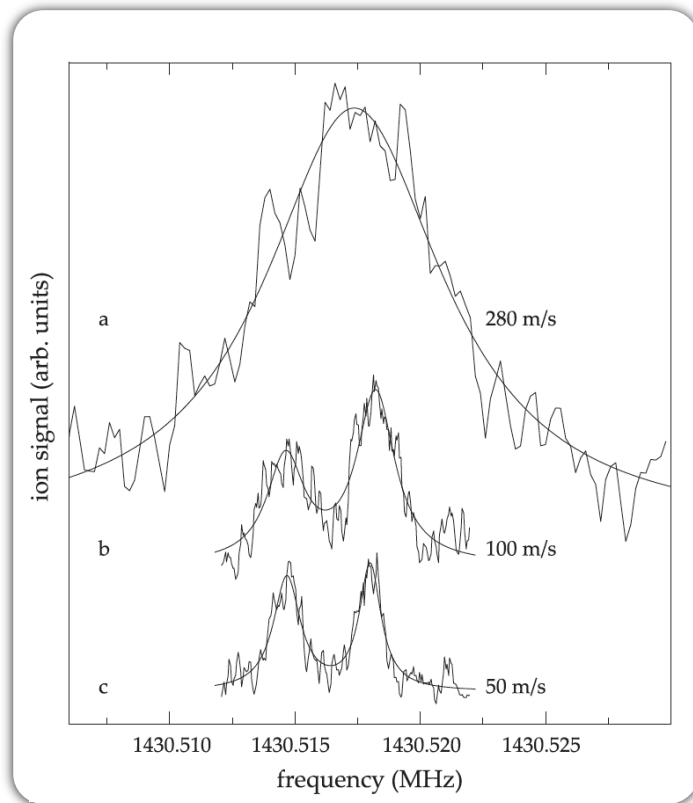
$$\Delta f \propto 1/\Delta t$$



Slow molecules provide longer measurement times

Hyperfine structure of ND₃

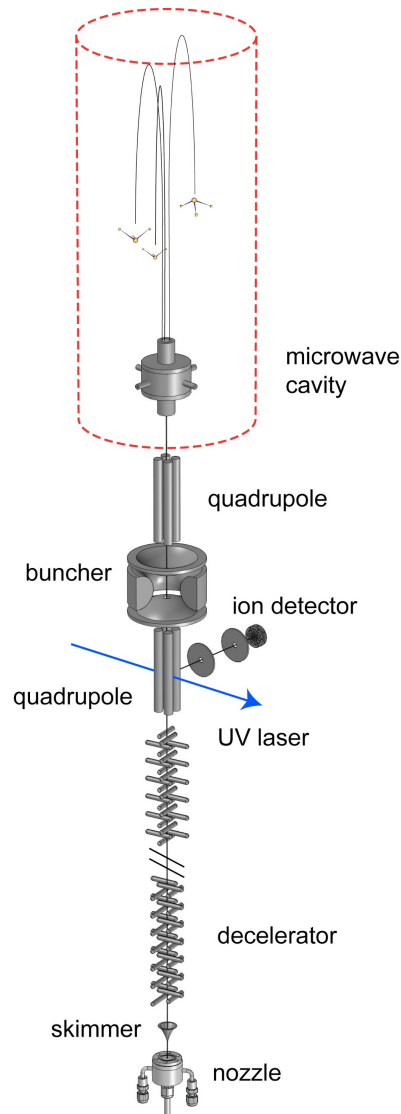
μ -wave spectroscopy on decelerated molecules



van Veldhoven, Jongma, Sartakov, Bongers,
and Meijer, Phys. Rev. A **66**, 032501 (2002).

Spectroscopy

In particular: Precision spectroscopy



Molecular fountain:

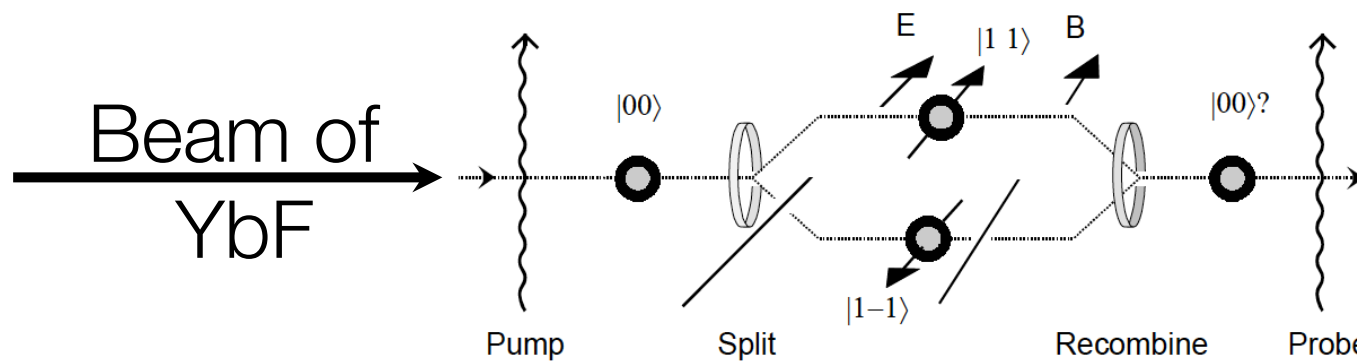
(R. Bethlem, VU Amsterdam)

Produce slow molecules in a vertical device, let them fly up and turn around under the influence of gravity. Perform Ramsey-type spectroscopy with very long flight times.

Spectroscopy

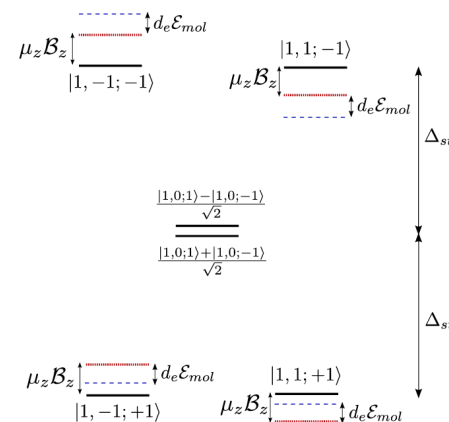
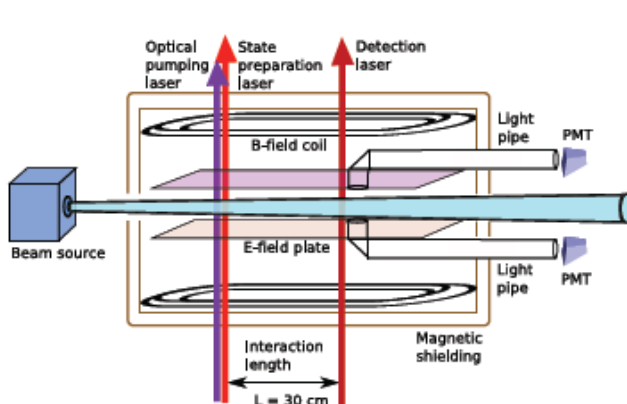
In particular: Precision spectroscopy

UCL experiment (Hinds, Tarbutt):



Hudson et al., arXiv 0509.169

Harvard/Yale experiment (DeMille, Doyle):



ThO
 $H^3\Delta_1(J=1)$

Vutha et al., arXiv 0908.2412

Experimental methods

Production of cold molecules

Methods for dynamics studies

How to control the motion of molecules?

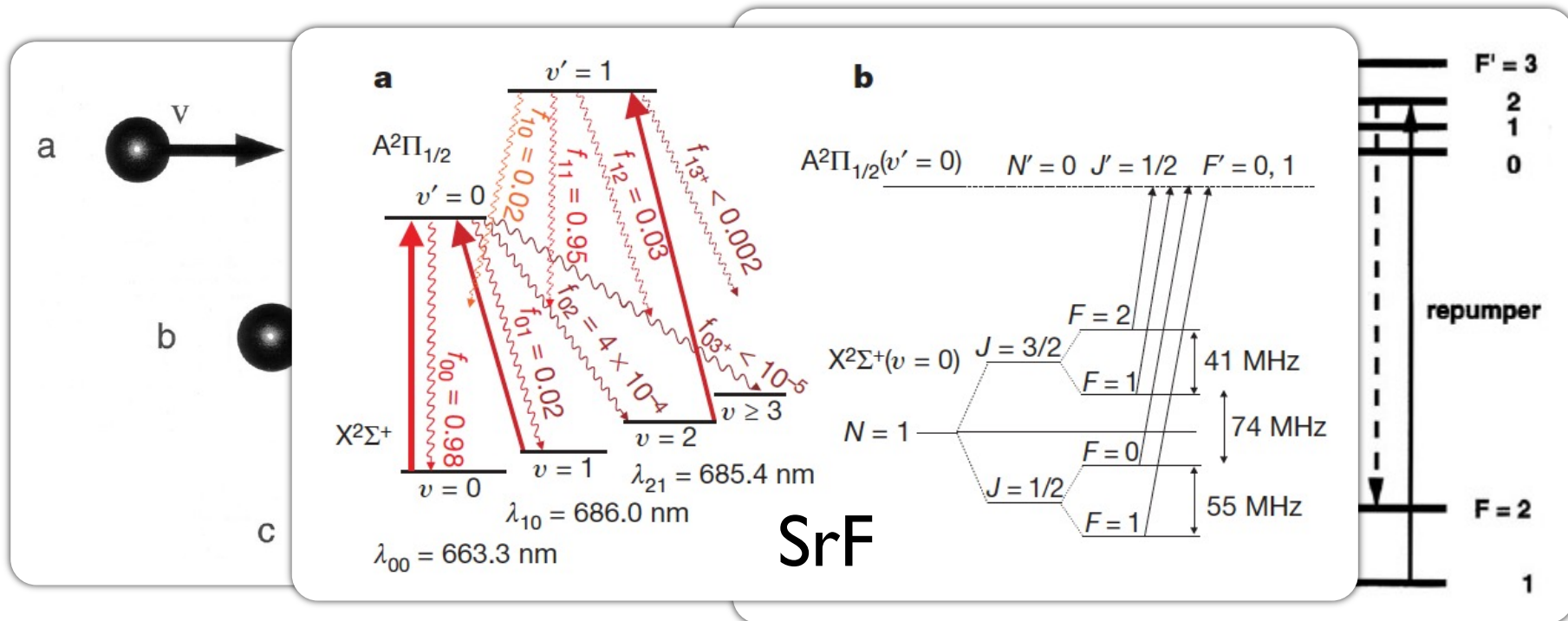
Forces can be applied through electric, magnetic, or electromagnetic fields



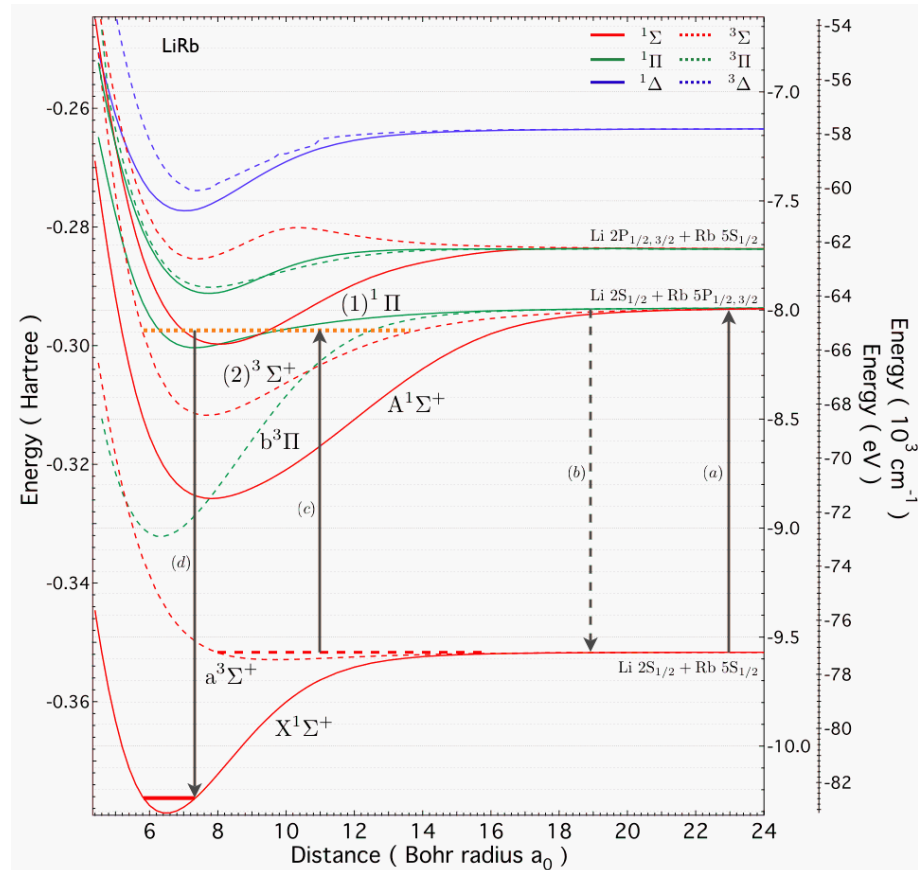
Methods

- Laser cooling
- Association from ultracold atoms
- Backward rotating nozzle, rotating paddle
- Billiard-like cooling
- Buffer-gas cooling
- Deceleration using electric fields
- Deceleration using magnetic fields
- Deceleration using optical fields
- Filtering of slow molecules from a thermal sample

Laser cooling

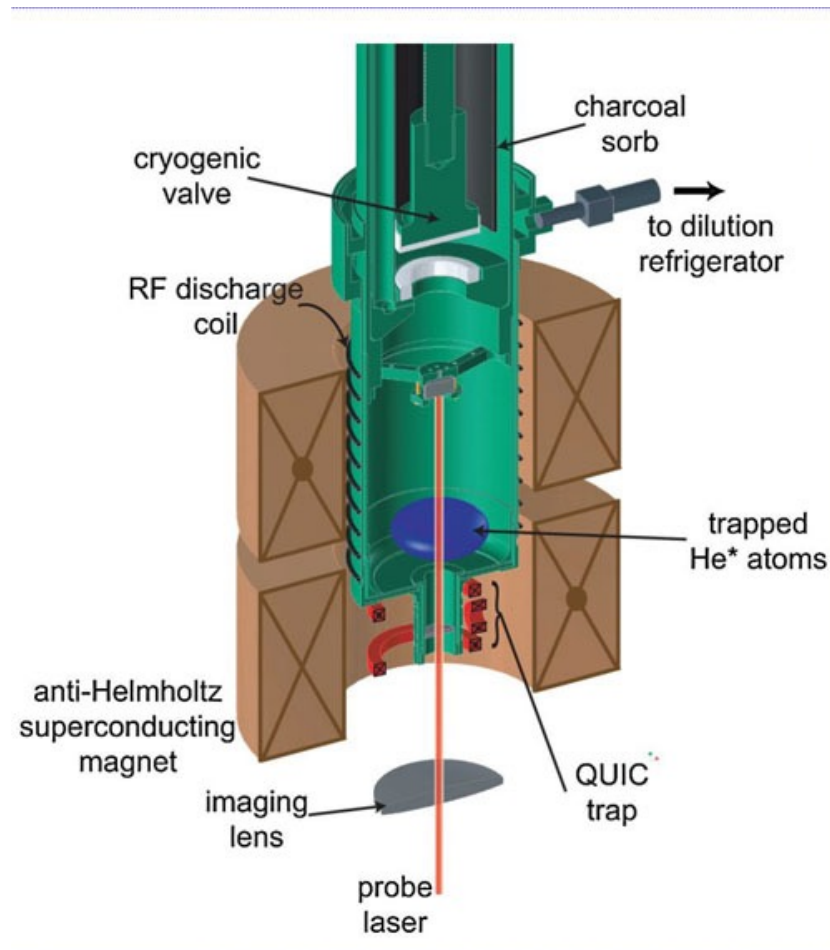


Photoassociation



LiRb potential curves

Buffer-gas cooling

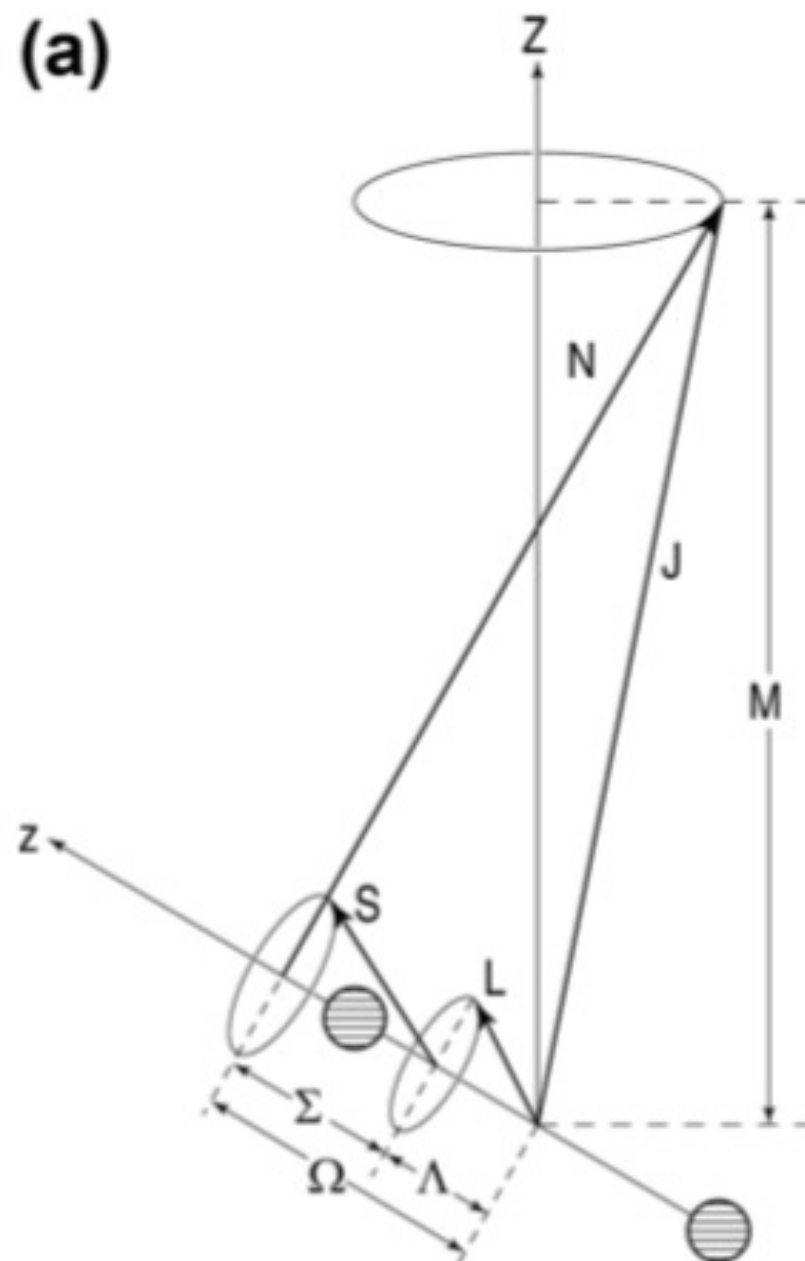


Doyle, Friedrich, Kim, and Patterson, Phys. Rev. A **52**, R2515 (1995).

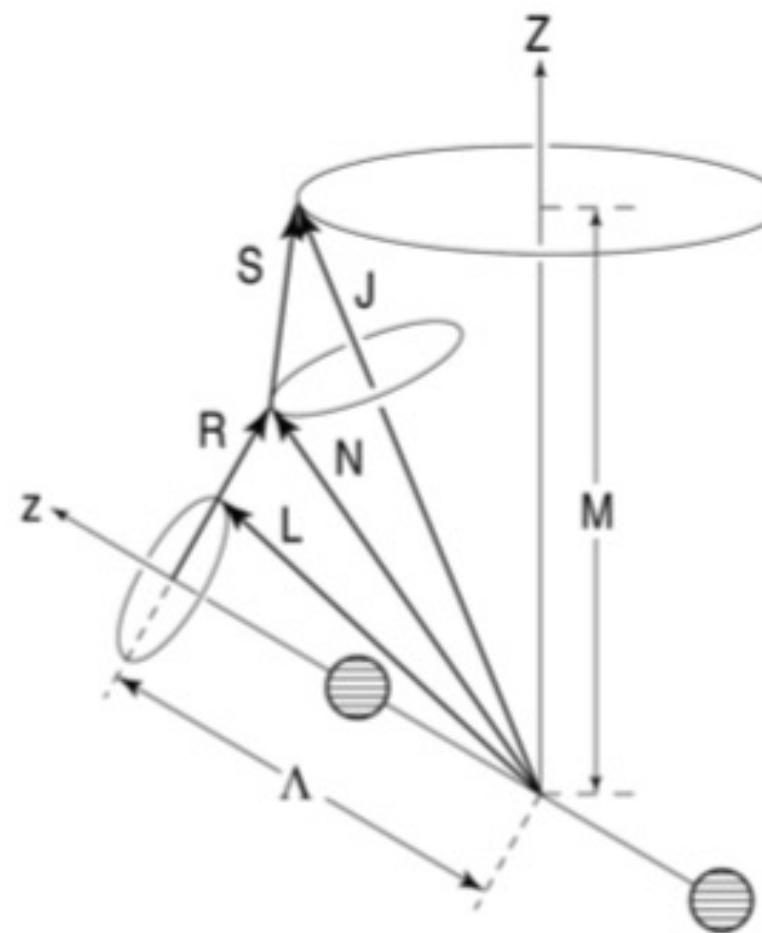
Electric field control of polar molecules

Using the Stark effect
(Energy level splitting and shifting in an electric field)

(a)



(b)



$$\langle J'K'M'|H_{\text{Stark}}|JKM\rangle$$

$$|JKM\rangle = \sqrt{\frac{2J+1}{8\pi^2}} \mathcal{D}_{MK}^{(J)*}(\phi, \theta, \chi)$$

$$\begin{aligned} \langle J'K'M'|H_{\text{Stark}}|JKM\rangle \\ = -E\sqrt{(2J+1)(2J'+1)} \sum_q (-1)^{K'-M'} \mu_q^e \\ \times \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix} \begin{pmatrix} J & 1 & J' \\ K & q & -K' \end{pmatrix} \end{aligned}$$

van de Meerakker, Bethlem, Vanhaecke, and Meijer, Chem. Rev. **112**, 4828 (2012).

$$\mu_{-1}^e = \frac{1}{\sqrt{2}}(\mu_x - i\mu_y)$$

$$\mu_0^e = \mu_z$$

$$\mu_1^e = -\frac{1}{\sqrt{2}}(\mu_x + i\mu_y)$$

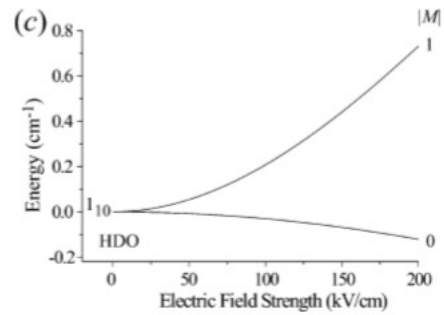
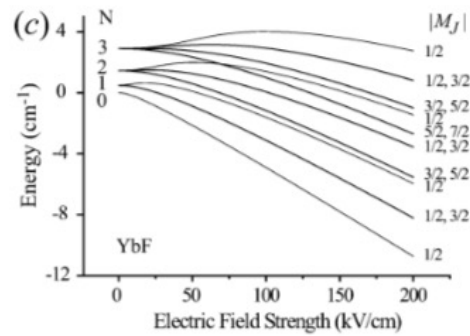
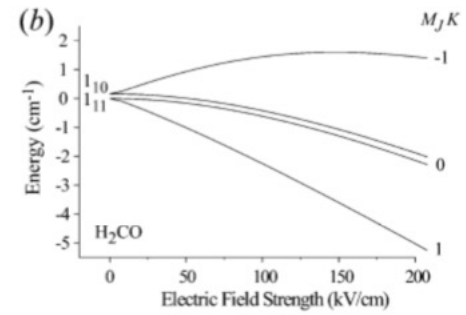
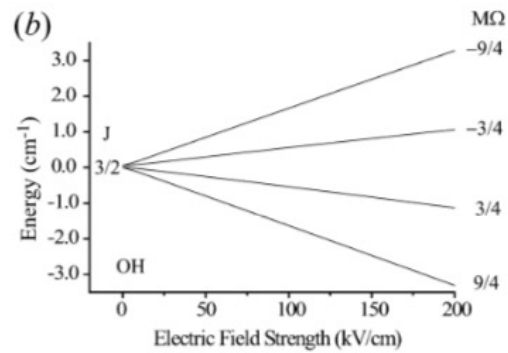
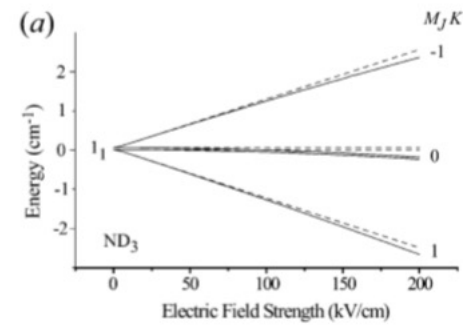
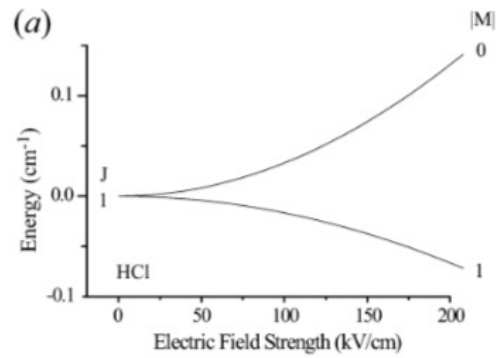
The selection rules follow from the 3- J symbols:

$$J = J' \quad \text{except} \quad J = J' = 0,$$

or

$$J = J' \pm 1, \quad M = M', \quad K' - K = 0, \pm 1$$

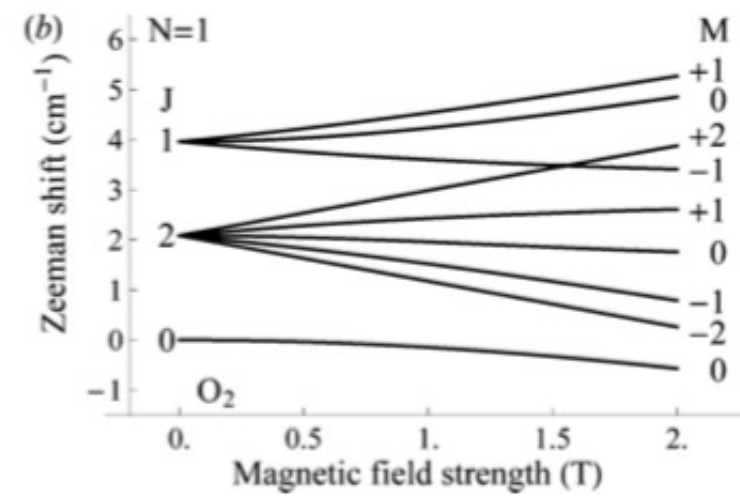
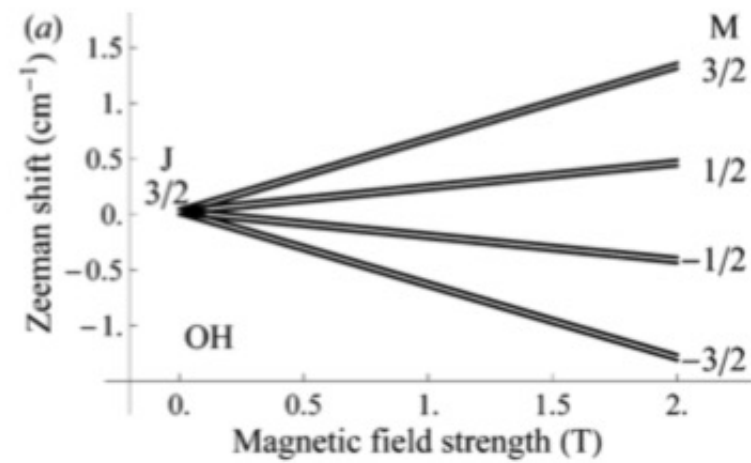
$$E_{\text{Stark}} = \frac{E_{\Lambda}}{2} \pm \sqrt{\left(\frac{E_{\Lambda}}{2}\right)^2 + \left(\mu^e E \cdot \frac{M\Omega_{\text{eff}}}{J(J+1)}\right)^2}$$



$$\begin{aligned}
& \left\langle n', {}^{2S'+1}L'_{J'}, M' | H_{\text{Zeeman}} | n, {}^{2S+1}L_J, M \right\rangle \\
&= \mu_{\text{B}} B \delta_{nn} \delta_{LL} \delta_{SS'} (-1)^{L+S+J'-M'} \times \sqrt{(2J'+1)(2J+1)} \\
&\quad \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix} \times \left[g_{\text{e}} (-1)^{-J} \sqrt{S(S+1)(2S+1)} \right. \\
&\quad \left. \begin{Bmatrix} S & L & J \\ J' & 1 & S \end{Bmatrix} + (-1)^{-J'} \sqrt{L(L+1)(2L+1)} \right. \\
&\quad \left. \begin{Bmatrix} L & S & J \\ J' & 1 & L \end{Bmatrix} \right]
\end{aligned}$$

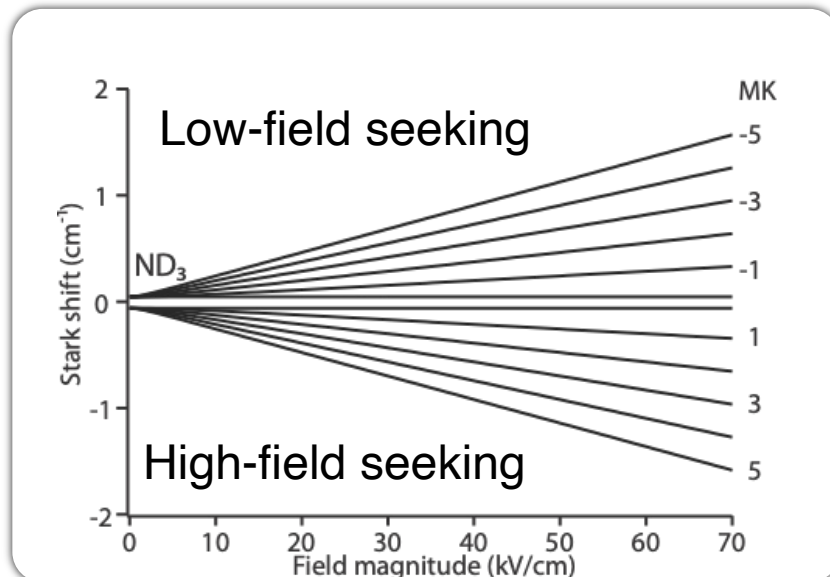
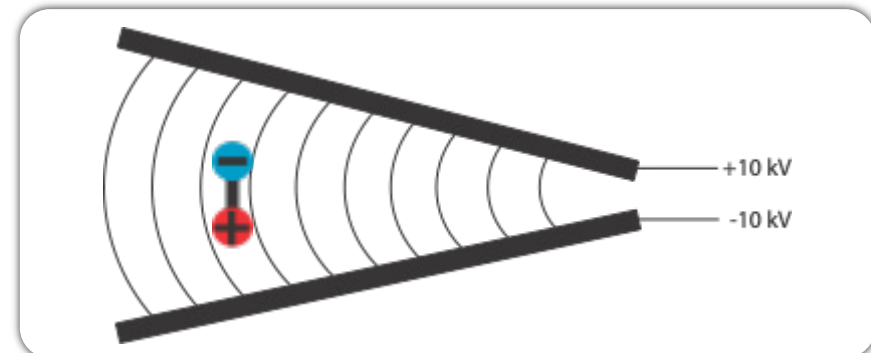
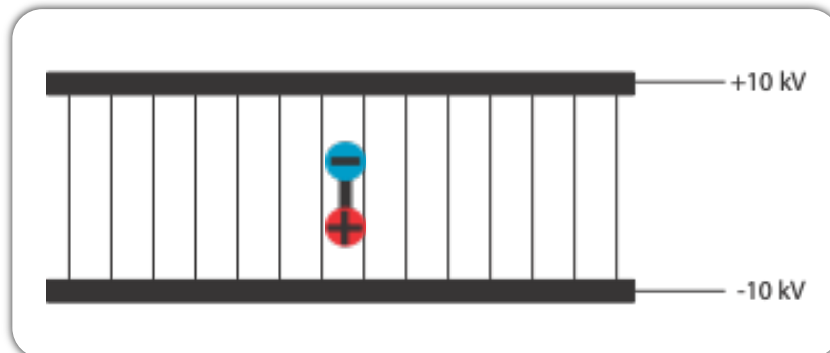
$$\begin{aligned}
& \langle \Lambda n S' J' \Omega' M' | H_{\text{Zeeman}} | \Lambda n S J \Omega M \rangle \\
&= \mu_{\text{B}} B \delta_{SS'} \sqrt{(2J' + 1)(2J + 1)} \begin{pmatrix} J & 1 & J' \\ M & 0 & -M' \end{pmatrix} \\
&\quad \times \left[g_{\text{e}} (-1)^{S-\Lambda+1+M'} \right. \\
&\quad \times \sqrt{S(S+1)(2S+1)} \begin{pmatrix} S & 1 & S' \\ \Sigma & \Omega' - \Omega & -\Sigma' \end{pmatrix} \\
&\quad \left. \begin{pmatrix} J & 1 & J' \\ \Omega & \Omega' - \Omega & -\Omega' \end{pmatrix} + \Lambda (-1)^{\Omega' - M'} \begin{pmatrix} J & 1 & J' \\ \Omega & 0 & -\Omega' \end{pmatrix} \right]
\end{aligned}$$

$$\mu_B B \frac{M\Omega(\Lambda + g_e \Sigma)}{J(J + 1)}$$



Polar molecules in fields

Electric fields: Stark effect



$$\Delta W = \frac{W_0}{2} \pm \sqrt{\left(\frac{W_0}{2}\right)^2 + \left(\mu_0 \frac{MK}{J(J+1)} E\right)^2}$$

Force: $\vec{F}_{Stark} = -\vec{\nabla} W$

$$\vec{F}_{Stark} = \mu_0 \frac{MK}{J(J+1)} \vec{\nabla} E$$

Focussing and Orientation of Polar Molecules

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Orienting Polar Molecules in Molecular Beams. Symmetric Tops*

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Department of Chemistry, Rice University, Houston, Texas 77001

(Received 31 March 1969)

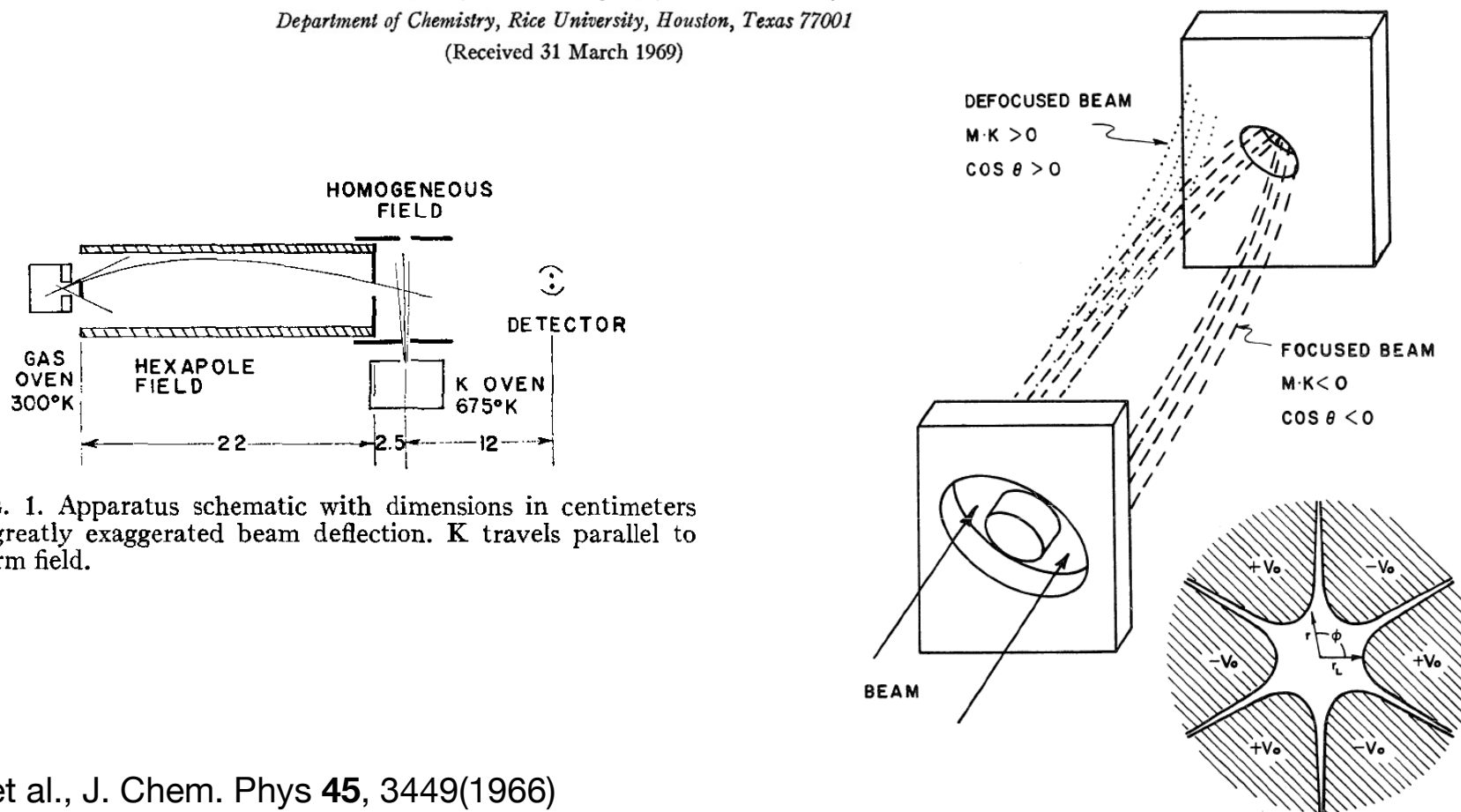
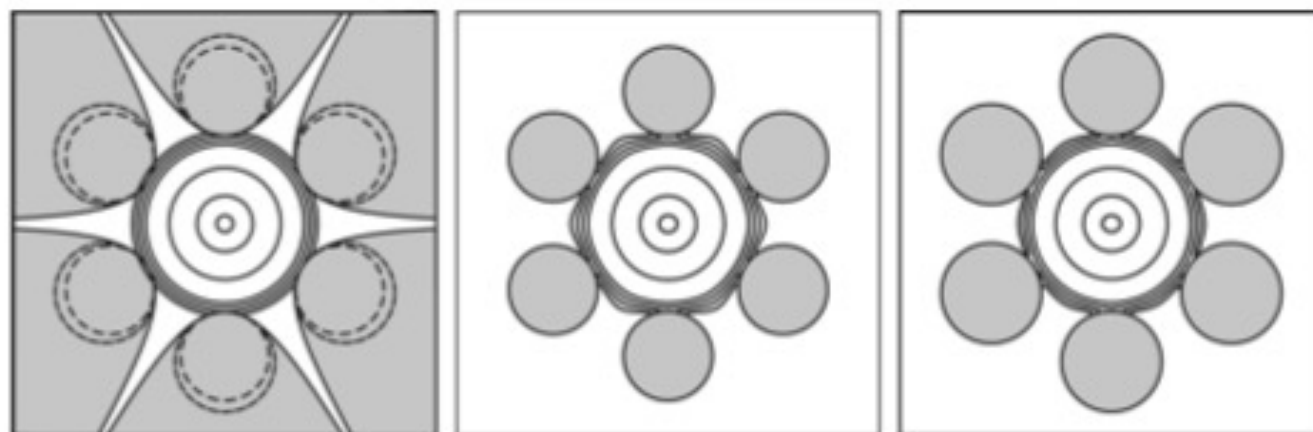


FIG. 1. Apparatus schematic with dimensions in centimeters and greatly exaggerated beam deflection. K travels parallel to uniform field.

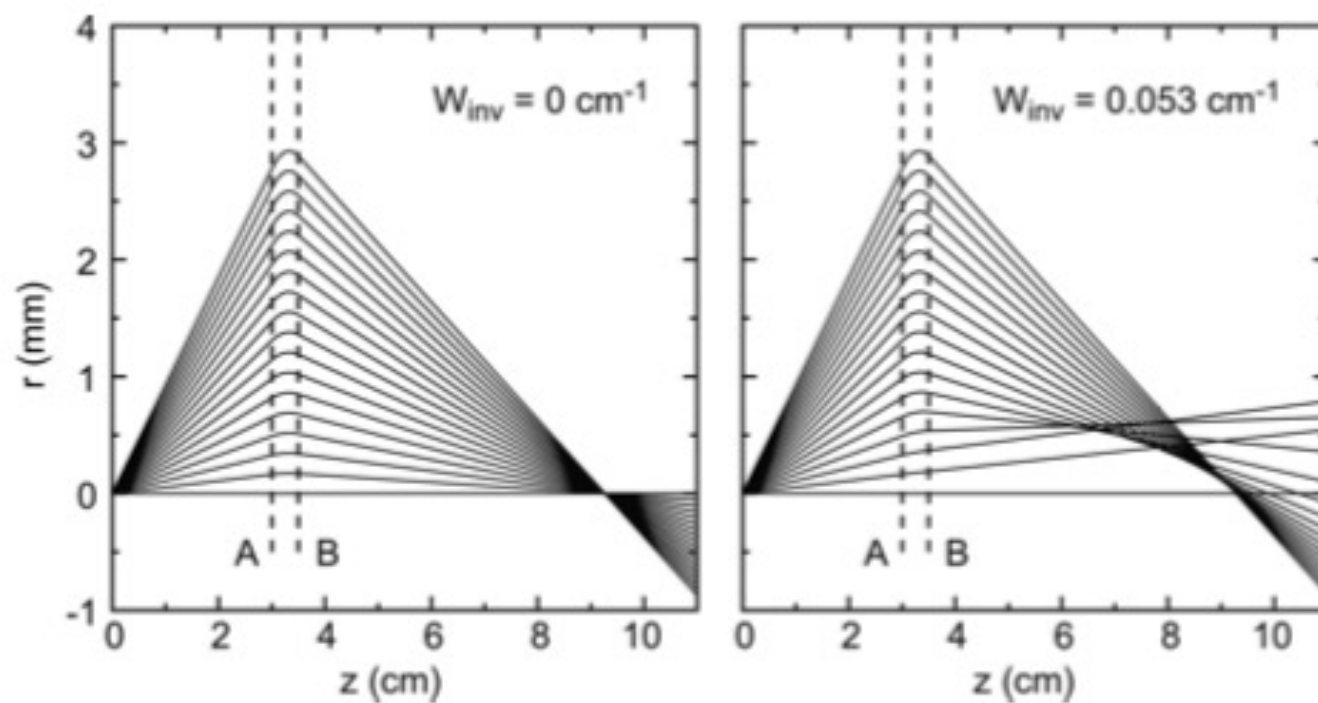


(a) Ideal hexapole

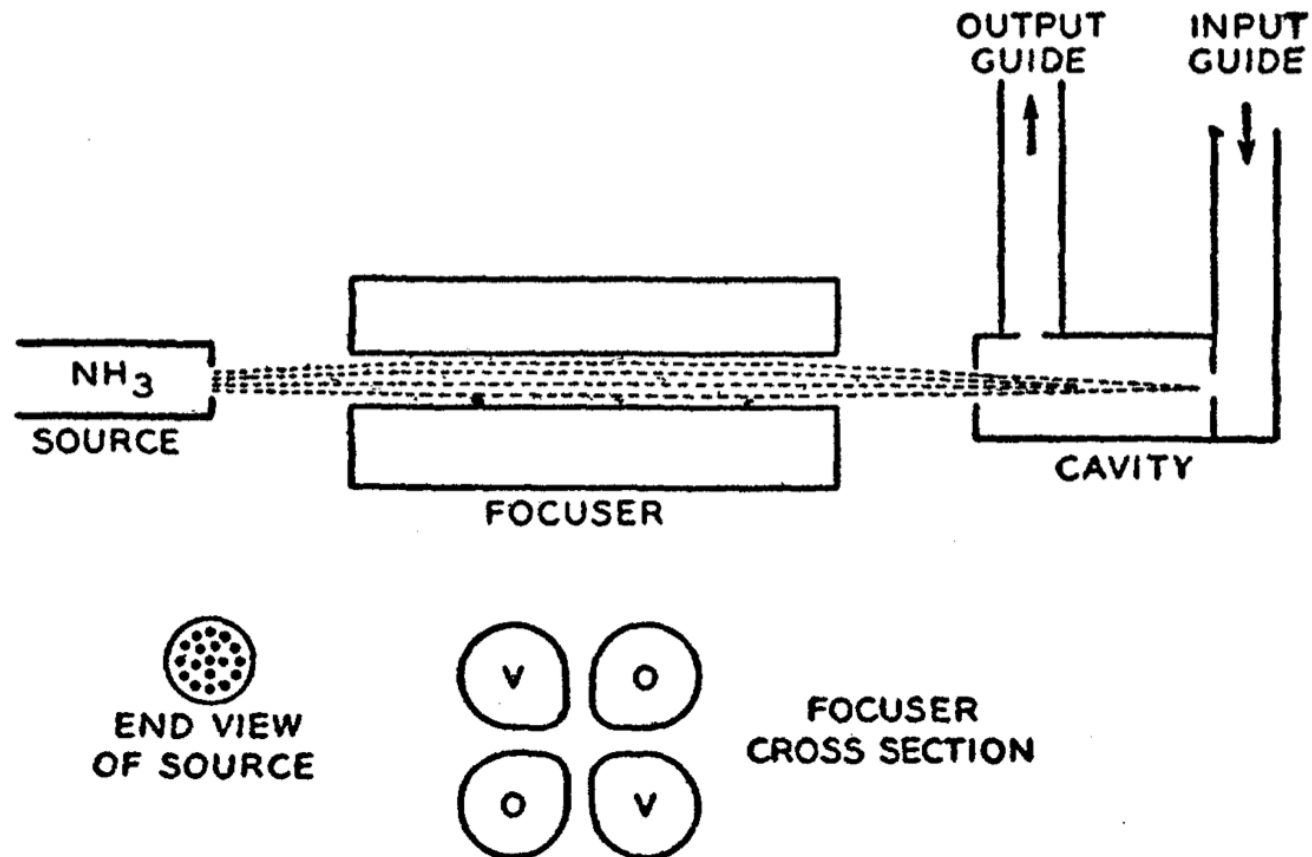
(b) Rod radius: $R/2$

(c) Rod radius: $0.565R$

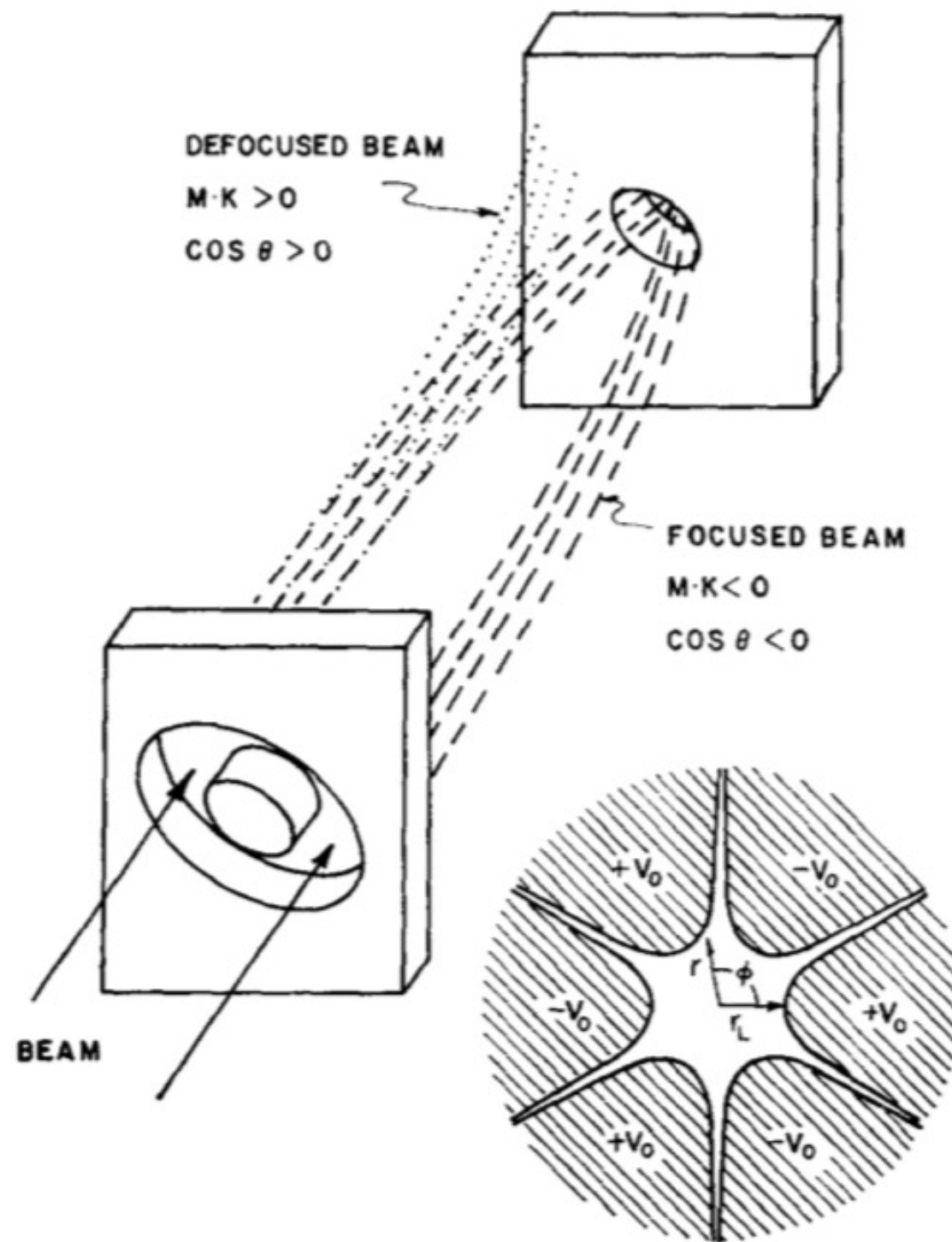
$$\vec{F} = -\vec{\nabla}W(E) = \mu_{\text{eff}}\vec{\nabla}E$$



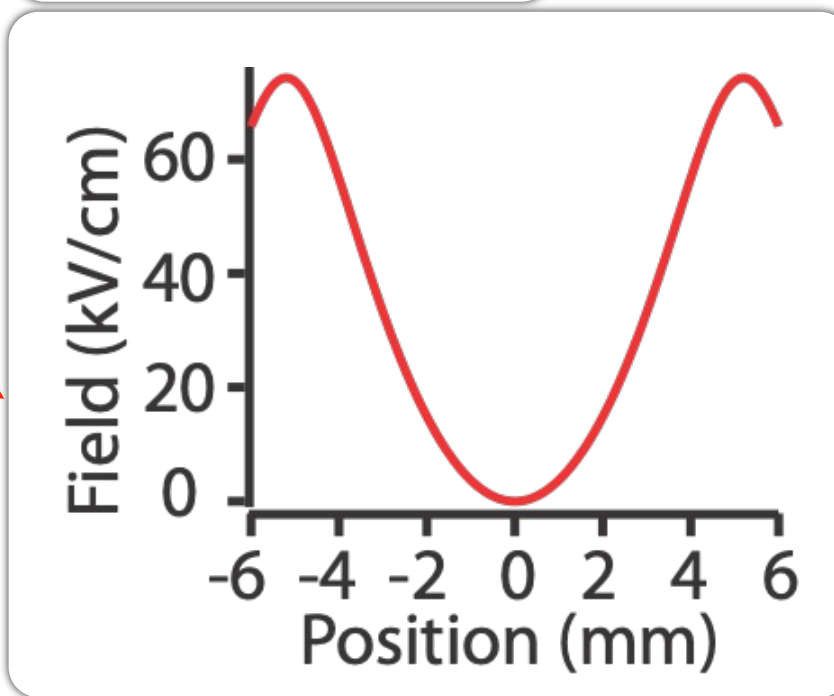
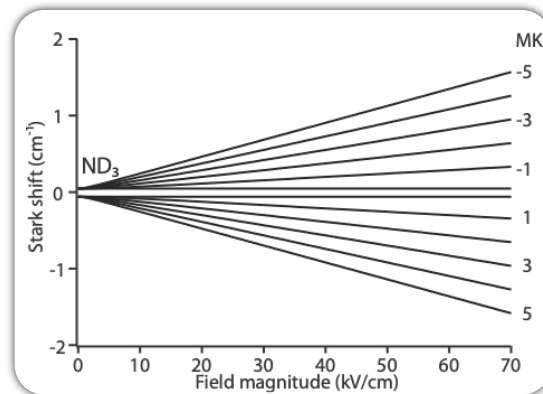
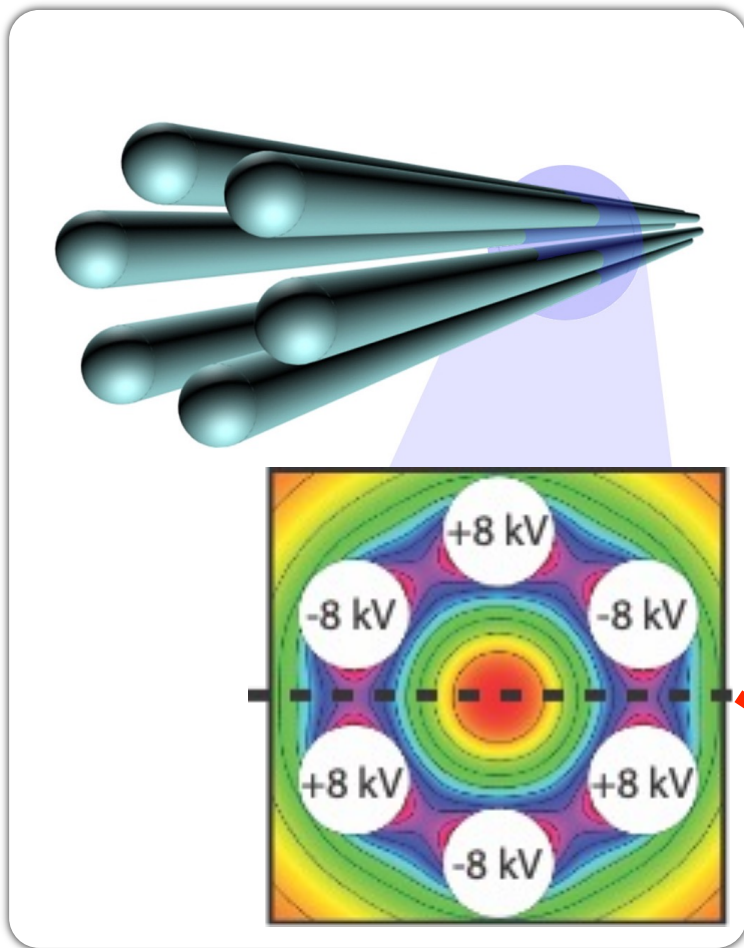
MASER



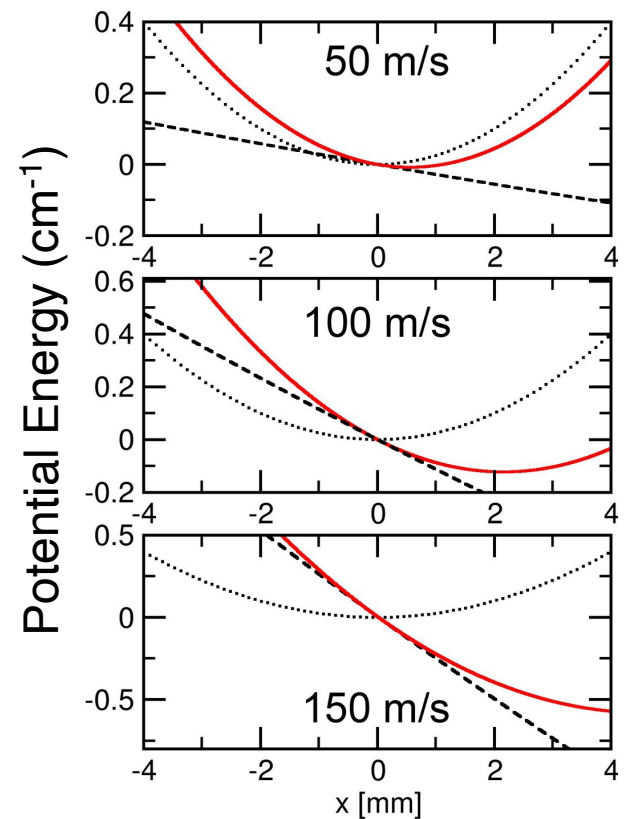
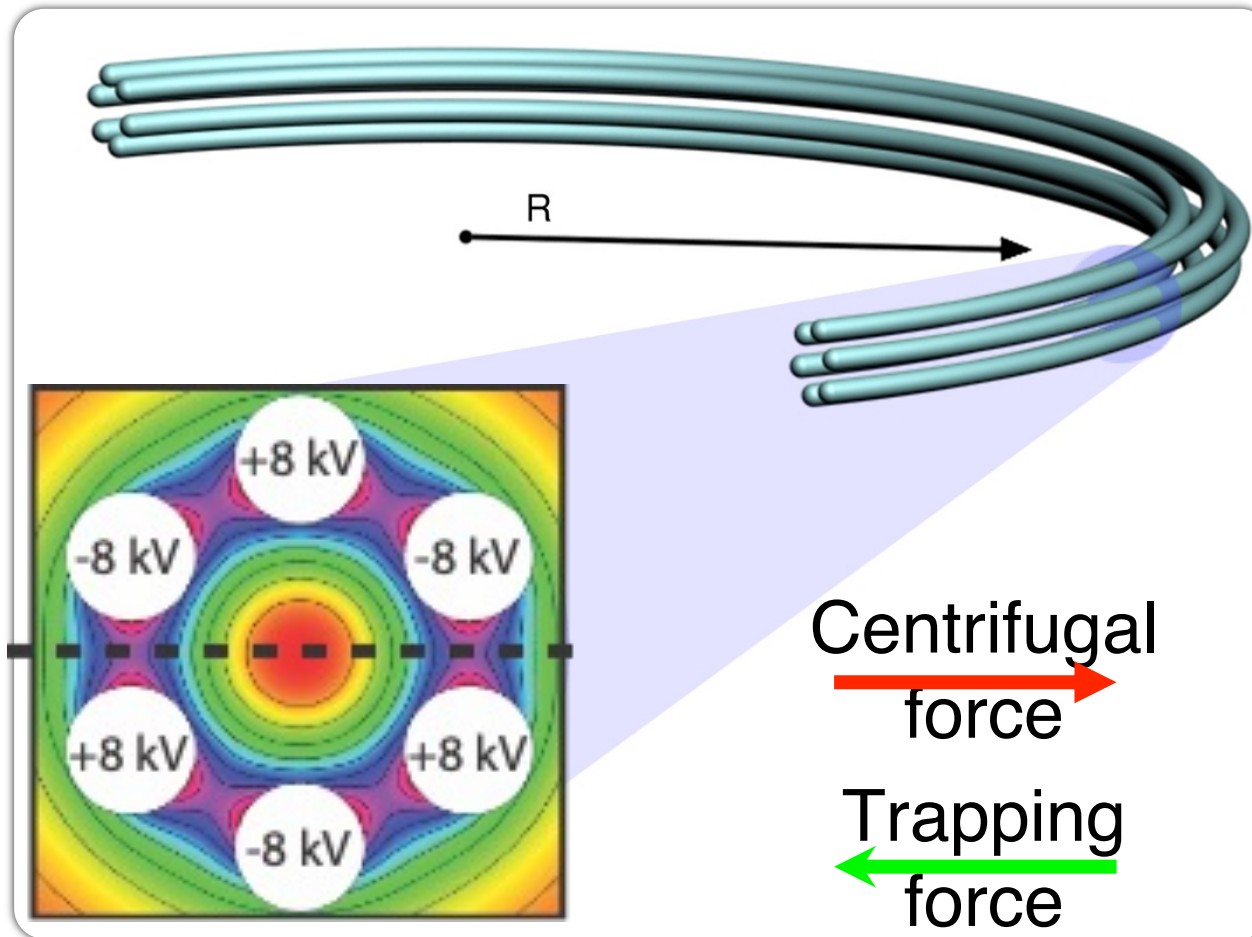
Gordon, Zeiger, and Townes, Phys. Rev. **99**, 1264 (1955).



Guide: 2D trap



Curved guide



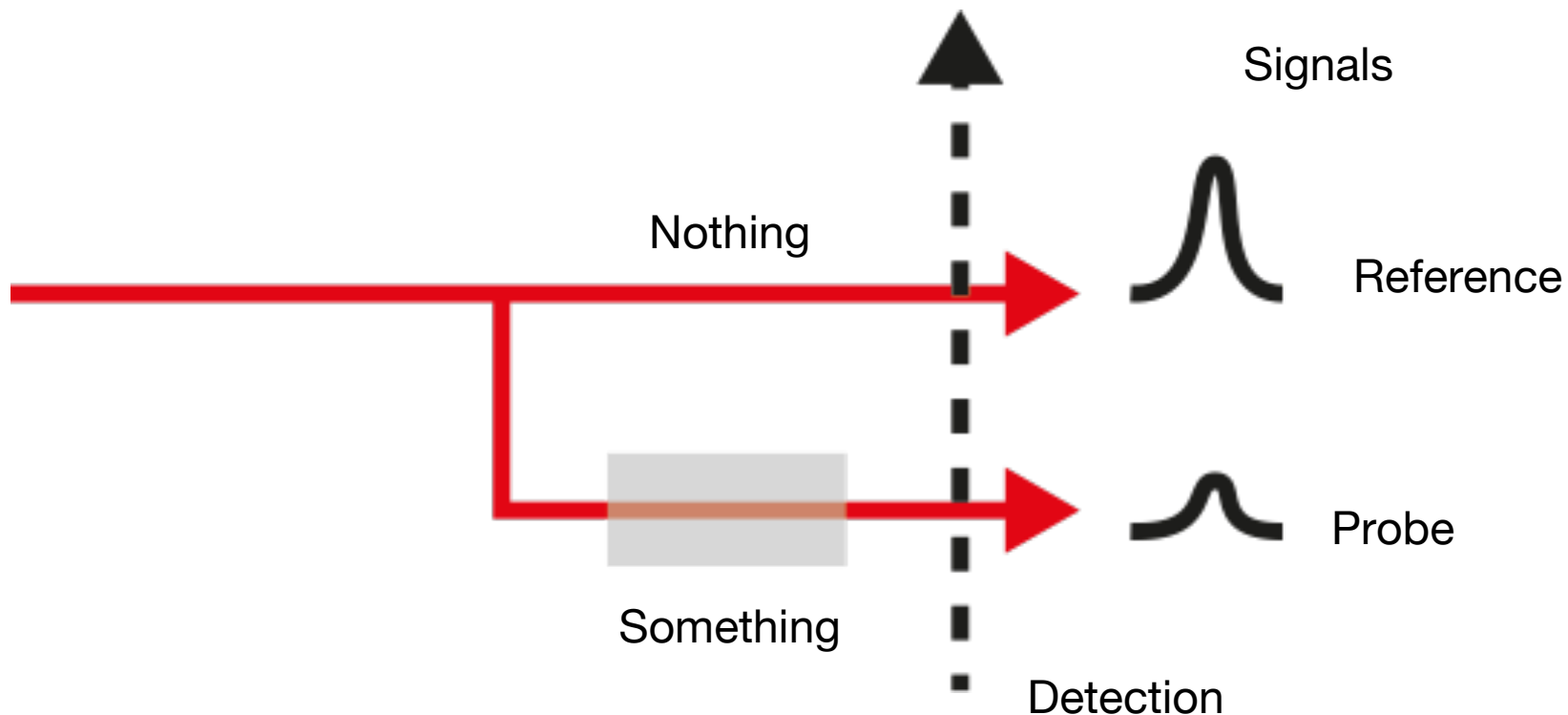
Velocity
threshold:

$$v_{max} = \sqrt{2 \frac{\mu M K E_{max}}{J(J+1)m} \left(1 + \frac{R}{r}\right)}$$

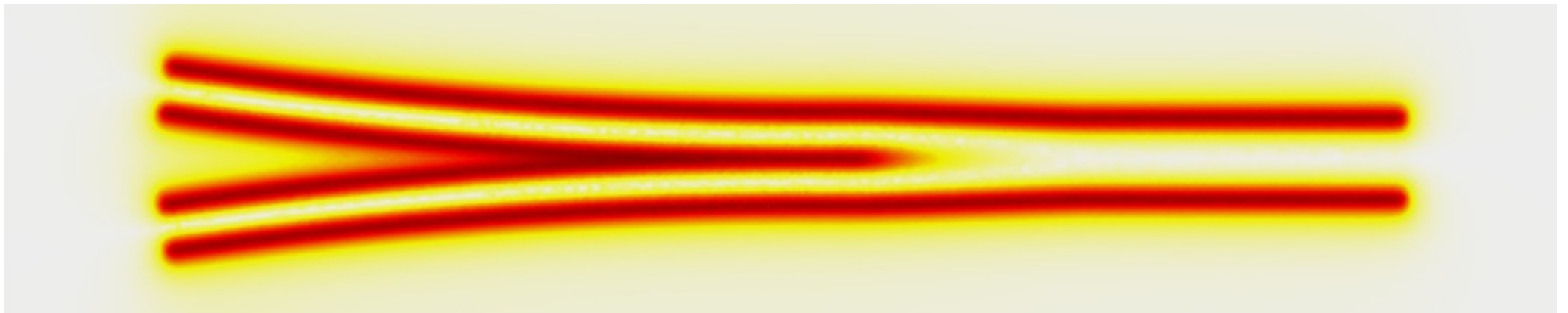
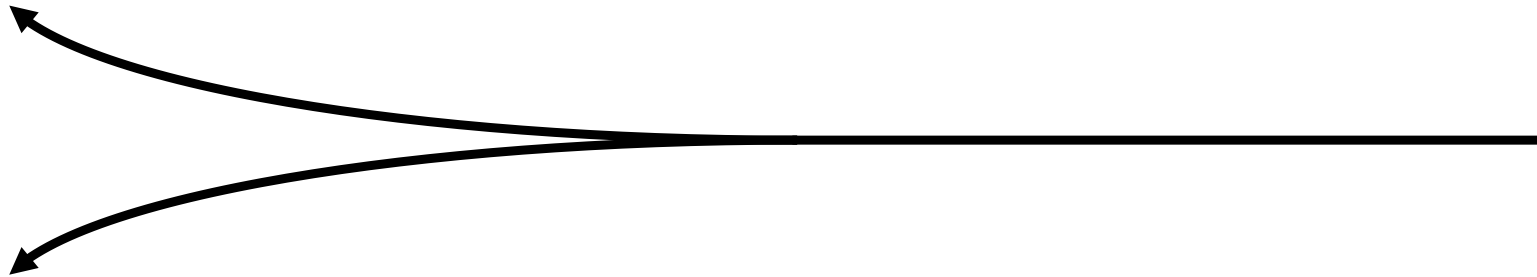
Splitting of a molecular beam

Idea:

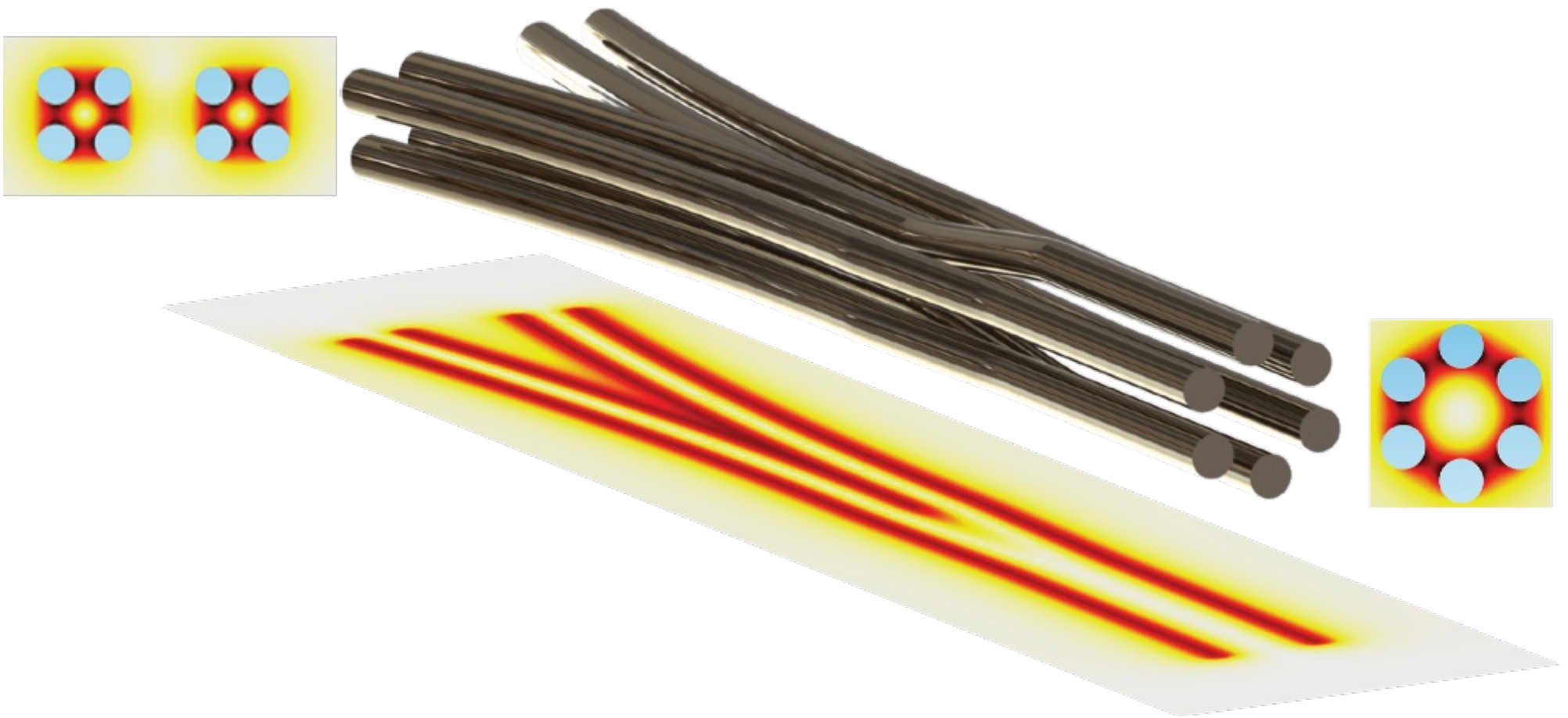
Split single beam into probe and reference beam



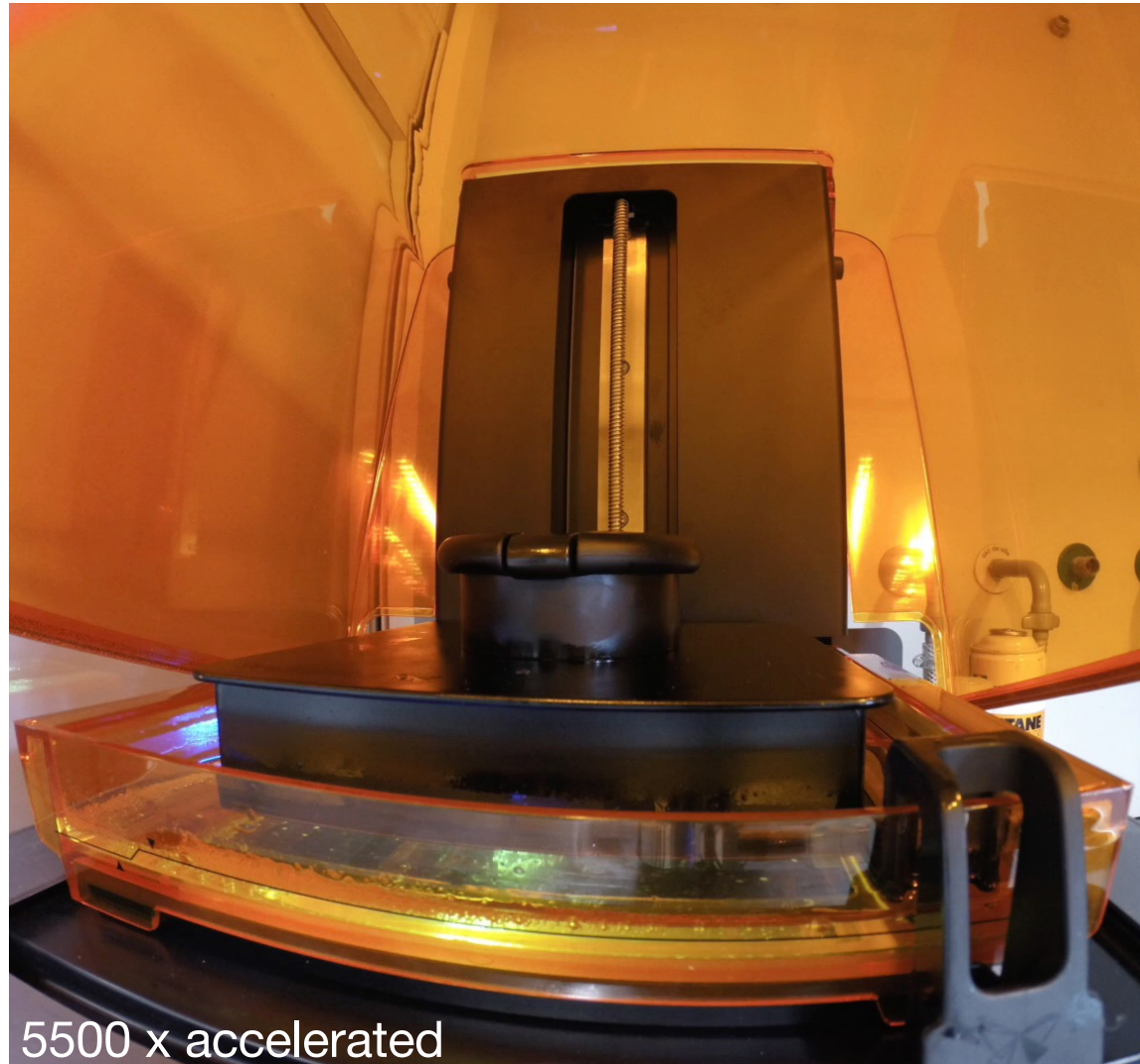
Splitting of a molecular beam



3D structure



Making a Molecular Beam Splitter

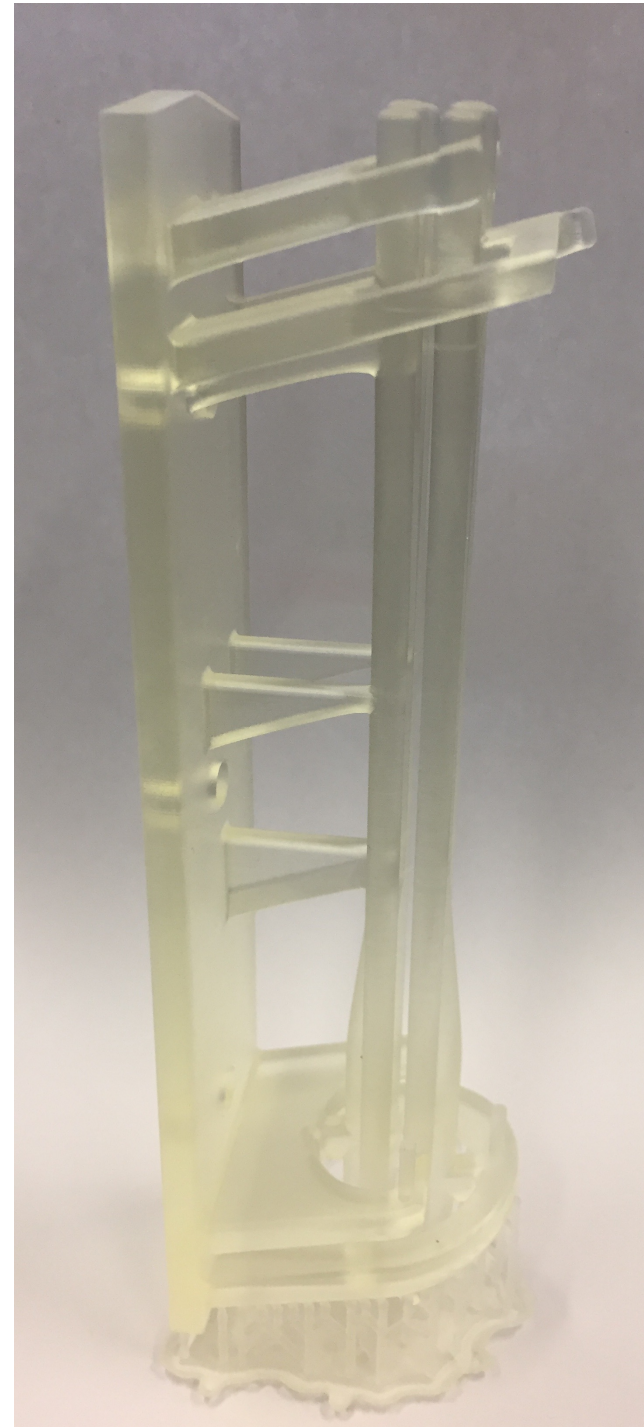


In reality: 25 h

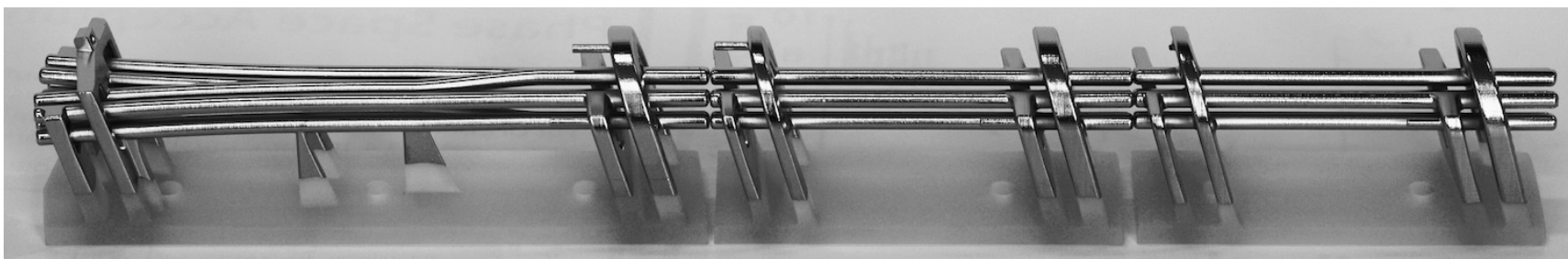
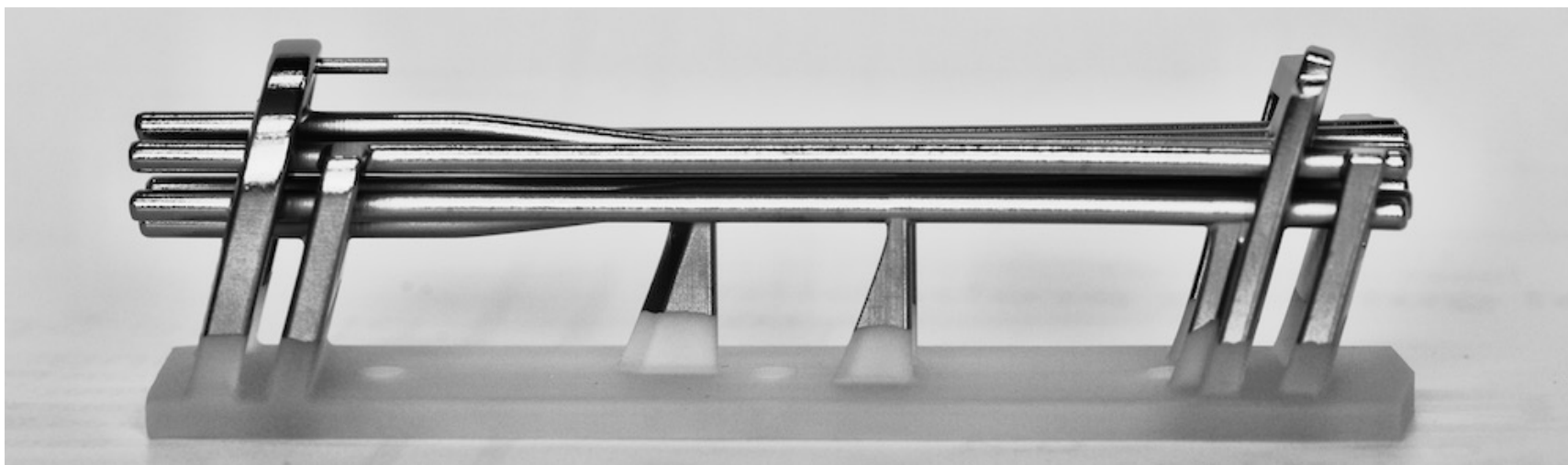
3D printed
PMMA (Plexiglass)
structure



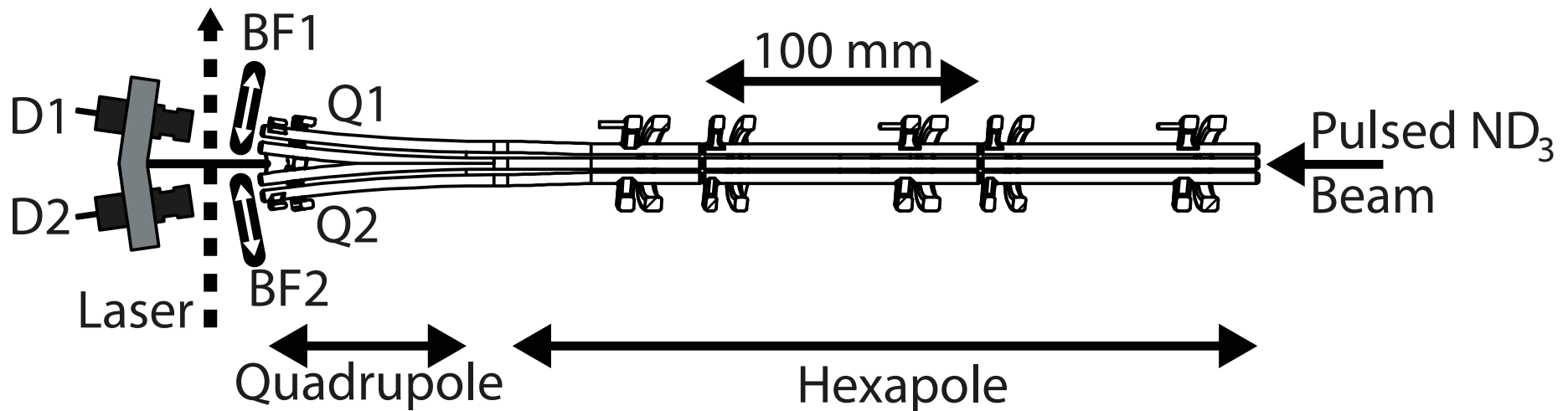
Obtain required
conductivity through
electroplating



A 3D-Printed Beam Splitter for Polar Neutral Molecules



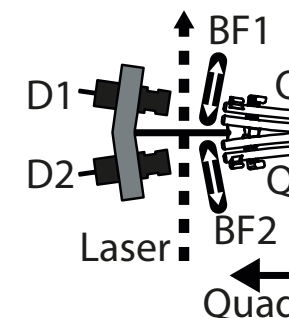
Experimental Setup



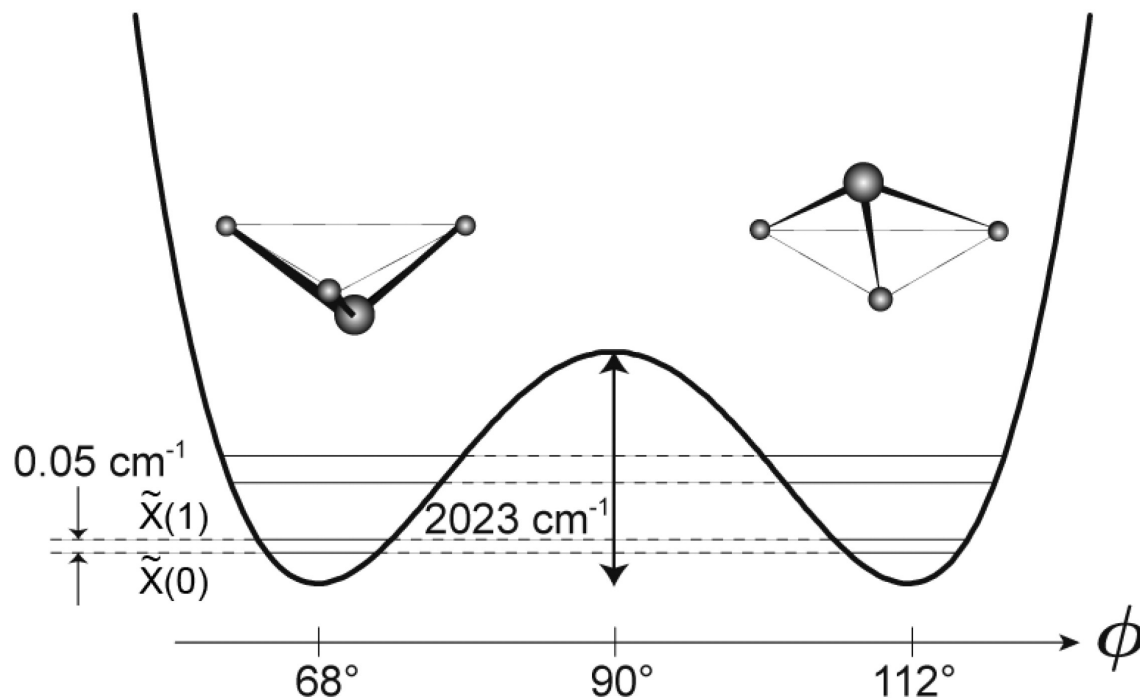
Beam-Splitter

Use REMPI for detection

One laser to ionise, two ion detectors to capture signals from each of the beam components



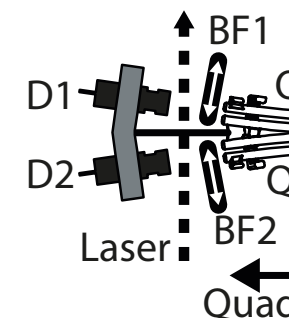
Inversion doubling in Ammonia



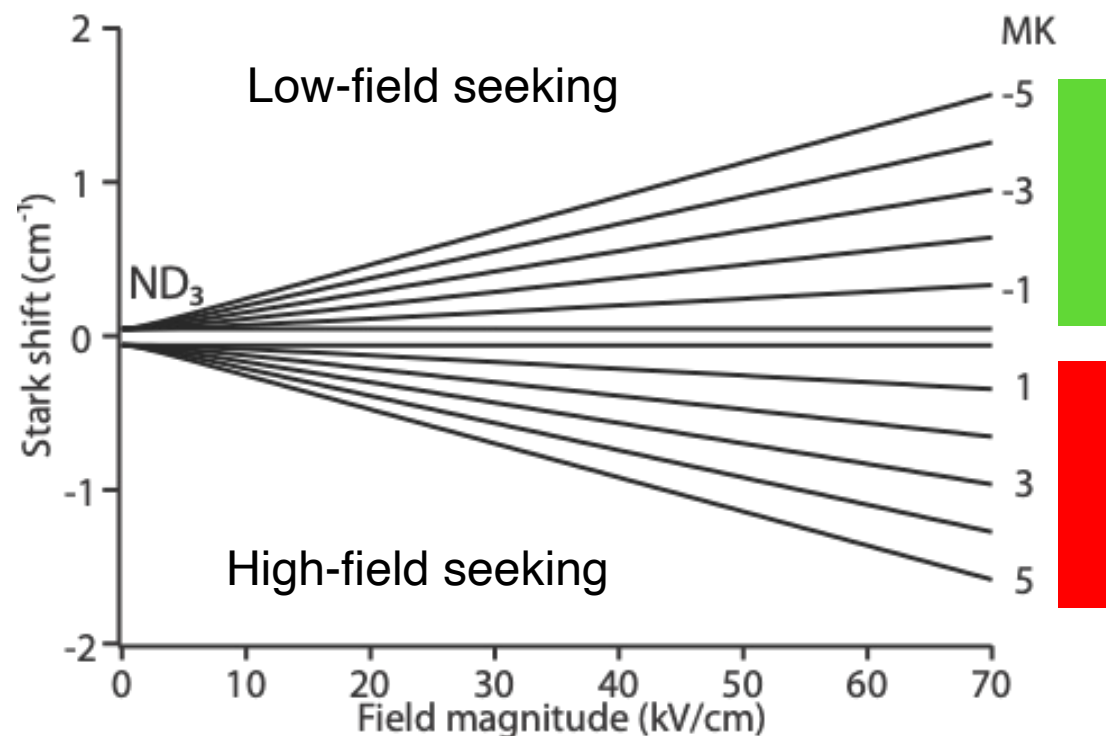
Beam-Splitter

Use REMPI for detection

One laser to ionise, two ion detectors to capture signals from each of the beam components



Stark Effect in Ammonia (again)



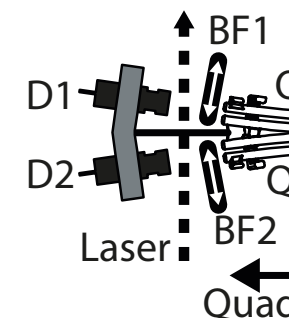
Can be guided in DC electric fields

Are not guided in DC electric fields

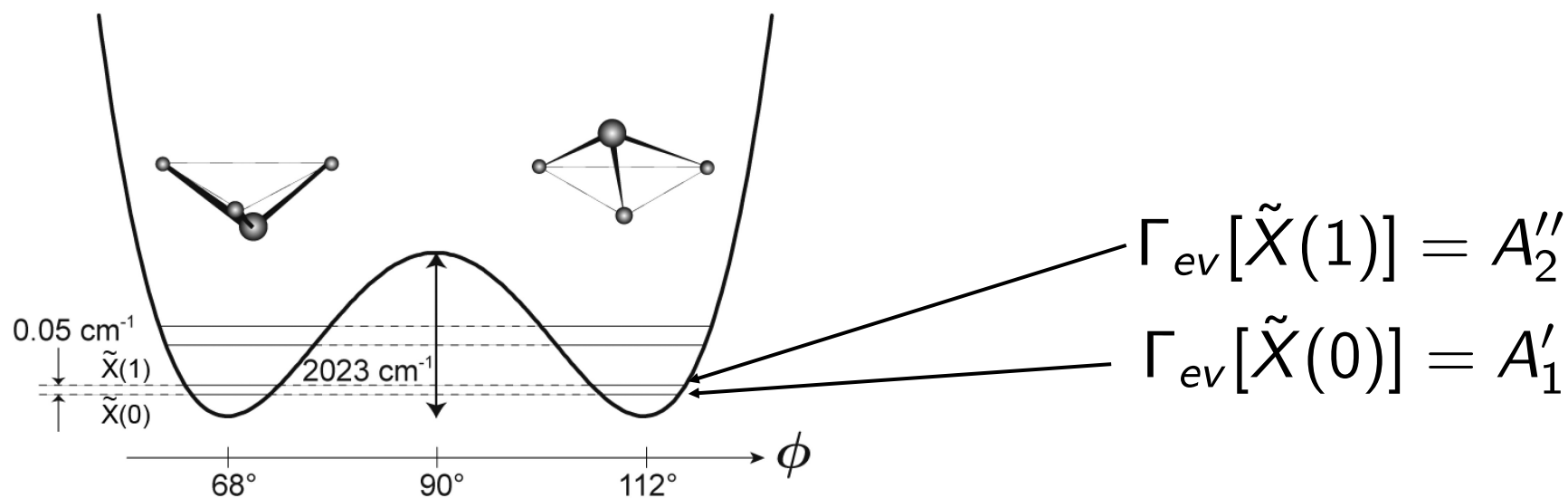
Beam-Splitter

Use REMPI for detection

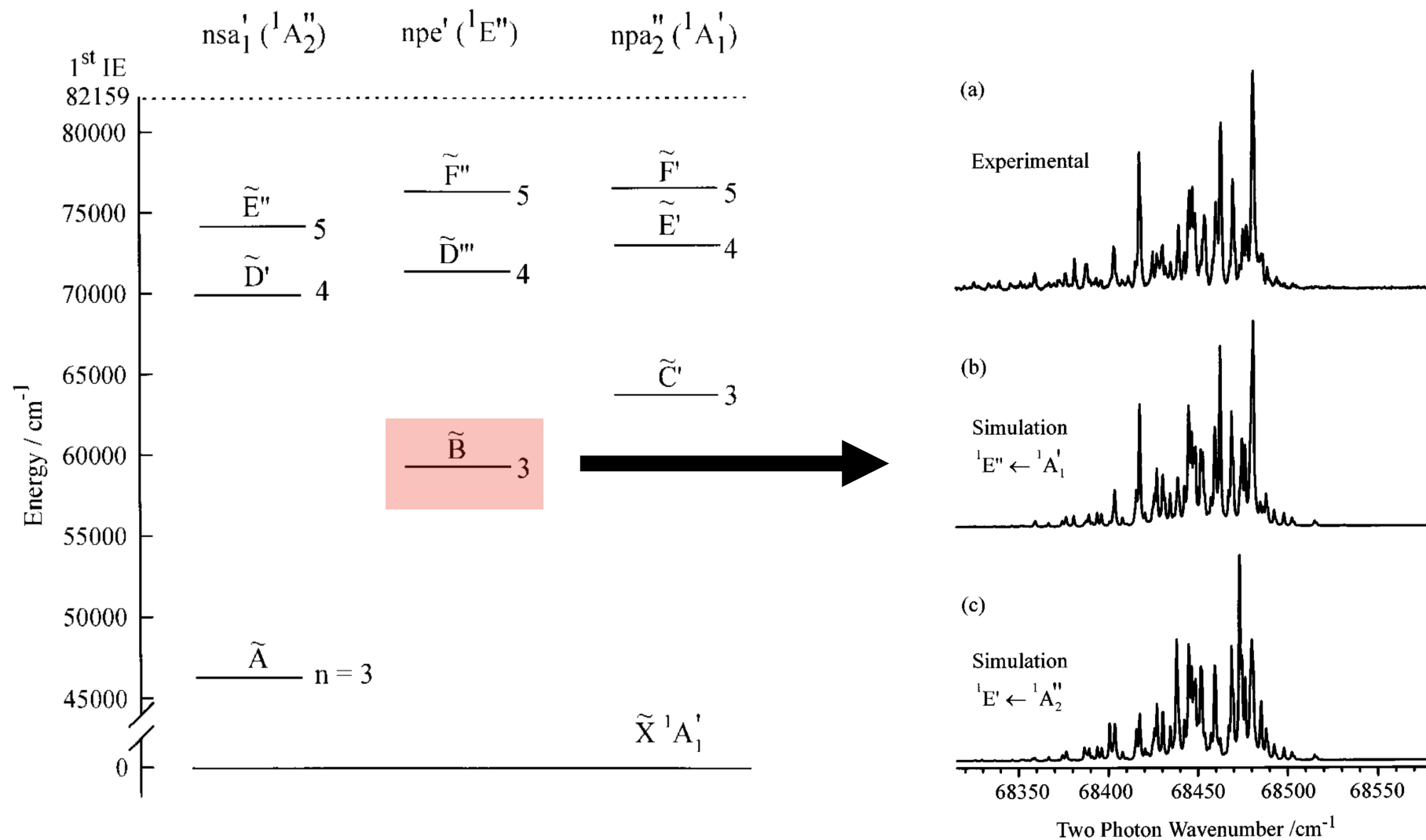
One laser to ionise, two ion detectors to capture signals from each of the beam components



REMPI of Ammonia (ND_3): vibronic symmetry selection rules



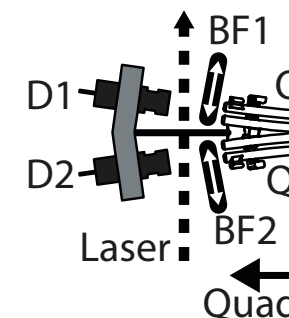
REMPI of ammonia



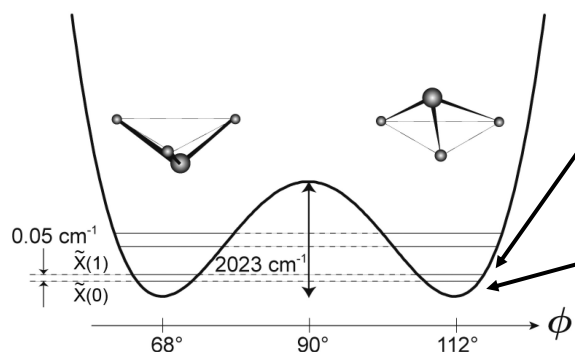
Beam-Splitter

Use REMPI for detection

One laser to ionise, two ion detectors to capture signals from each of the beam components



REMPI of Ammonia: vibronic symmetry selection rules



$$\Gamma_{ev}[\tilde{X}(1)] = A_2''$$

$$\Gamma_{ev}[\tilde{X}(0)] = A_1'$$

$$\Gamma_v[\tilde{B}(v_2 = \text{even})] = A_1'$$

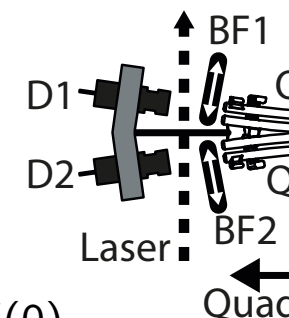
$$\Gamma_v[\tilde{B}(v_2 = \text{odd})] = A_1''$$

$$\tilde{B}(v_2 = \text{even}) \leftarrow \tilde{X}(0); \tilde{B}(v_2 = \text{odd}) \not\leftarrow \tilde{X}(0)$$

$$\tilde{B}(v_2 = \text{odd}) \leftarrow \tilde{X}(1); \tilde{B}(v_2 = \text{even}) \not\leftarrow \tilde{X}(1)$$

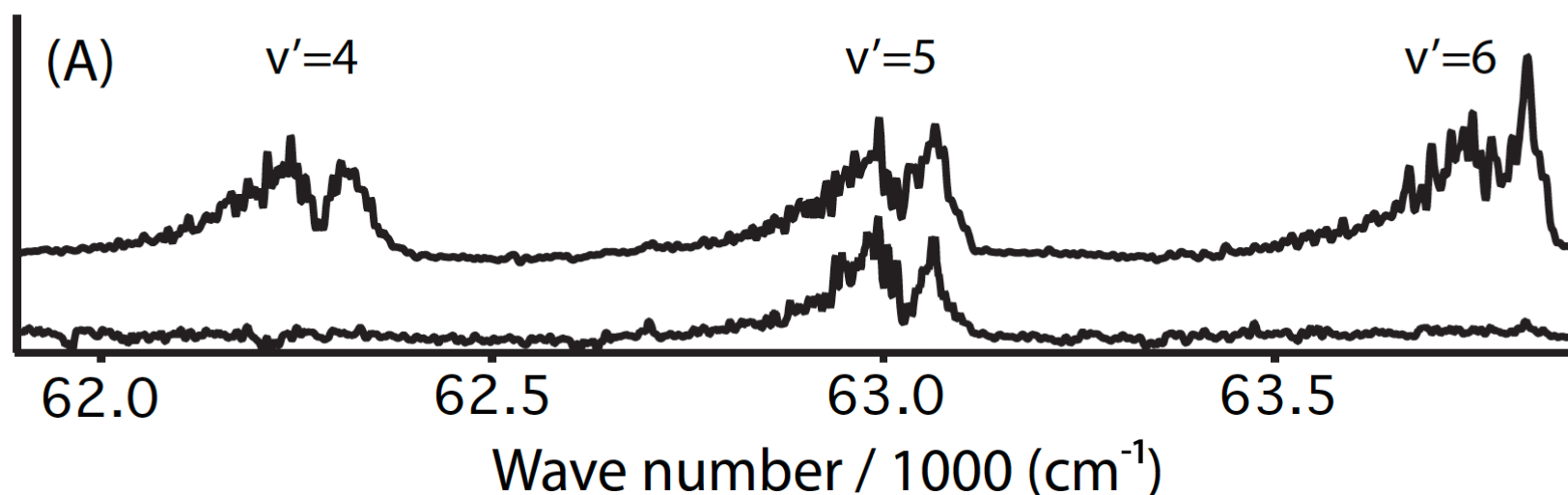
Beam-Splitter

Use REMPI for detection
One laser to ionise, two ion detectors to capture signals
from each of the beam components



REMPI of Ammonia:
vibronic symmetry selection rules

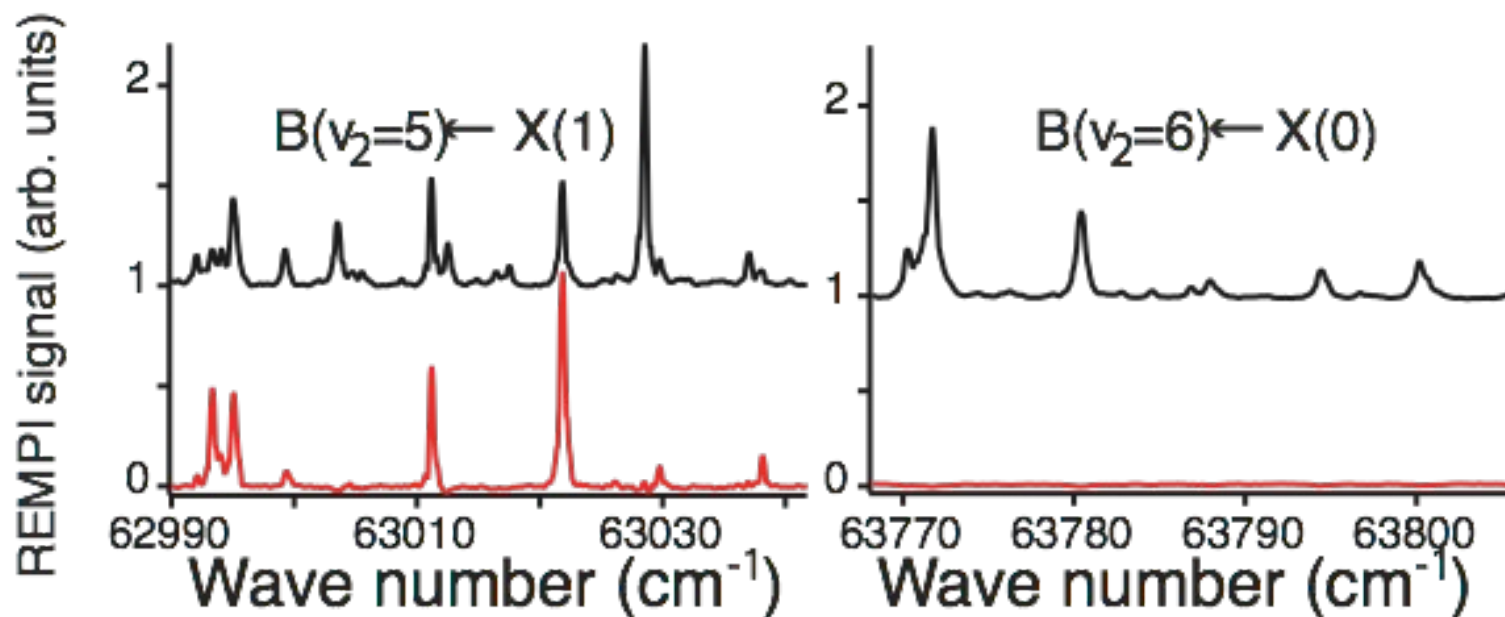
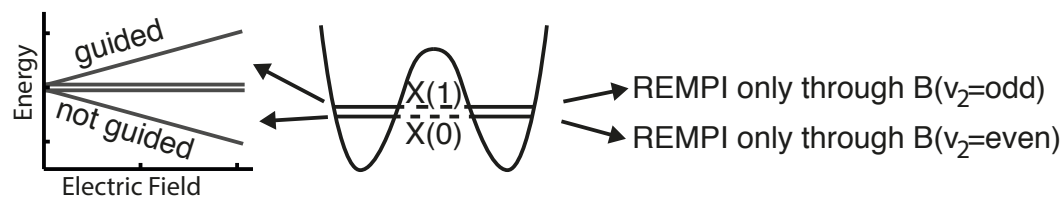
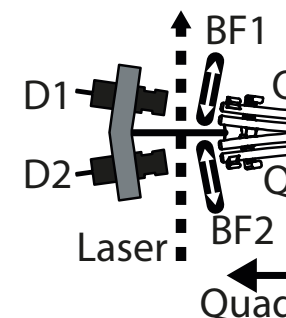
$$\tilde{B}(v_2 = \text{even}) \leftarrow \tilde{X}(0); \tilde{B}(v_2 = \text{odd}) \not\leftarrow \tilde{X}(0)$$

$$\tilde{B}(v_2 = \text{odd}) \leftarrow \tilde{X}(1); \tilde{B}(v_2 = \text{even}) \not\leftarrow \tilde{X}(1)$$


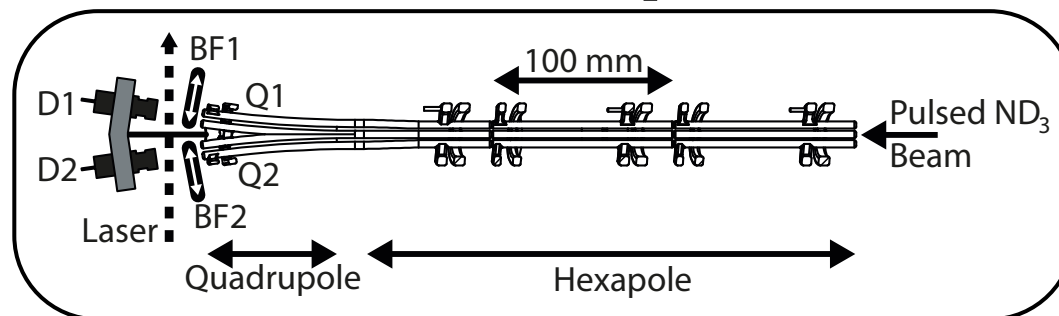
Beam-Splitter

Use REMPI for detection

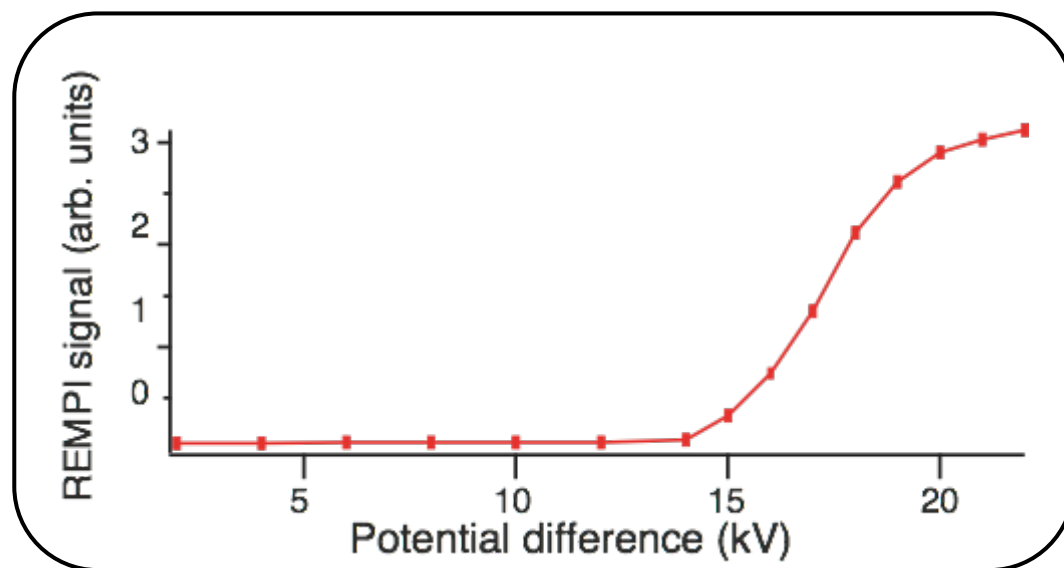
One laser to ionise, two ion detectors to capture signals from each of the beam components



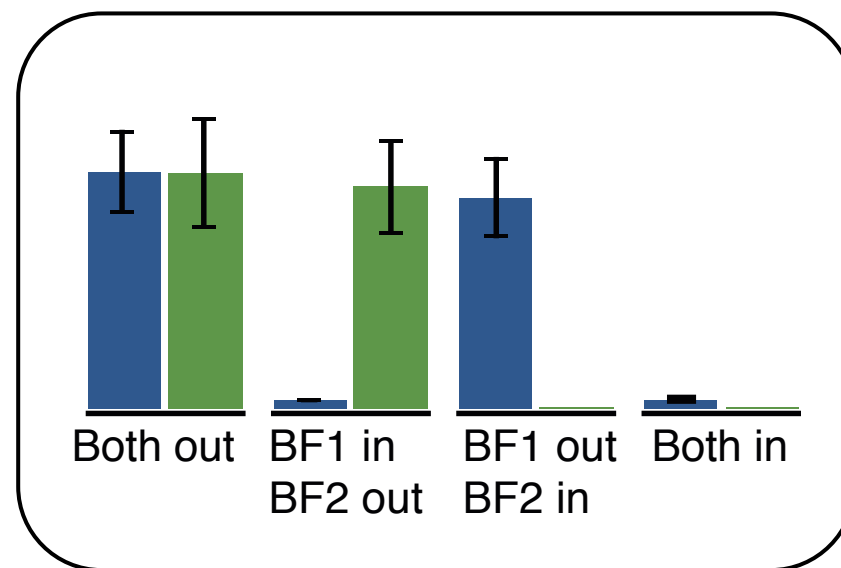
Beam-Splitter



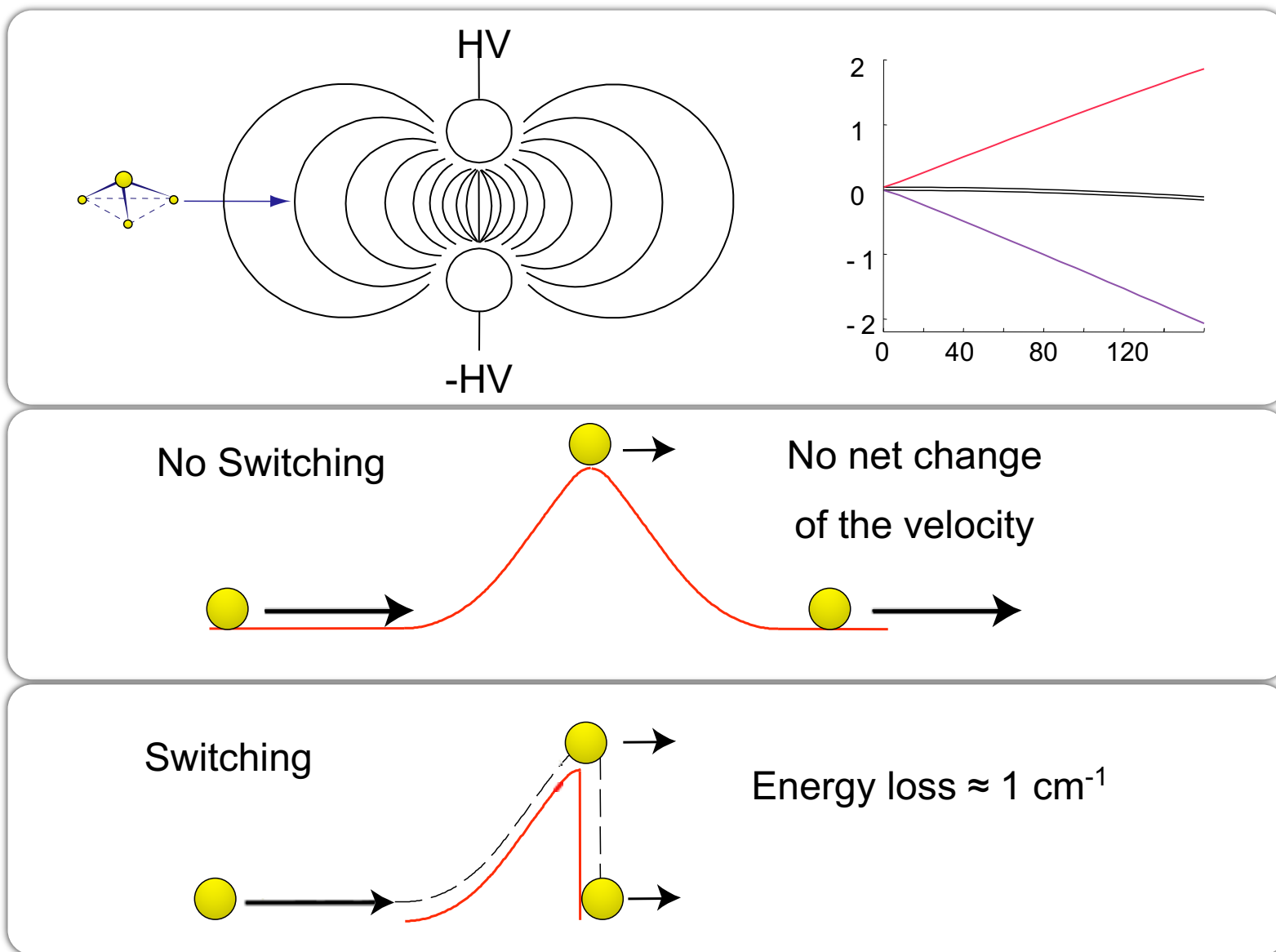
Guiding force increases with electric field



Mechanical blocking of beams



Stark deceleration

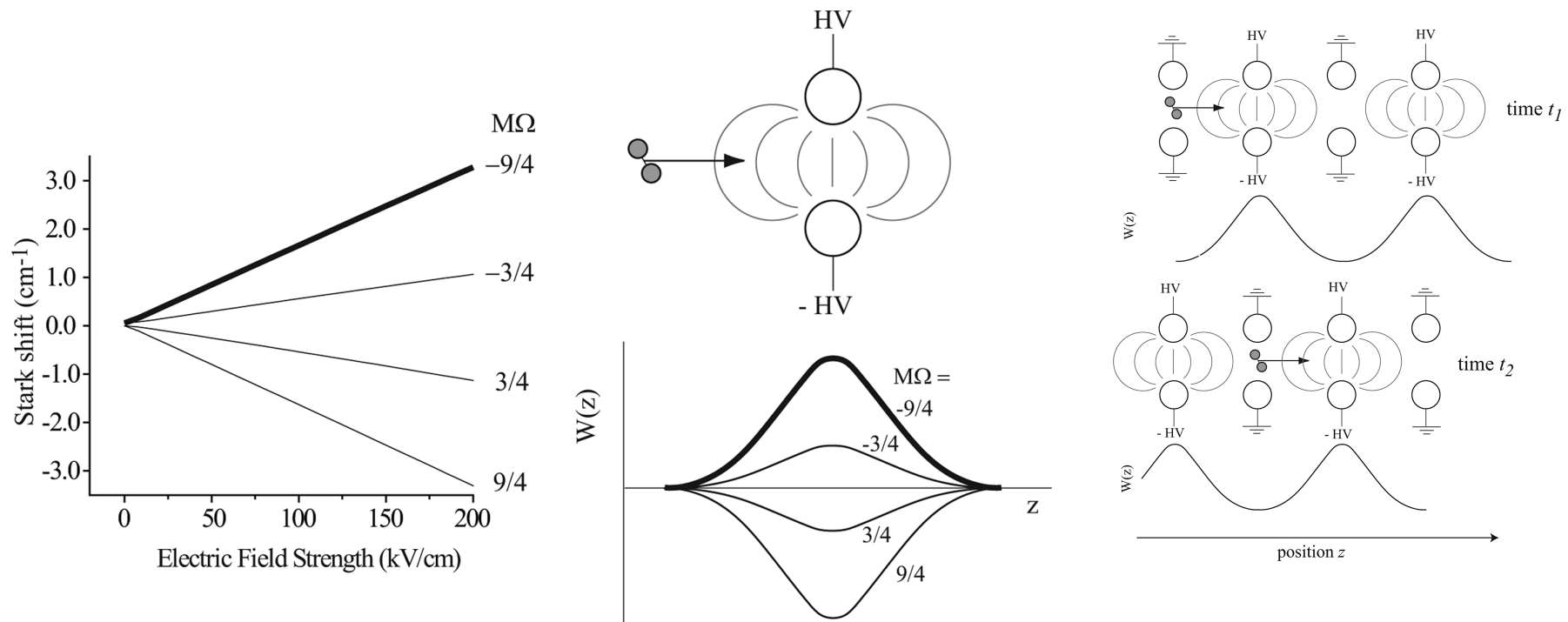


Stark deceleration

H. L. Bethlem and G. Meijer, Int. Rev. Phys. Chem. 22, 73 (2003).

H. L. Bethlem et al., Phys. Rev. Lett. **84**, 5744 (2000).

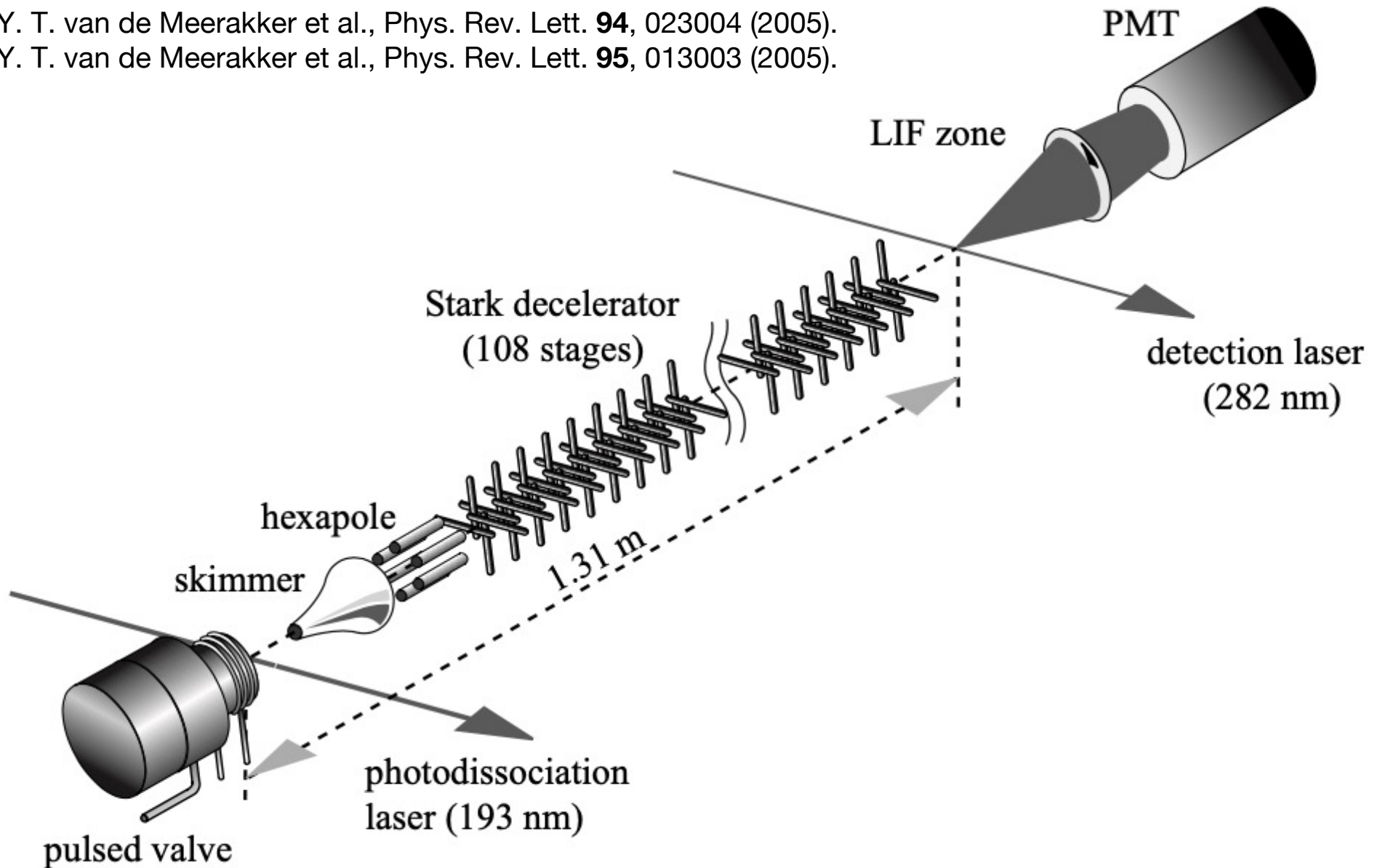
H. L. Bethlem et al., Phys. Rev. Lett. **83**, 1558 (1999).



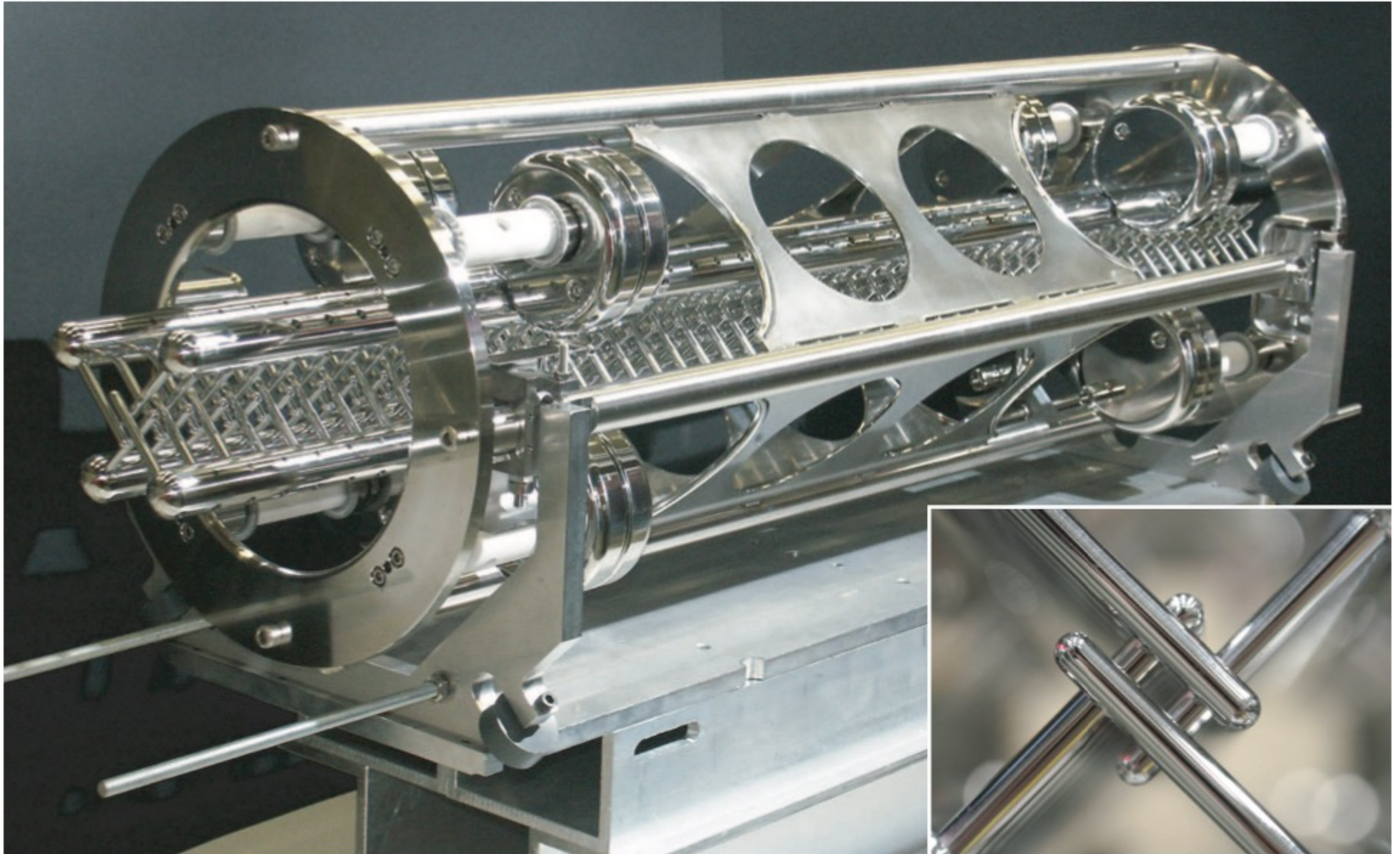
Stark deceleration

S. Y. T. van de Meerakker et al., Phys. Rev. Lett. **94**, 023004 (2005).

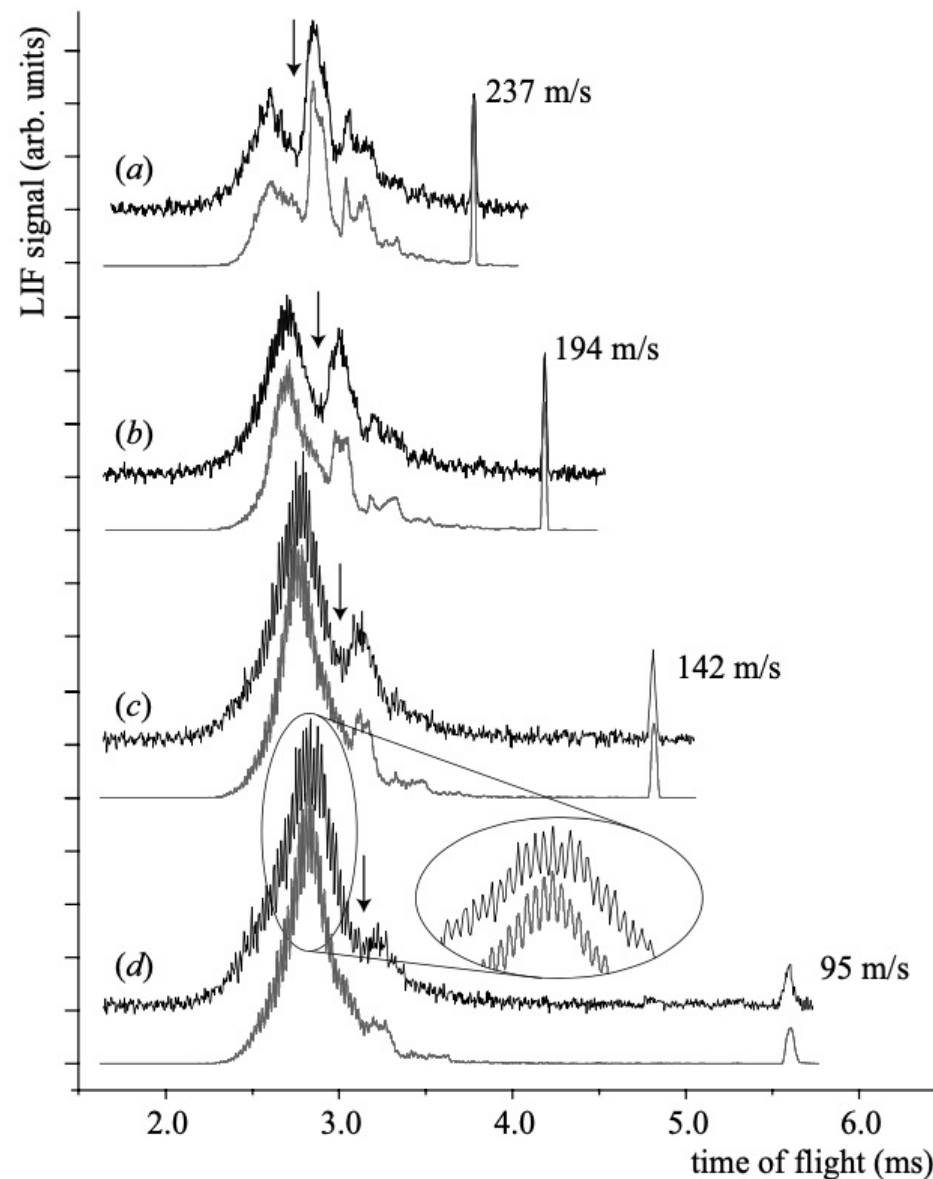
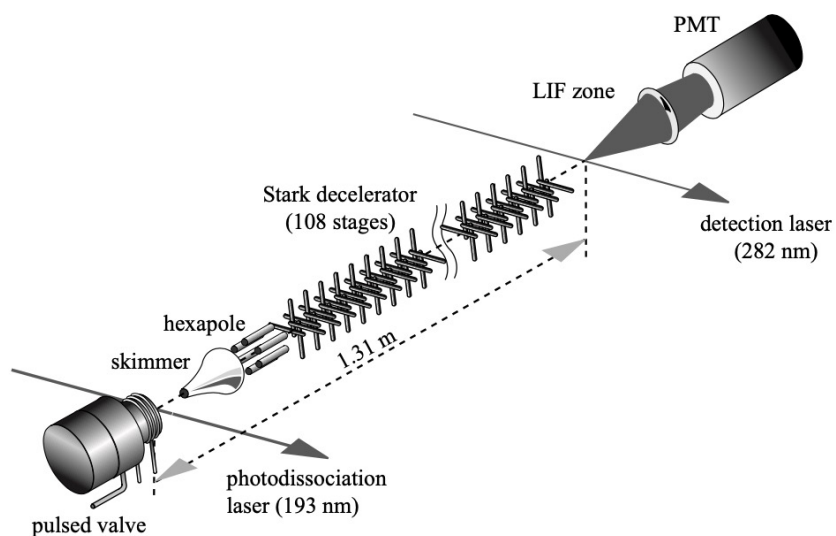
S. Y. T. van de Meerakker et al., Phys. Rev. Lett. **95**, 013003 (2005).



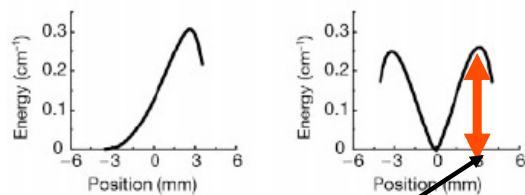
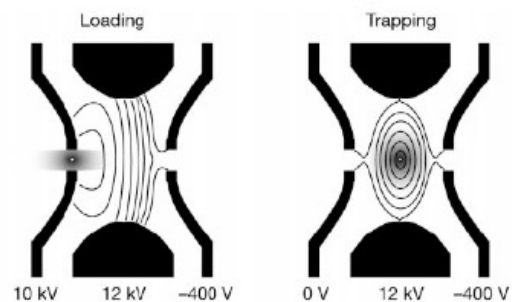
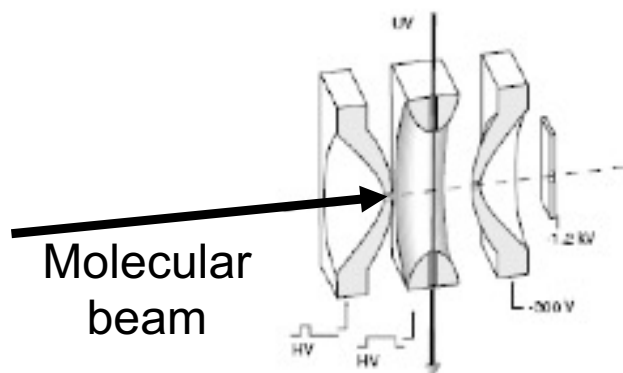
Stark deceleration



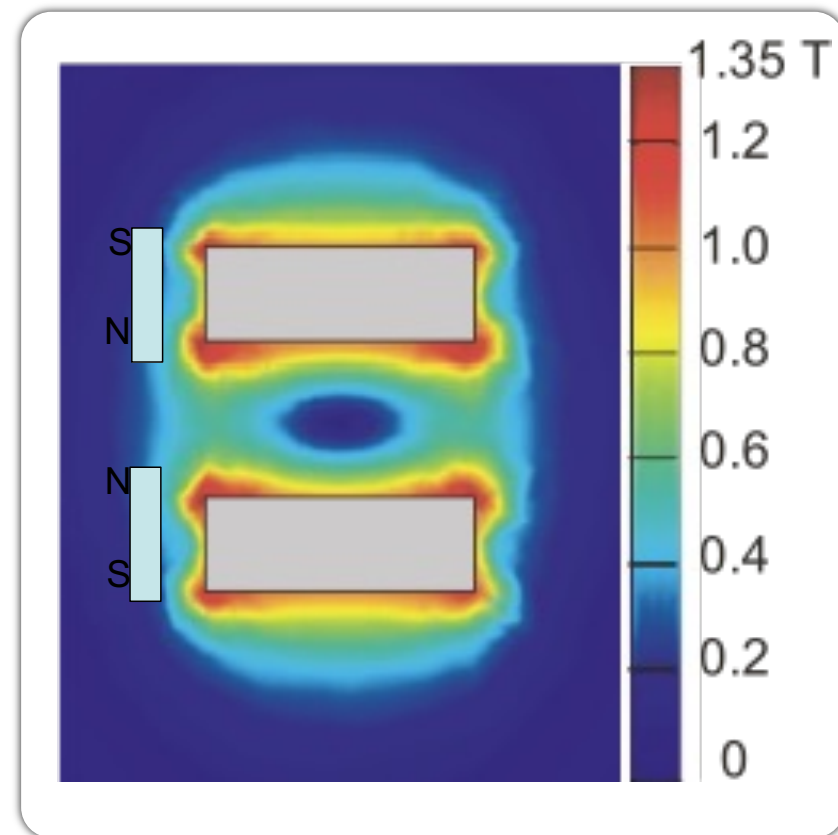
Stark deceleration



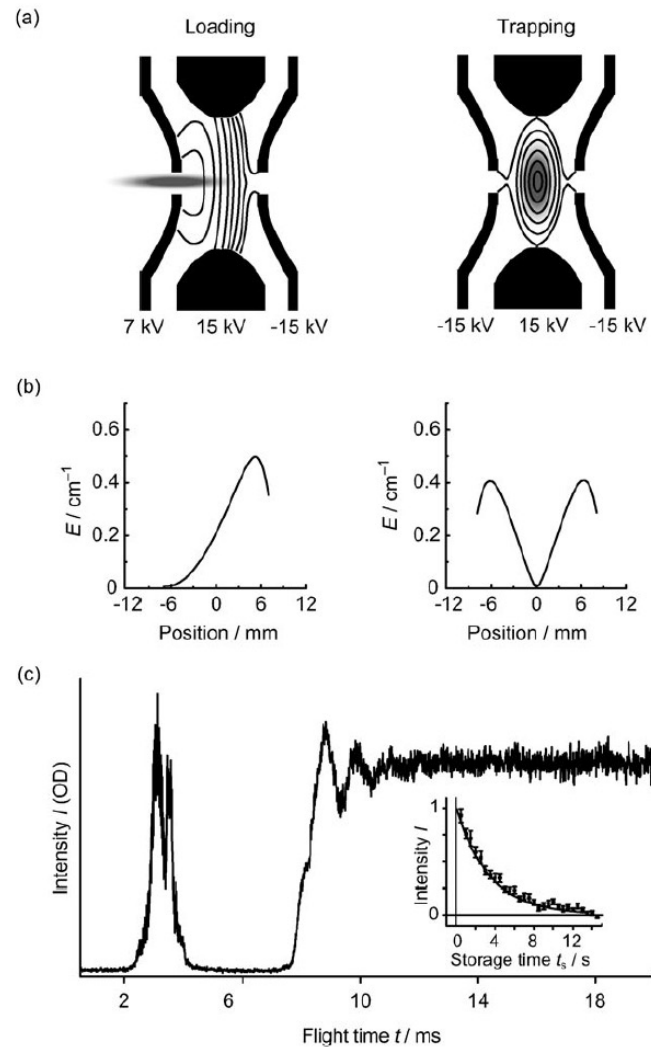
Trapping of molecules



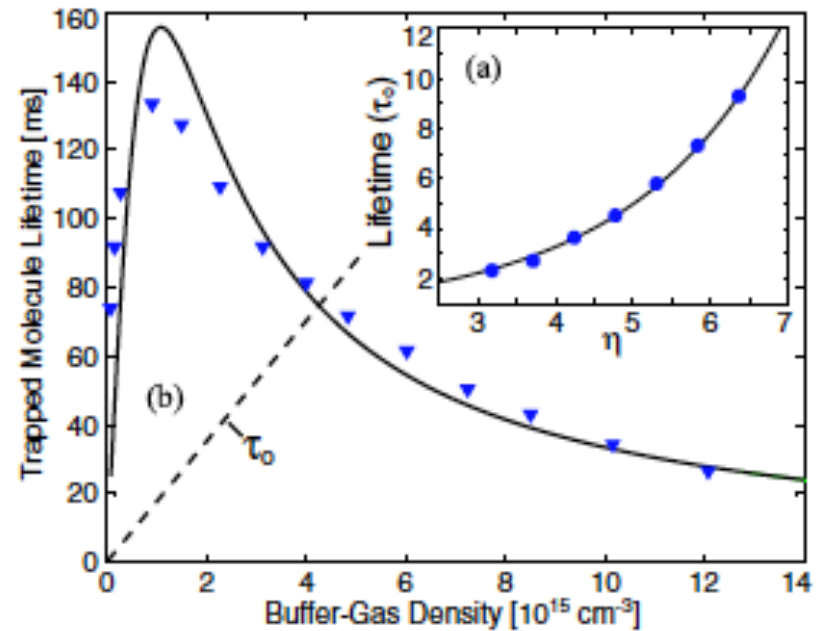
up to 500 mK deep



Trapping of molecules

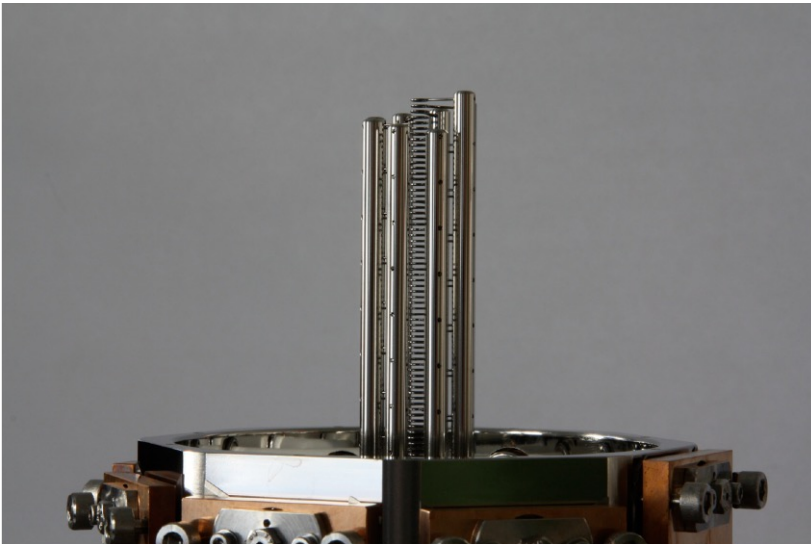


Electrostatic trapping of OH



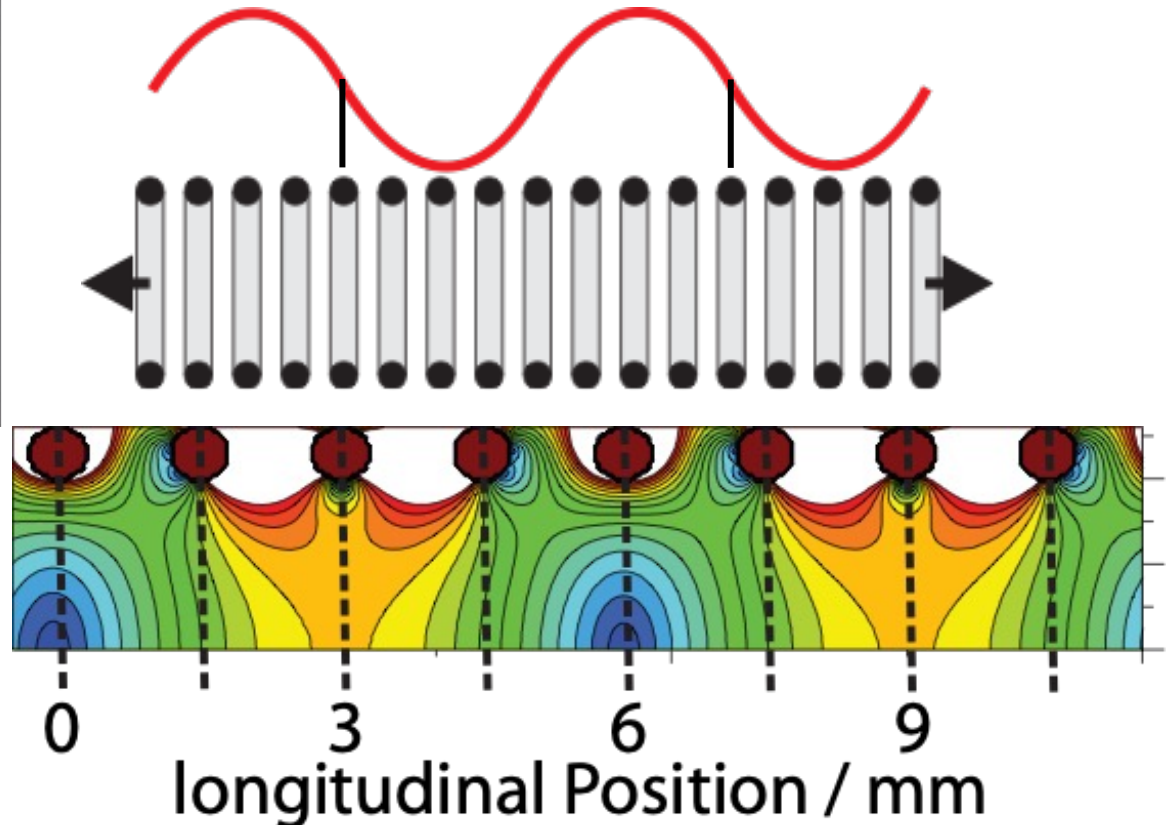
Magnetic trapping of NH

Stark deceleration: Traveling 3D traps

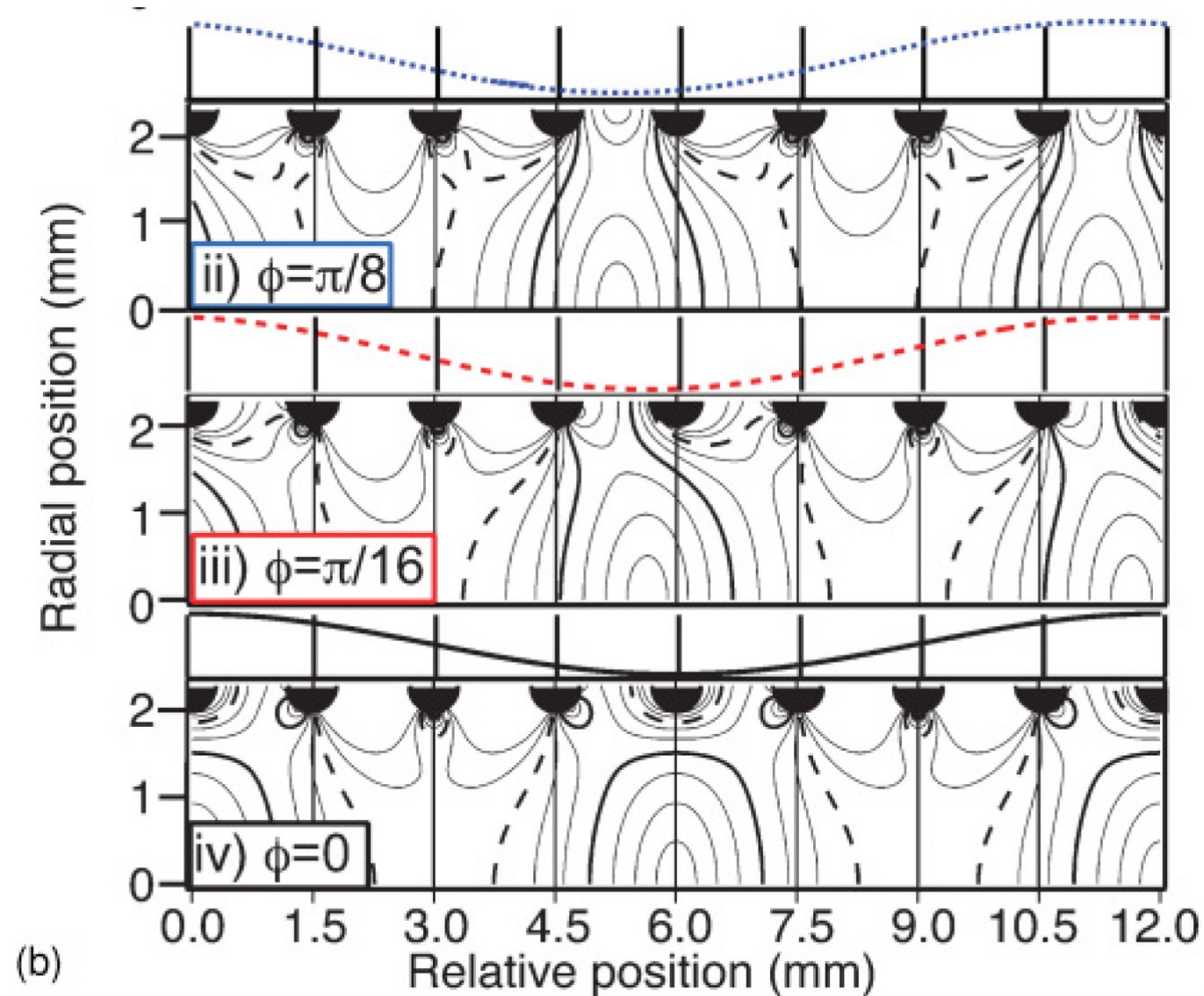


Array of
ring-electrodes

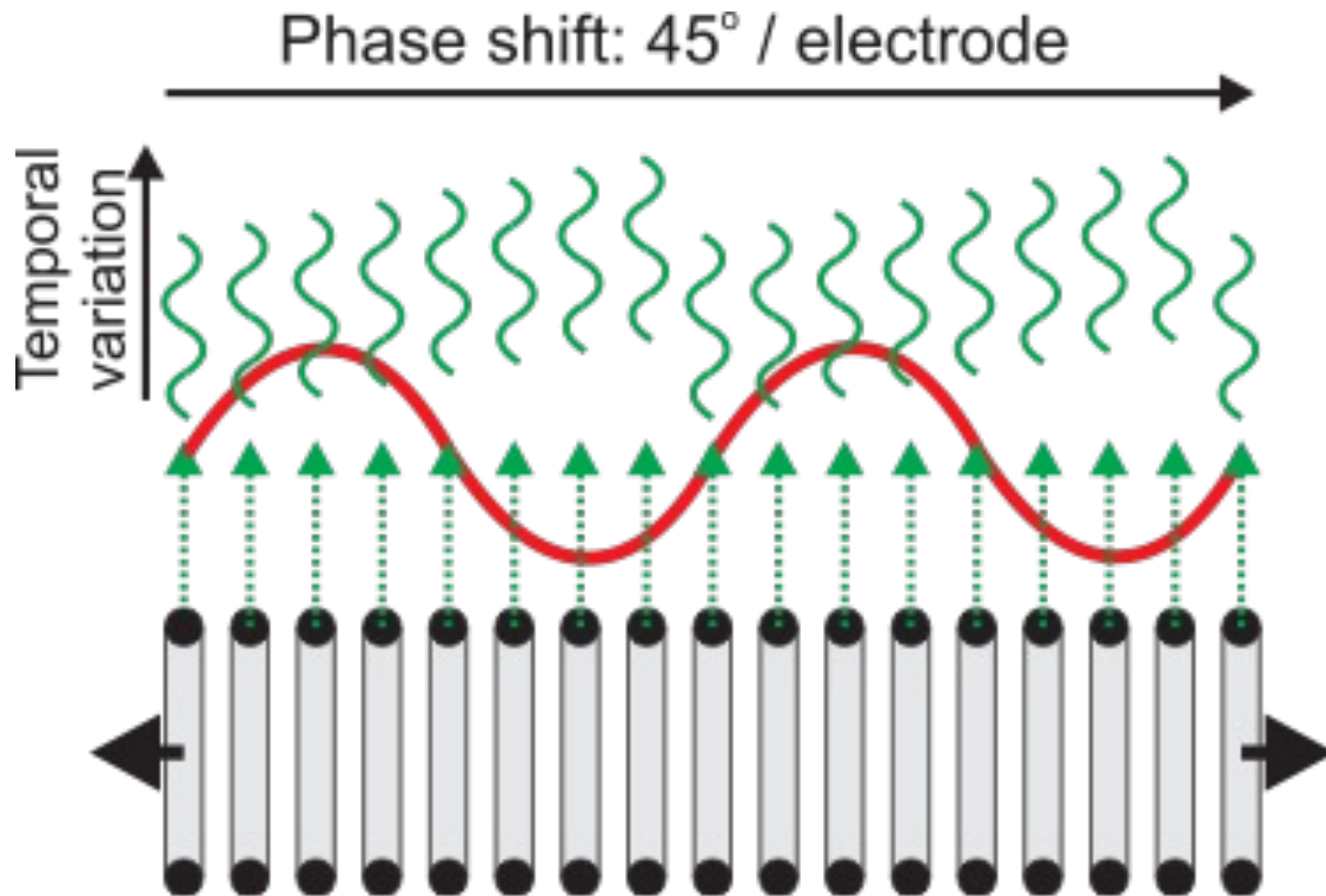
$$V_n = V_0 \cos(\Phi + n\pi/4)$$



$$V_n = V_0 \cos(\Phi(t) + n\pi/4)$$

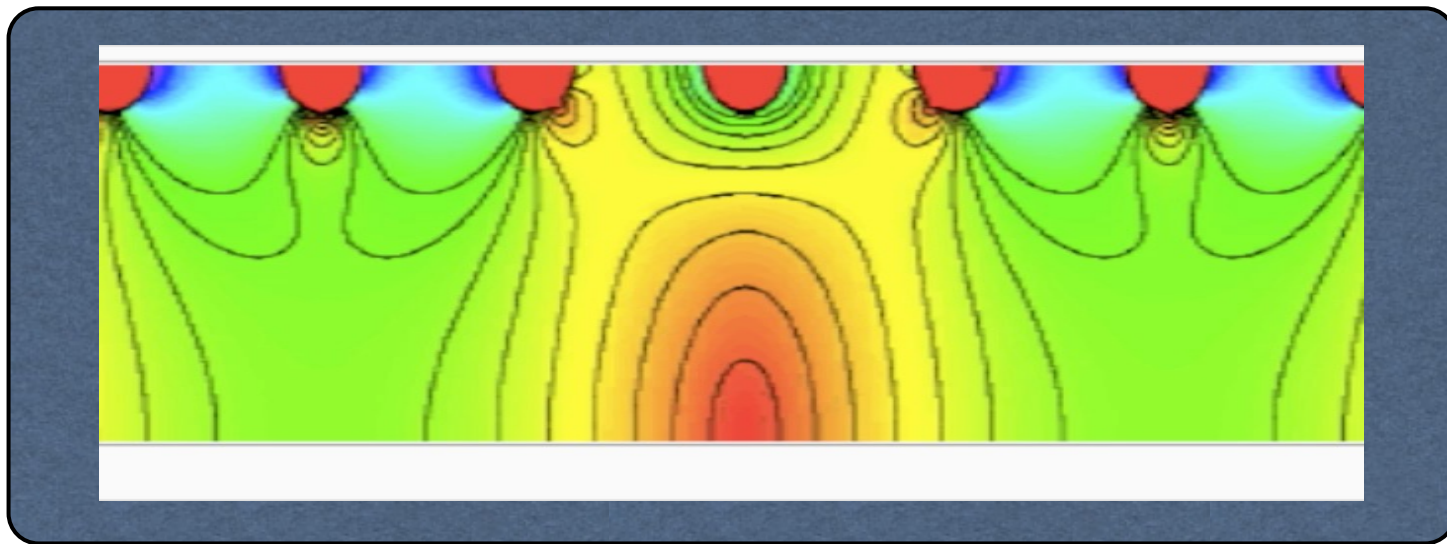


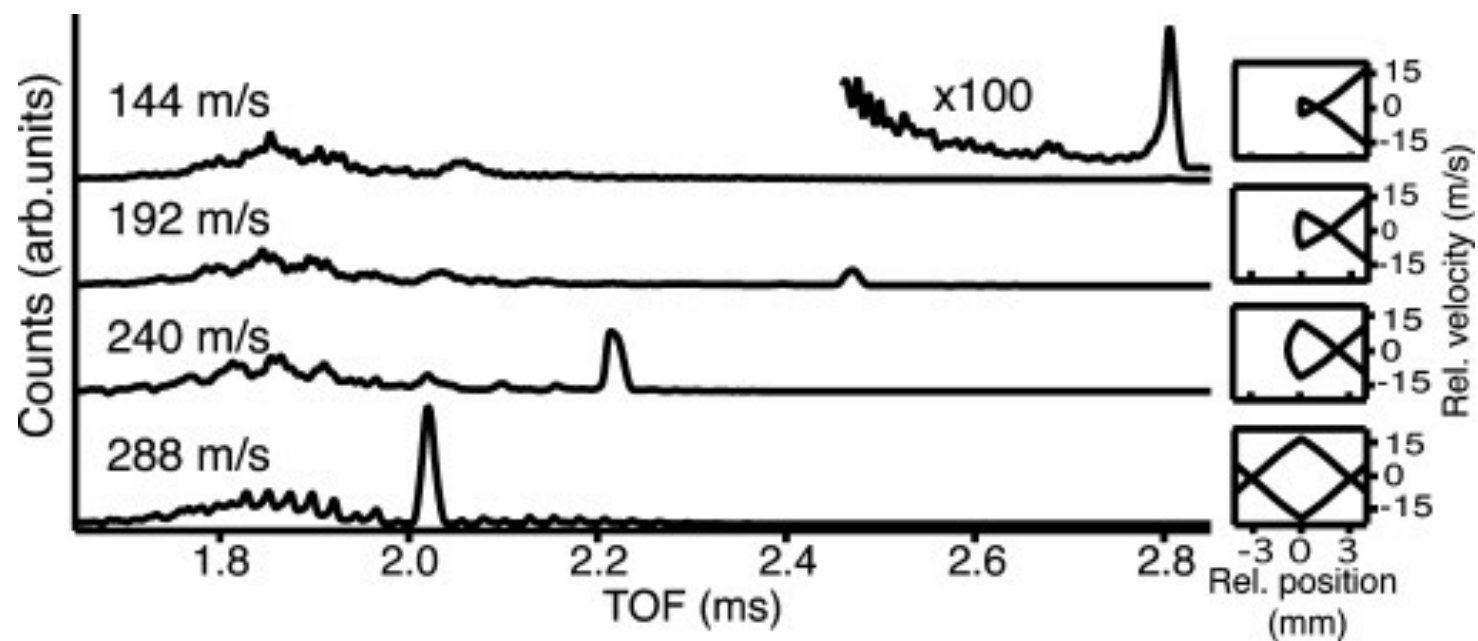
Traveling traps



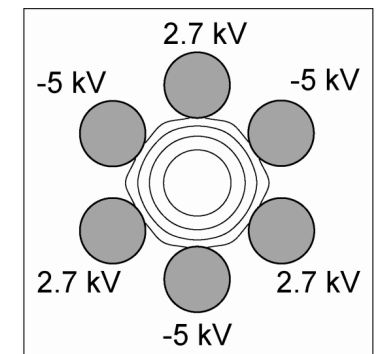
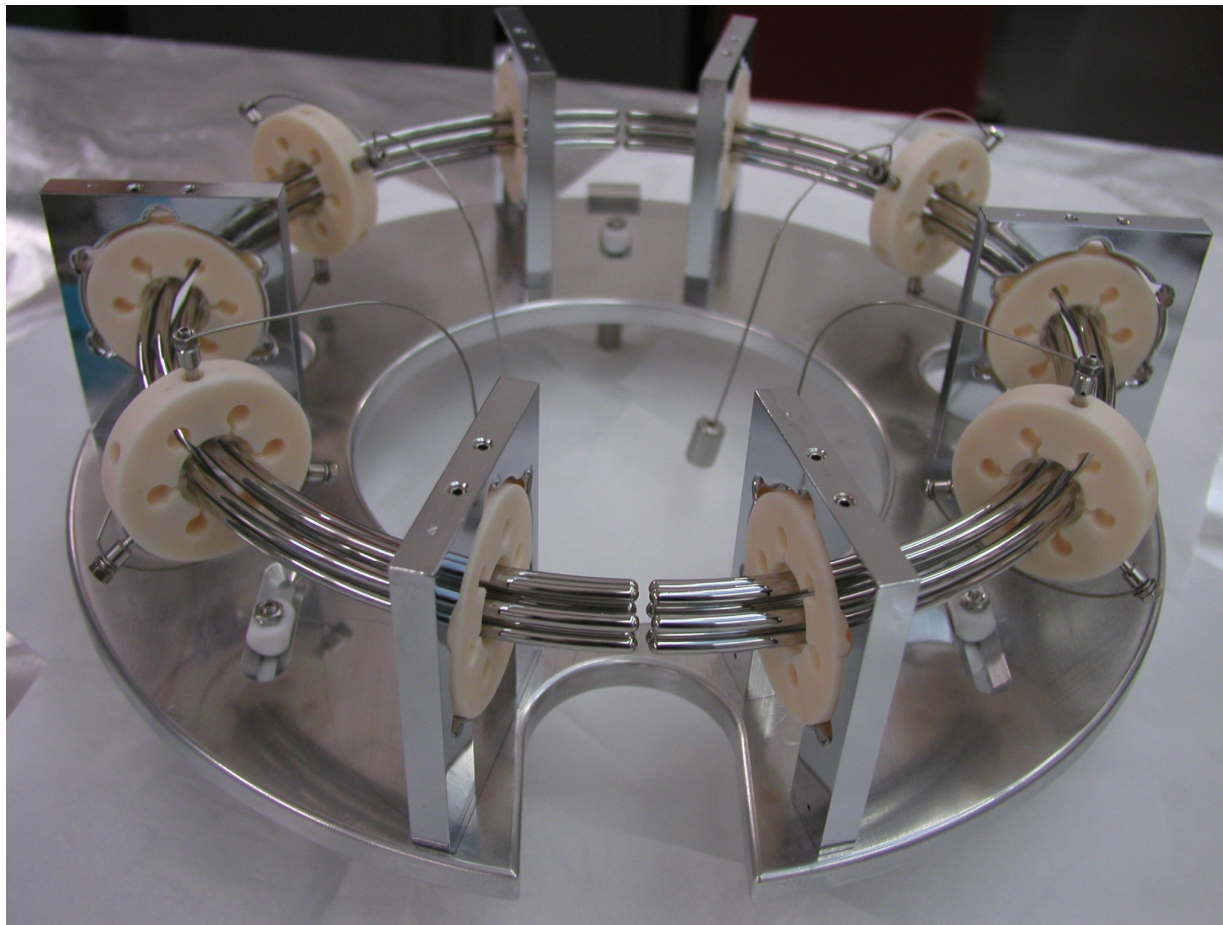
magnetic field-version also exists

Traveling traps

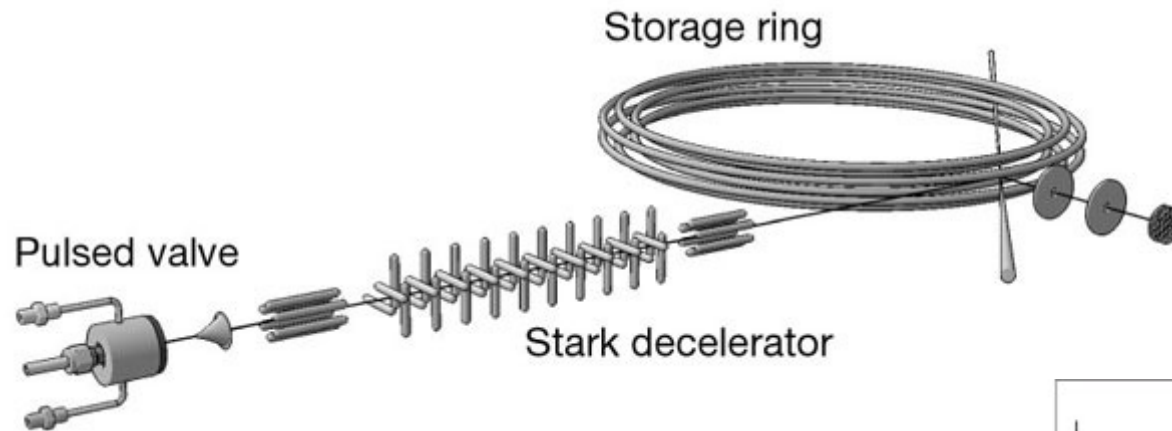




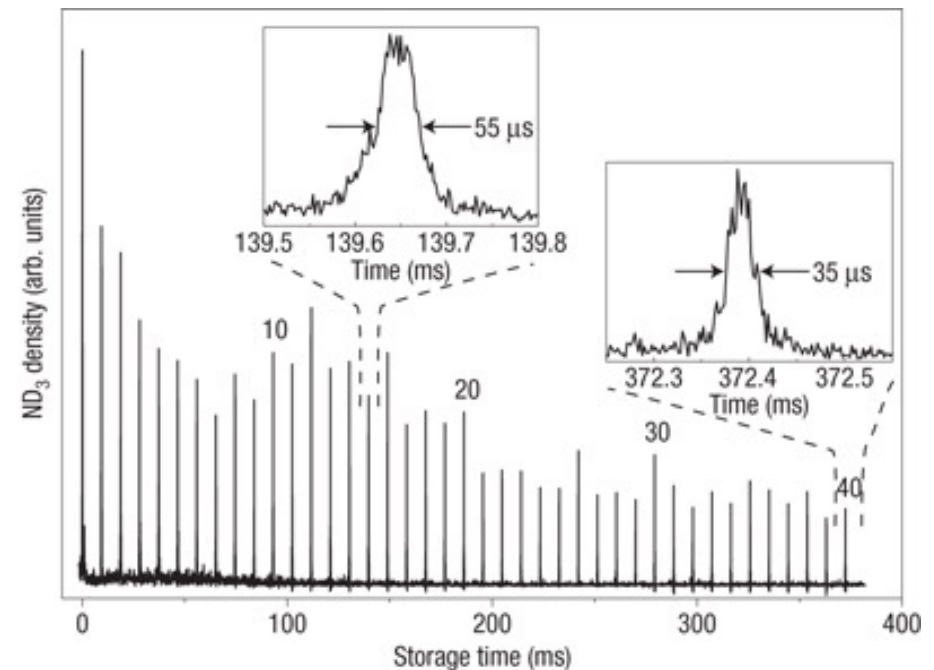
Storage ring for neutral molecules (molecular synchrotron)



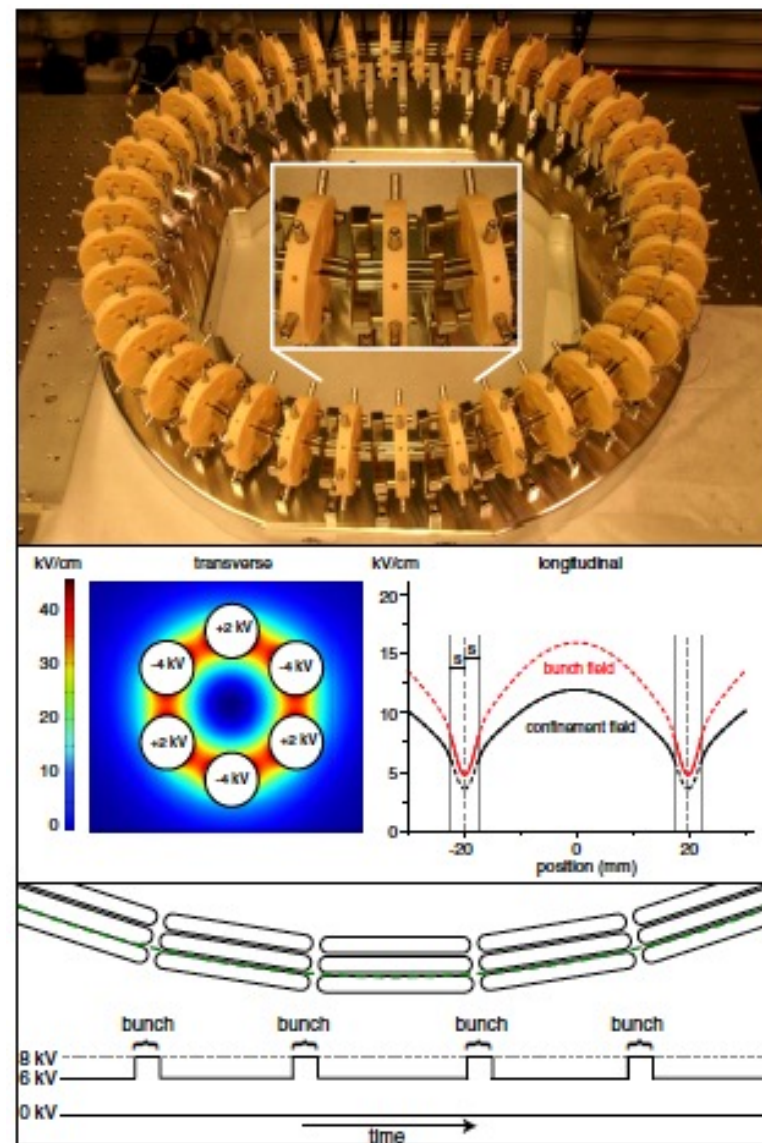
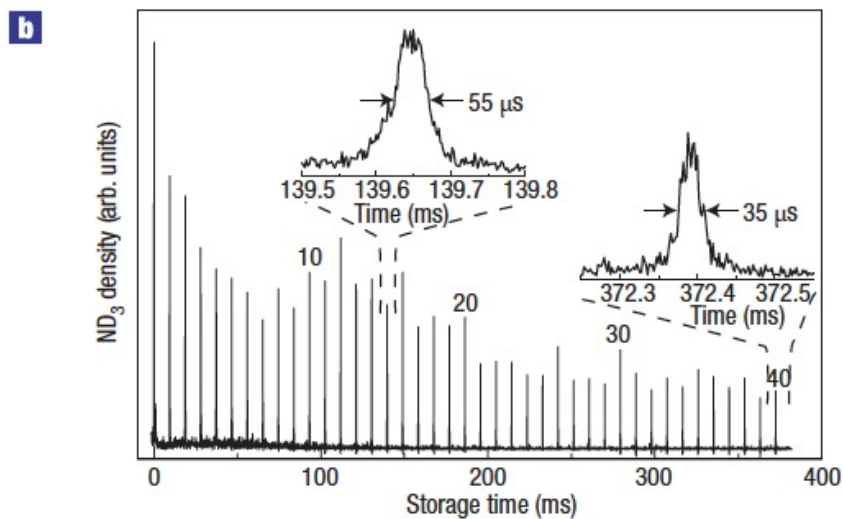
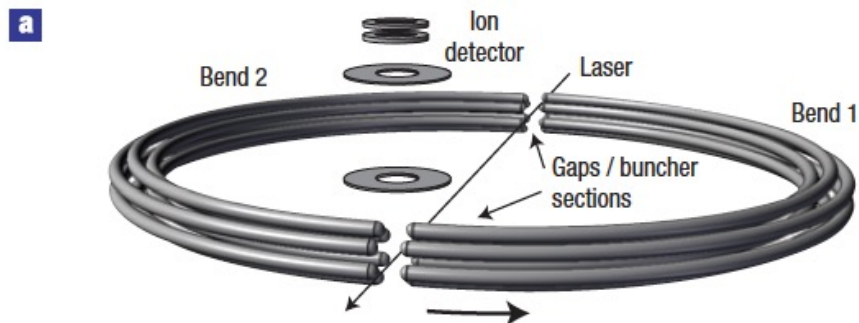
Storage ring for neutral molecules (molecular synchrotron)



Decelerate Molecules prior to loading
Keep packets stored and focused by bunching
techniques

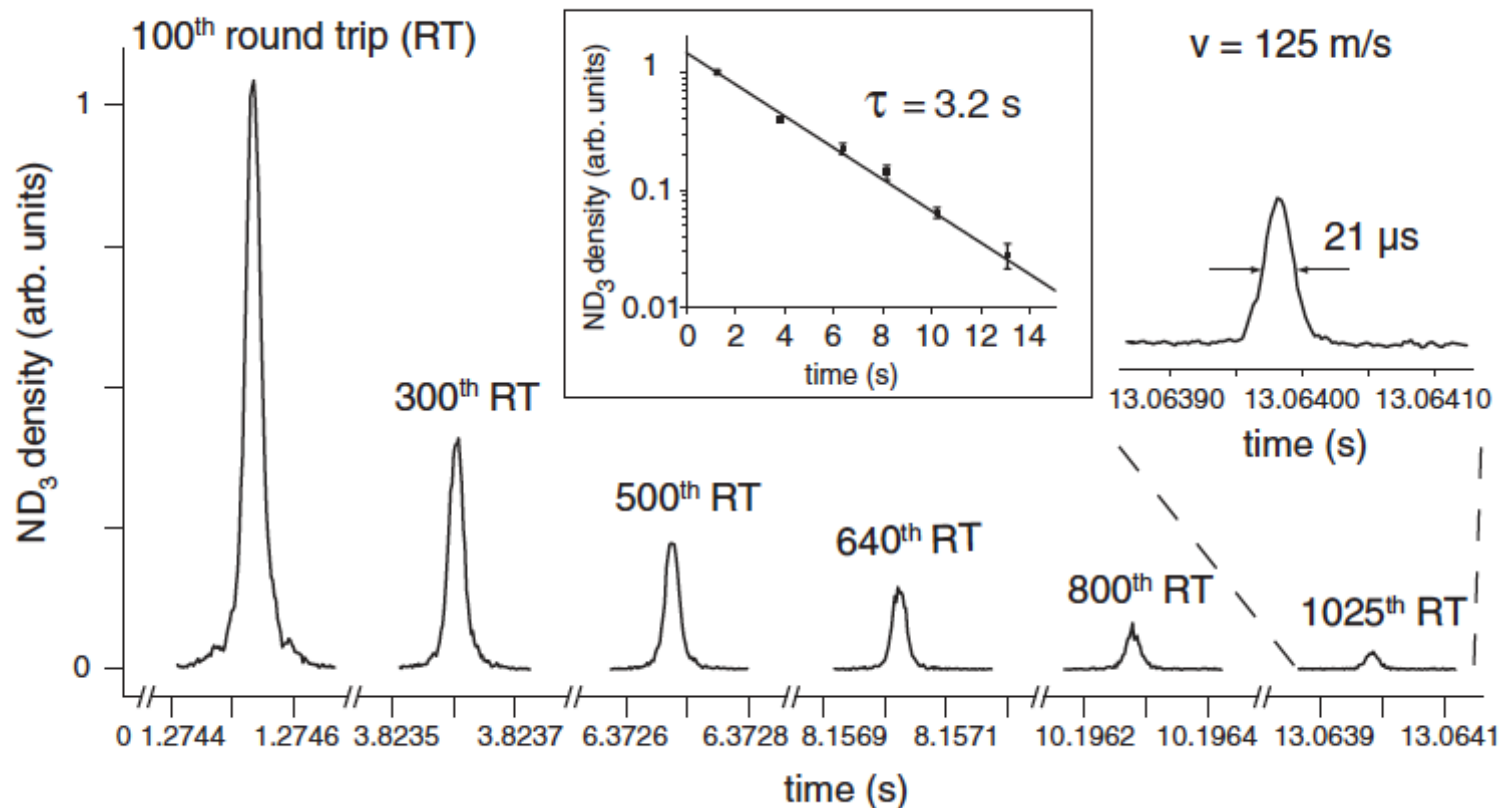


Crompvoets et al., Nature **411**, 174(2001)
Heiner et al., Nature Physics **3**, 115(2007)



Multiple Packets of Neutral Molecules Revolving for over a Mile

Peter C. Zieger,¹ Sebastiaan Y. T. van de Meerakker,¹ Cynthia E. Heiner,¹ Hendrick L. Bethlem,²
André J. A. van Roij,³ and Gerard Meijer¹

a
 Ion
**b**

Multiple Packets of Neutral Molecules Revolving for over a Mile

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 André J. A. van Roij,³ and Gerard Meijer¹

Collision experiments: techniques

Crossed (molecular) beams

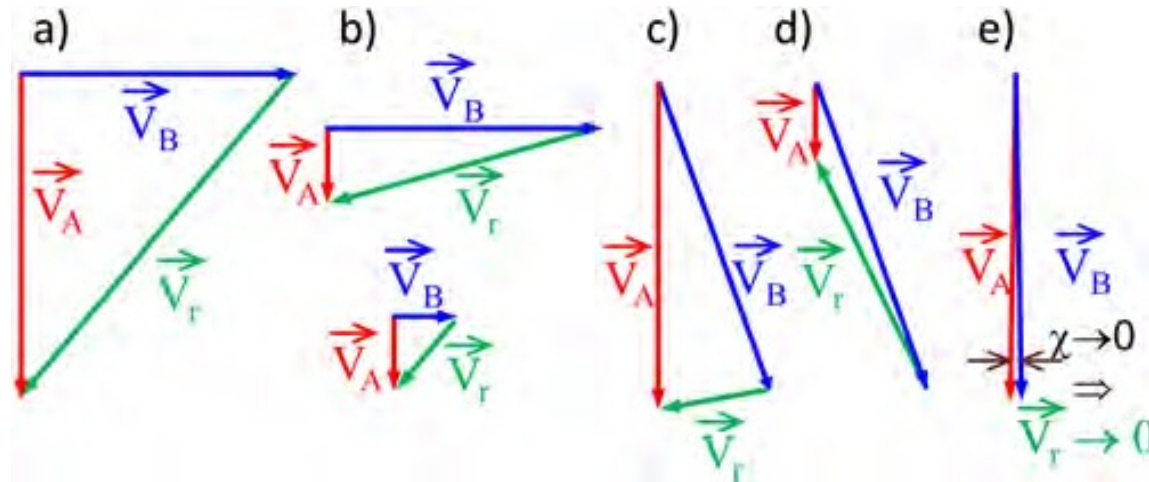
Collisions of trapped molecules with beam

Collisions of cold molecules with trapped ions

Co-trapped molecules

Low-energy collisions in Merged Beams

How to reach low collision energies?



$$\begin{aligned} E_{coll} &= \frac{\mu |\vec{v}_{rel}|^2}{2} \\ &= \frac{\mu}{2} (\vec{v}_1 - \vec{v}_2)^2 \\ &= \frac{\mu}{2} (|v_1|^2 + |v_2|^2 - 2v_1 v_2 \cos(\theta)) \end{aligned}$$

Crossed Beams

Collision Energy:

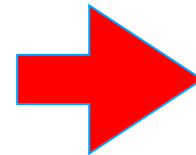
$$\begin{aligned} E_{coll} &= \frac{\mu |\vec{v}_{rel}|^2}{2} \\ &= \frac{\mu}{2} (\vec{v}_1 - \vec{v}_2)^2 \\ &= \frac{\mu}{2} (|v_1|^2 + |v_2|^2 - 2v_1 v_2 \cos(\theta)) \end{aligned}$$

Realistic numbers:

m_1, m_2 : ca. 20 amu

v_1, v_2 : ca. 500-1000 m/s

θ : 90 degrees



E_{coll} around 500 K

Crossed Beams

Collision Energy:

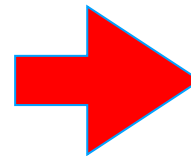
Get to low collision energies either through a reduction of the v_i or through a reduction of the angle.

Realistic numbers:

m_1, m_2 : ca. 20 amu

v_1, v_2 : ca. 500-1000 m/s

θ : 90 degrees



E_{coll} around 500 K

Crossed Beams

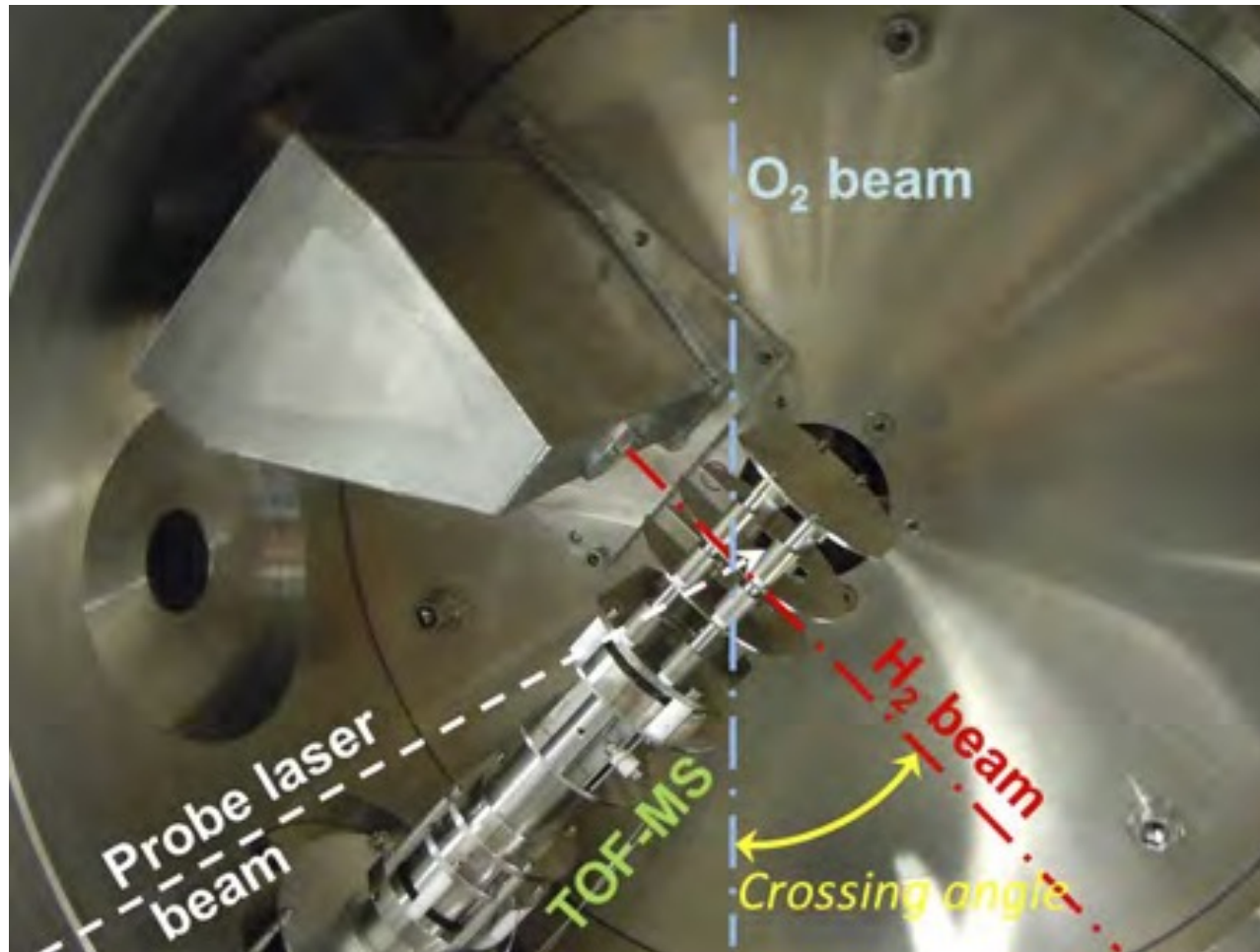
Collision Energy:

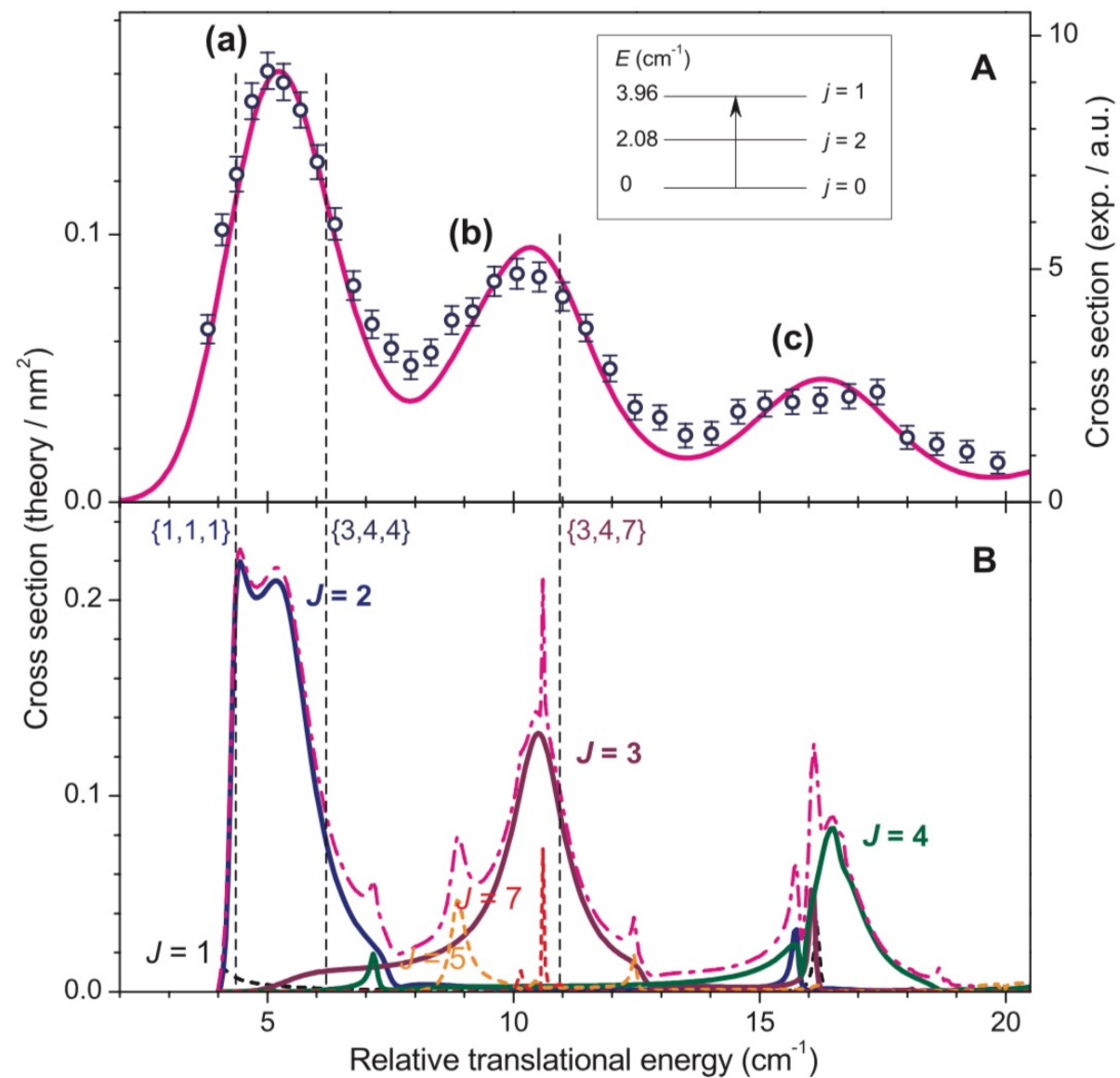
Get to low collision energies either through a reduction of the v_i or through a reduction of the angle.

	regular crossed	slow crossed	low-angle crossed	merged
m1 (amu)	20	20	20	20
m2 (amu)	20	20	20	20
mu (amu)	10	10	10	10
v1 (m/s)	500	50	500	500
v2 (m/s)	500	50	500	500
theta	90	90	12	0
Energy (K)	688	7	15	0

Crossed Beams

Low angles

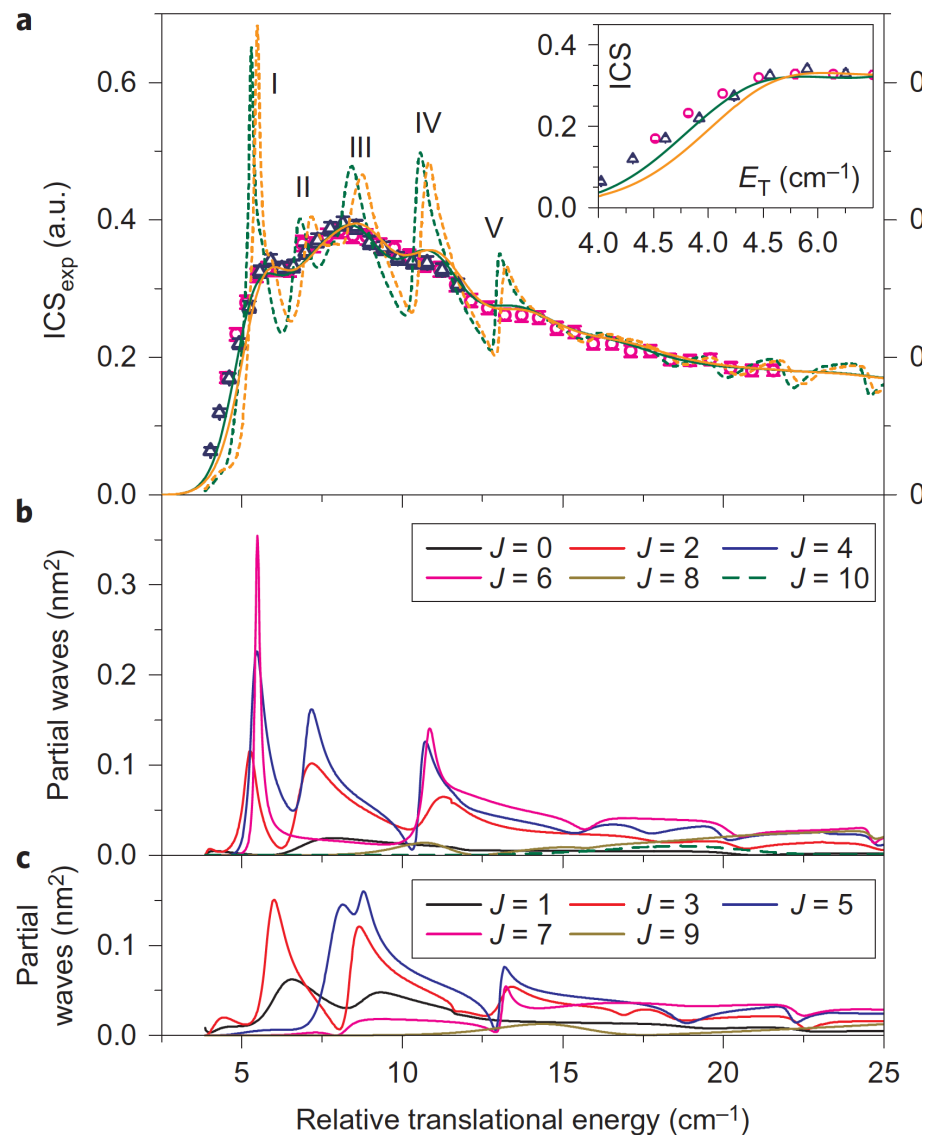




Chefdeville, Kalugina, van de Meerakker, Naulin, Lique, and Costes, *Science* **341**, 1094 (2013).

Crossed Beams

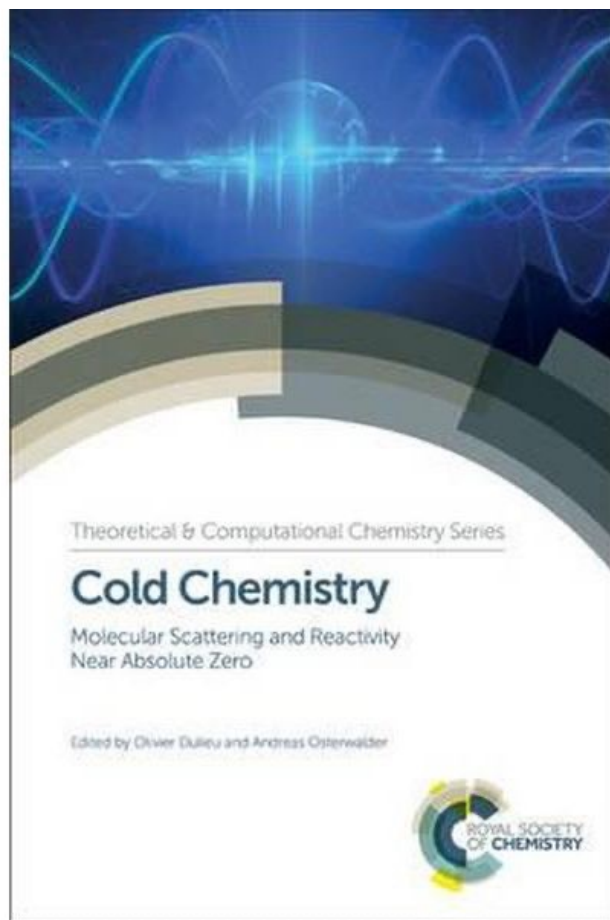
Low angles



Bergeat, Onvlee, Naulin, van der Avoird, and Costes, Nature Chem 7, 349 (2015).

Crossed Beams

Low angles



CHAPTER 3

Low-energy Scattering in Crossed Molecular Beams

C. NAULIN^{a,b} AND A. BERGEAT^{*a,b}

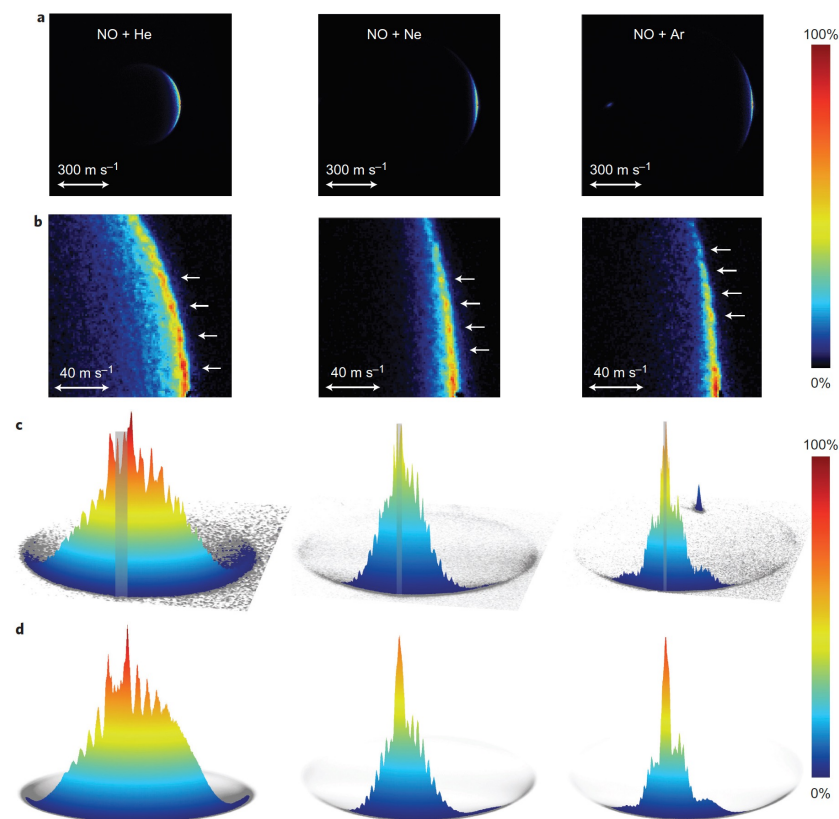
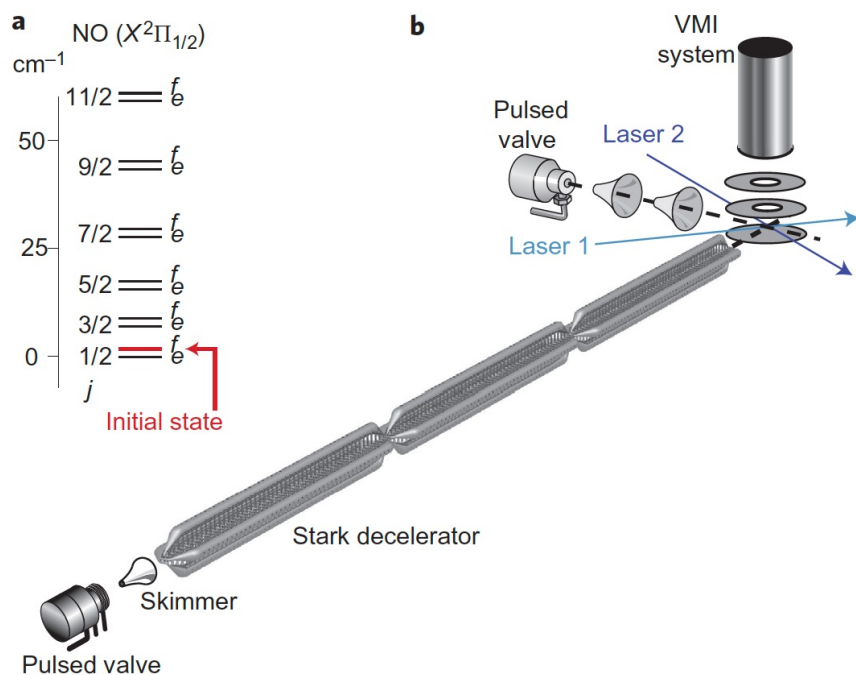
^aUniv. Bordeaux, ISM, UMR 5255, F-33400 Talence, France; ^bCNRS, ISM, UMR 5255, F-33400 Talence, France

*E-mail: astrid.bergeat@u-bordeaux.fr

Cold Chemistry, edited by O. Dulieu and A. Osterwalder (Royal Society of Chemistry, Cambridge, 2017), pp. 1–45.

Examples

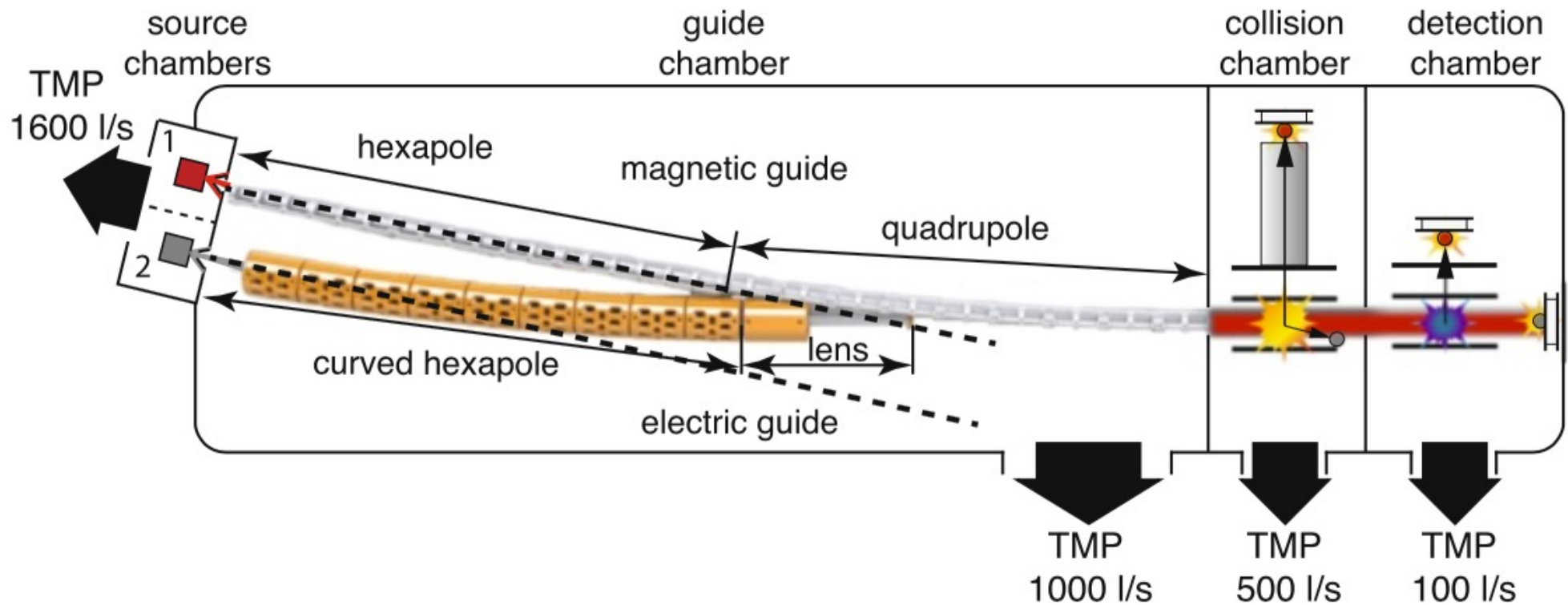
Inelastic collisions of NO with rare gases



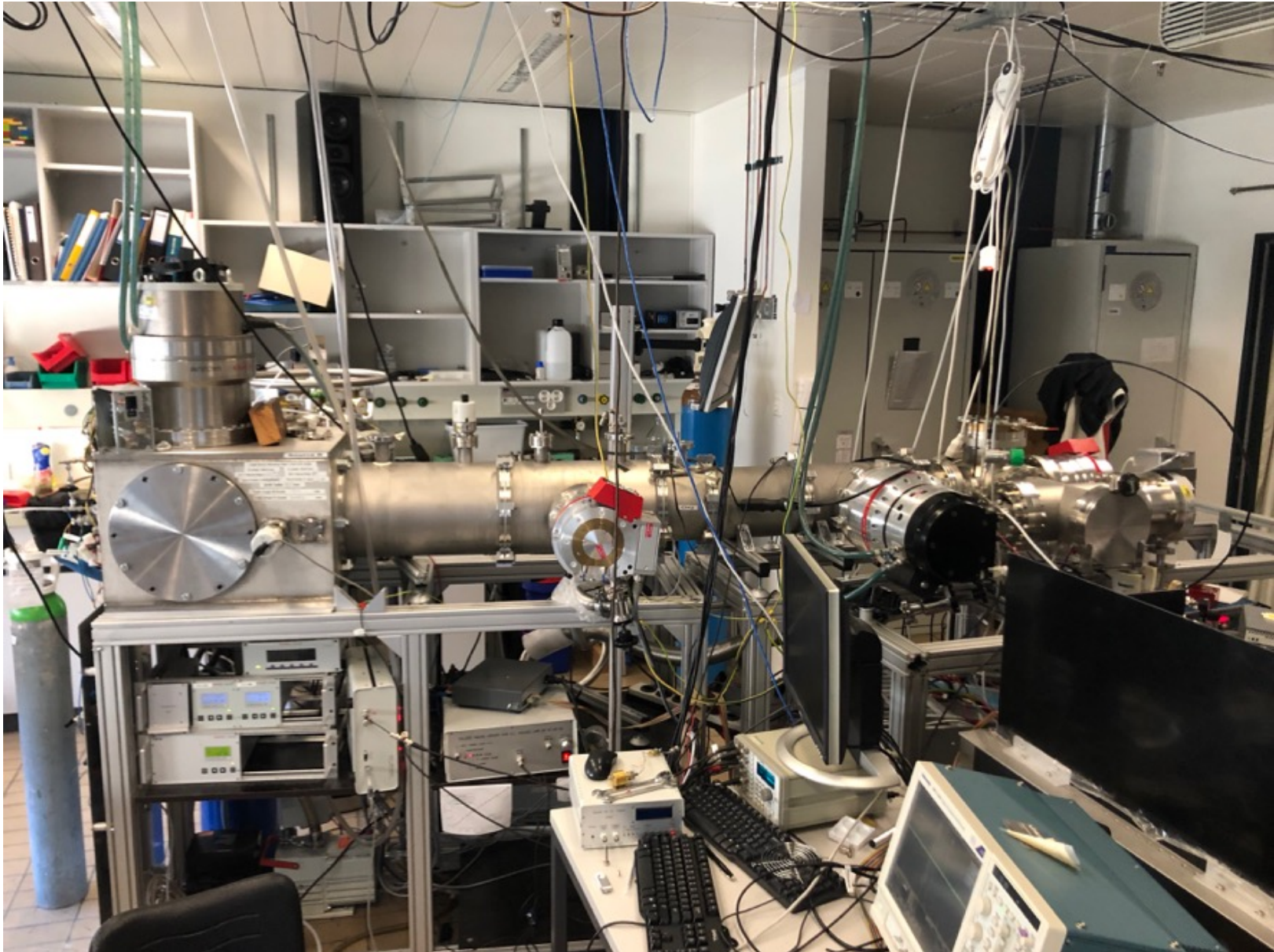
von Zastrow, Onvlee, Vogels, Groenenboom, van der Avoird, and van de Meerakker, Nature Chem **6**, 216 (2014).

Merged beams

Intrabeam angle is zero

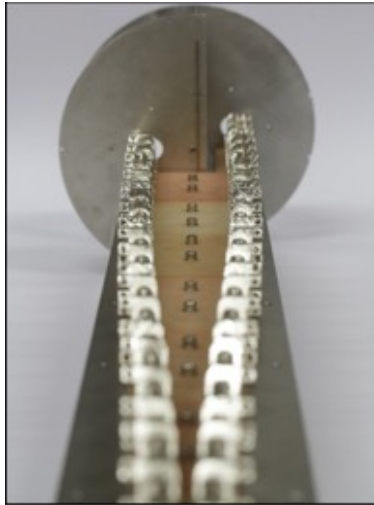


Merged beams

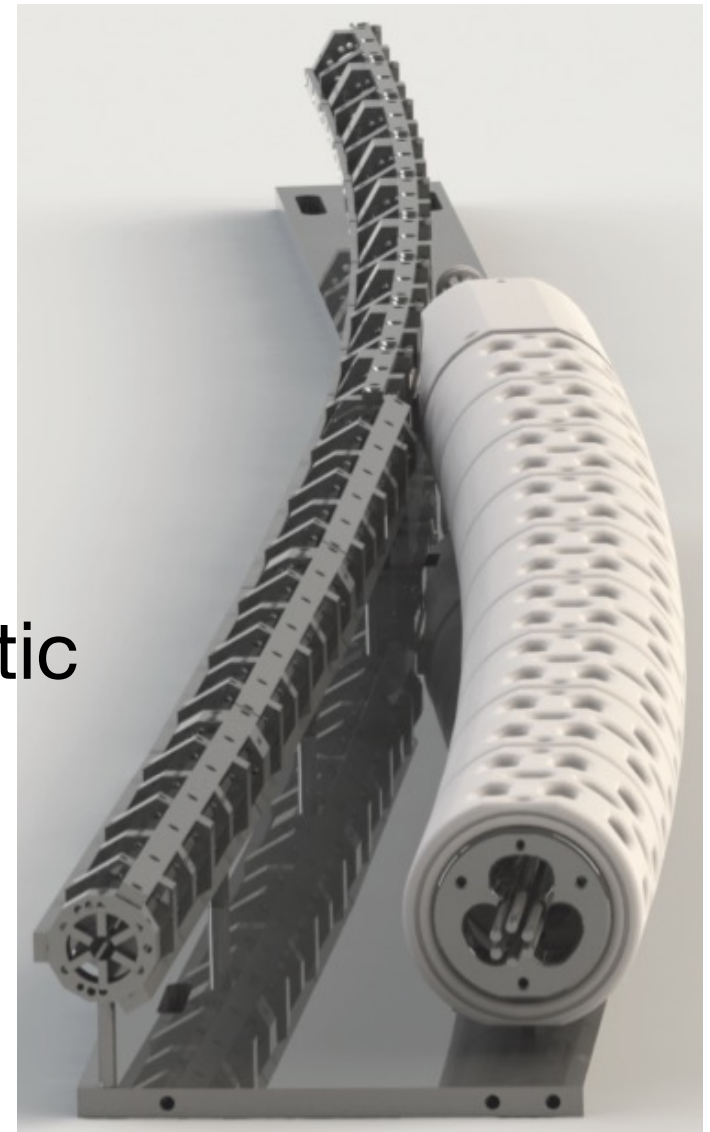
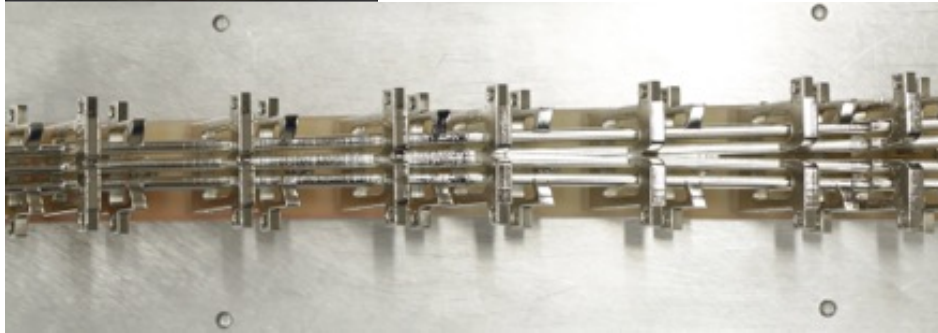


Merged beams

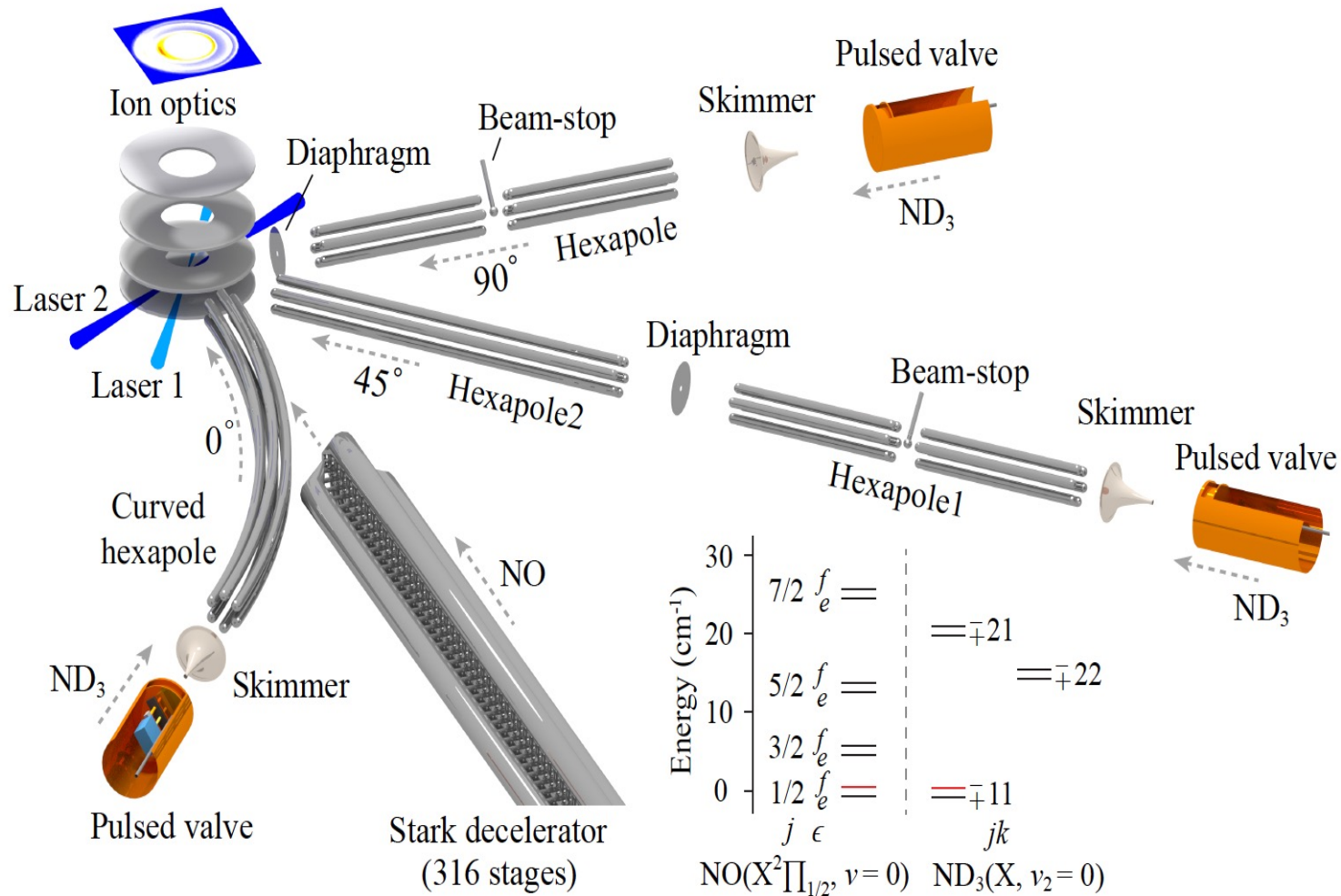
Intrabeam angle is zero



Electric+Electric
Electric+Magnetic



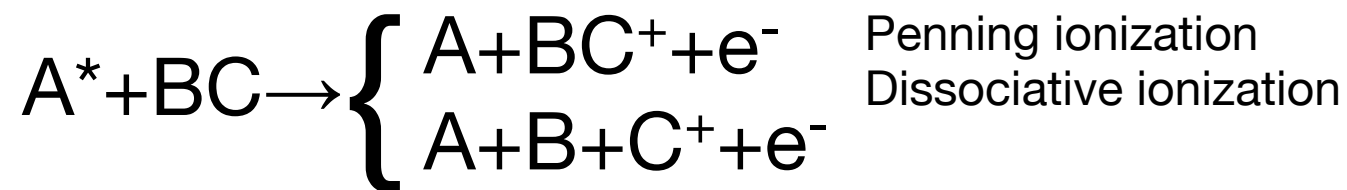
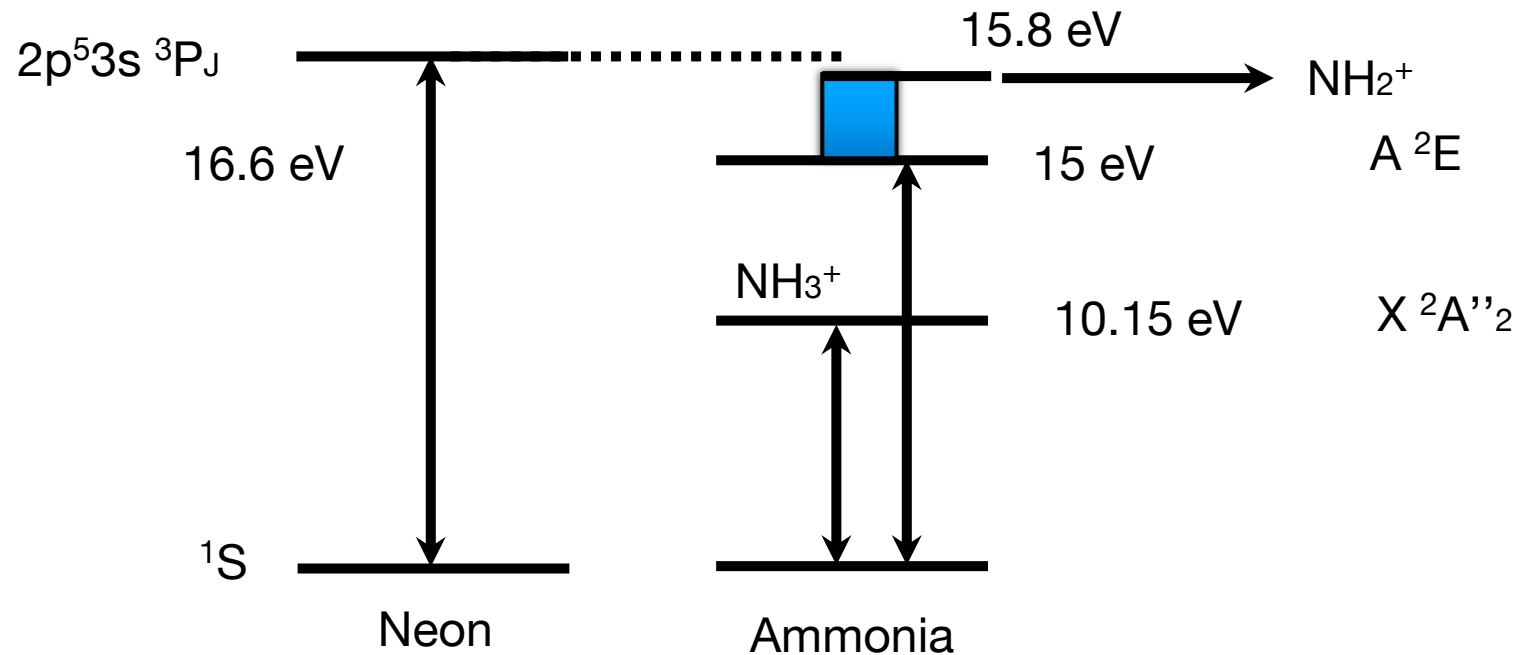
Merged beams



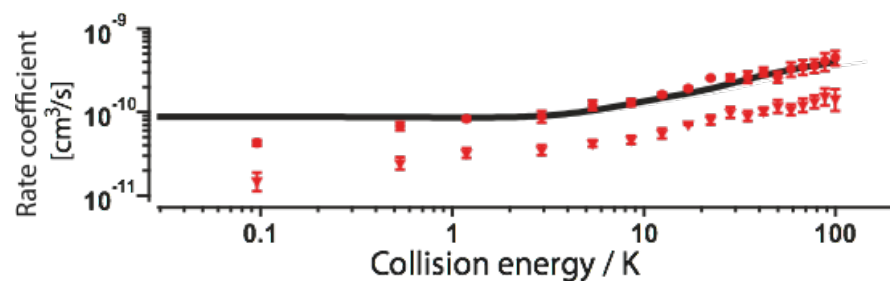
Merged beams

Applications

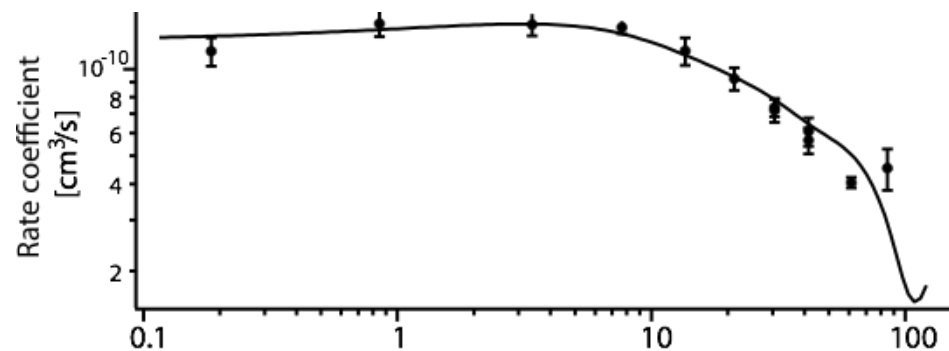
Penning Ionization:

$$\text{Ne}(^3\text{P}_2) + \text{NH}_3 \rightarrow \text{Ne}(^1\text{S}) + \text{NH}_3^+ + \text{e}^-$$


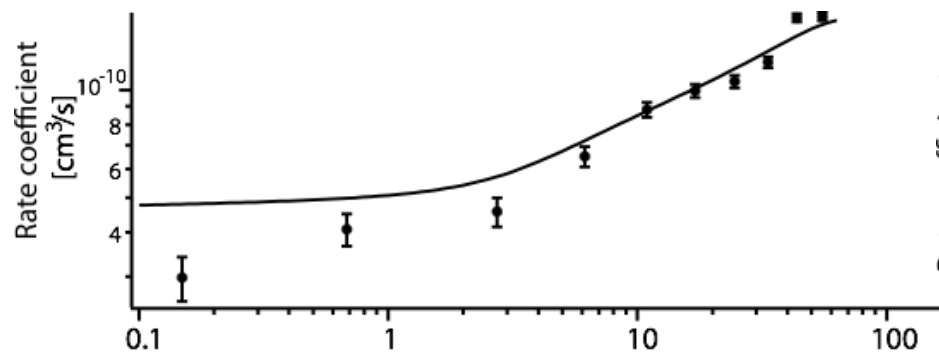
$\text{Ne}^* + \text{NH}_3$



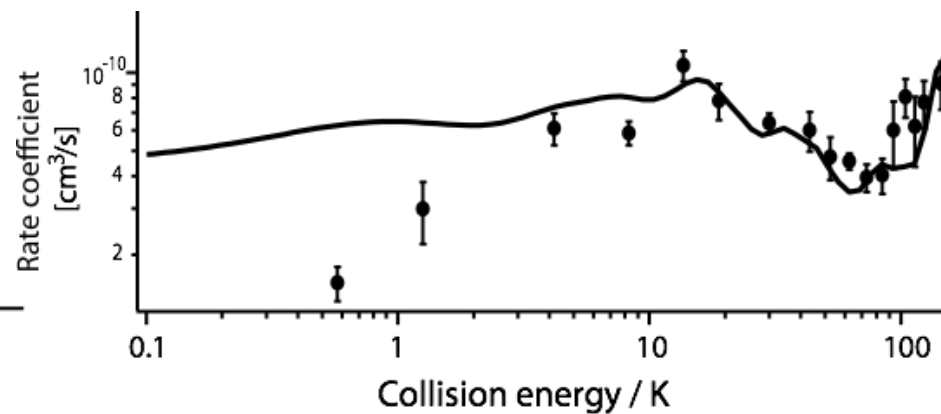
$\text{Ne}^* + \text{CHF}_3$



$\text{Ne}^* + \text{CH}_3\text{F}$



$\text{He}^* + \text{CHF}_3$



JCP **140**, 244302(14)

JPC **118**, 3875(14)

EPJTI **2**, 10(15)

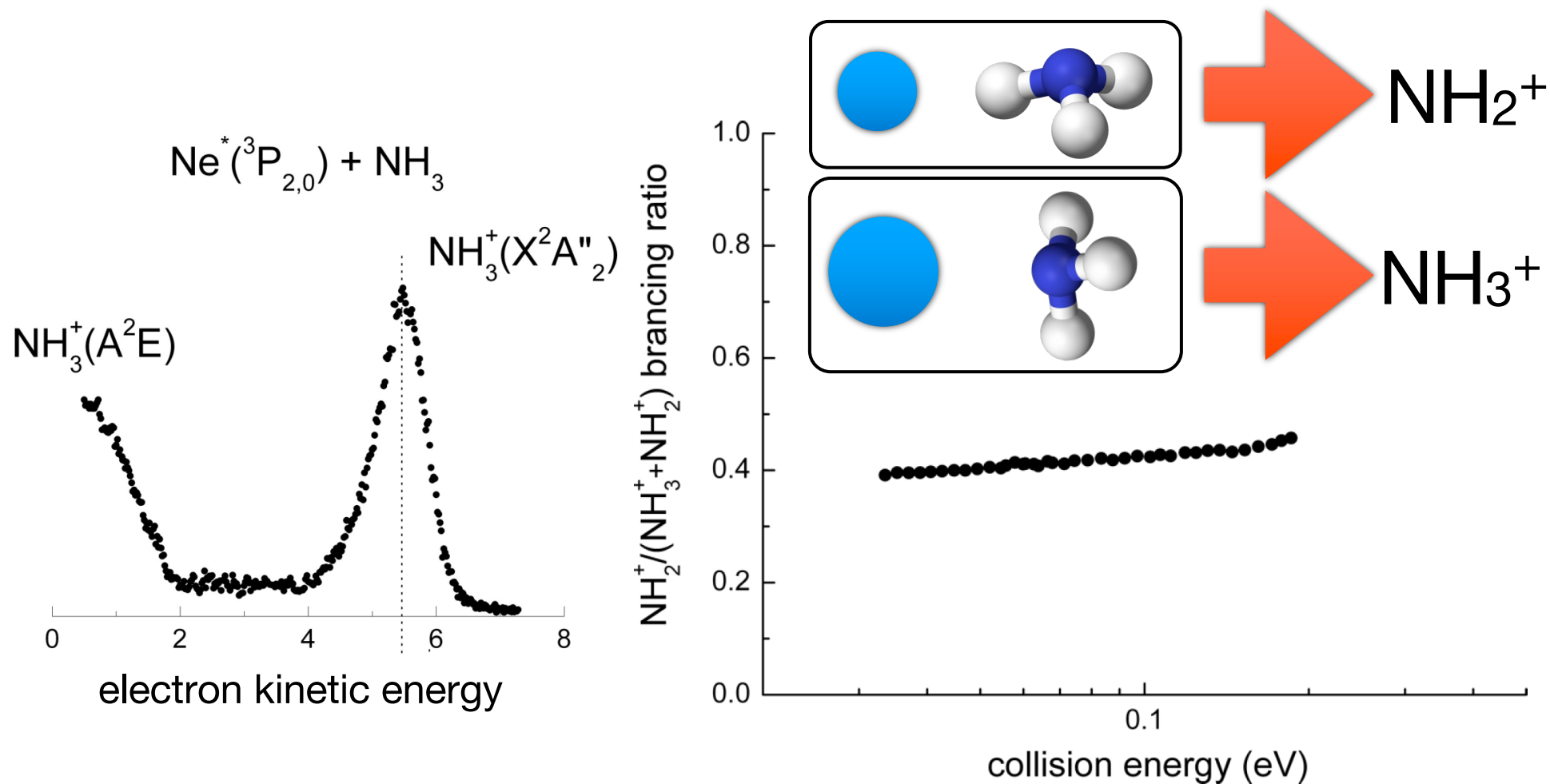
JCP **144**, 221102(16)

Chem.Phys.Chem. **17**, 3776(16)

Stereodynamics

Stereodynamics in crossed beams

Ne^{*}+NH₃ Penning ionisation



Falcinelli et al., JCP **143**, 164306 (2015)

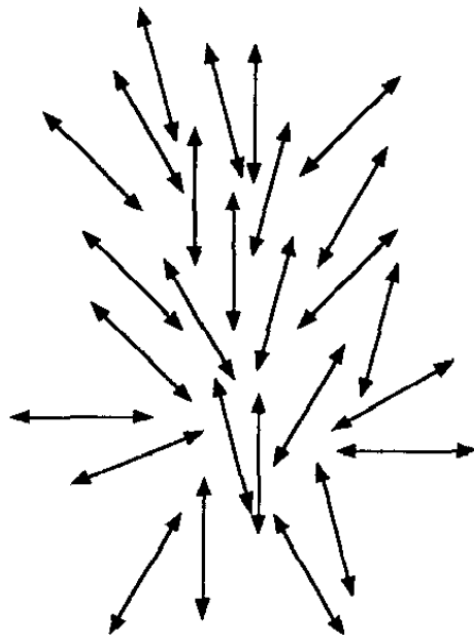
Orientation and Alignment of Molecules

ORIENTATION AND ALIGNMENT OF REACTION PRODUCTS

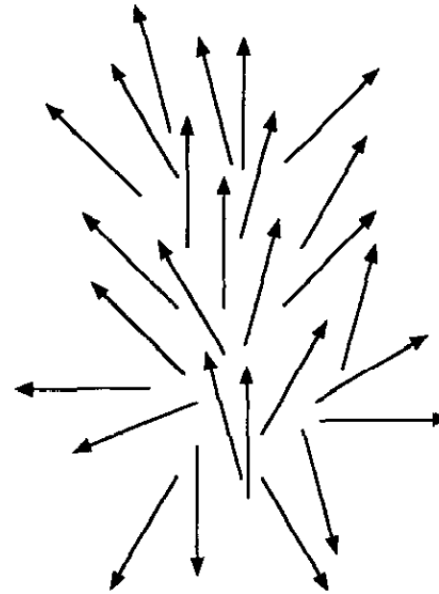
Andrew J. Orr-Ewing¹ and Richard N. Zare

Department of Chemistry, Stanford University, Stanford,
California 94305

Annu. Rev. Phys. Chem. 1994. 45: 315–66

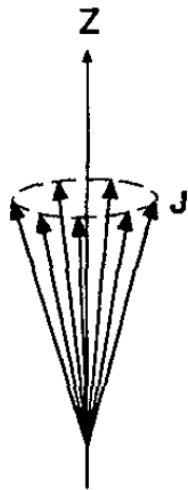


Alignment



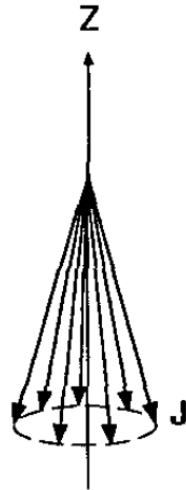
Orientation

Alignment Parameters $A_q^k(J)$



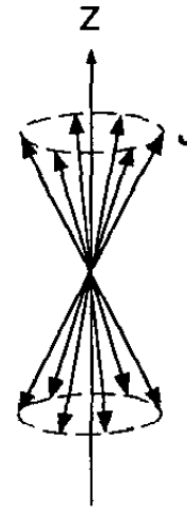
Positive orientation

$$A_0^{(1)} \rightarrow 1$$



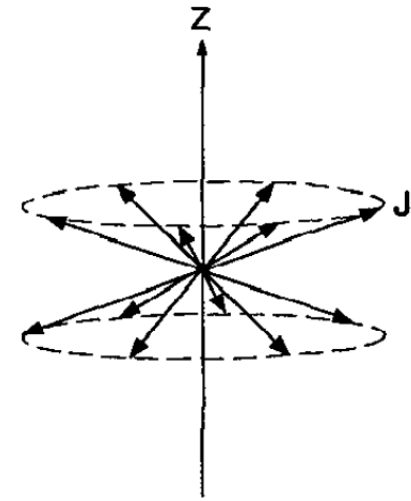
Negative orientation

$$A_0^{(1)} \rightarrow -1$$



Positive alignment

$$A_0^{(2)} \rightarrow 2$$



Negative alignment

$$A_0^{(2)} \rightarrow -1$$

Diagram of positive and negative orientation and alignment

Classical:

$$\hat{\mathbf{J}} \cdot \hat{\mathbf{Z}} = \cos \theta$$

$$P_1(\hat{\mathbf{J}} \cdot \hat{\mathbf{Z}}) = P_1(\cos \theta) = \cos \theta$$

$$P_2(\hat{\mathbf{J}} \cdot \hat{\mathbf{Z}}) = P_2(\cos \theta) = \frac{1}{2}[3 \cos^2 \theta - 1]$$

$$A_0^{(1)} = \langle P_1(\hat{\mathbf{J}} \cdot \hat{\mathbf{Z}}) \rangle = \langle \cos \theta \rangle$$

$$A_0^{(2)} = 2 \langle P_2(\hat{\mathbf{J}} \cdot \hat{\mathbf{Z}}) \rangle = \langle 3 \cos^2 \theta - 1 \rangle$$

Distribution of angles

$$N(\hat{\mathbf{J}} \cdot \hat{\mathbf{Z}}) = \frac{1}{4\pi} \sum_n a_n P_n(\cos \theta)$$

The angular distribution of $\mathbf{J}$ can be expanded in terms of the multipolar moments as

$$N(J, \theta) = \frac{1}{4\pi} \{ A_0^{(0)}(J) + 3A_0^{(1)}(J)P_1(\cos \theta) + \frac{5}{2}A_0^{(2)}(J)P_2(\cos \theta) \\ + 7A_0^{(3)}(J)P_3(\cos \theta) + 9A_0^{(4)}(J)P_4(\cos \theta) + \dots \}. \quad 16.$$

QM description using density matrix

Angular momentum spherical-tensor operator

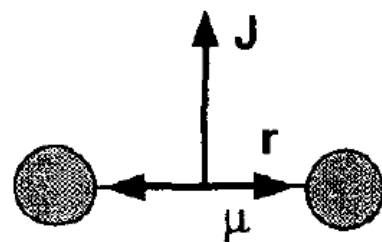
$$\langle J_q^{(k)} \rangle = \langle (J | J_q^{(k)} | J) \rangle = \sum_{M, M'} \rho_{M' M} \langle JM | J_q^{(k)} | JM' \rangle,$$

Density Matrix elements

$$A_q^{(k)}(J) = \frac{c(k)}{\langle JM | \mathbf{J}^2 | JM \rangle^{k/2}} \text{Re} \langle J_q^{(k)} \rangle.$$

$$\mathcal{A}_q^{(k)}(J) = \frac{c(k)}{\langle JM | \mathbf{J}^2 | JM \rangle^{k/2}} \langle J_q^{(k)} \rangle$$

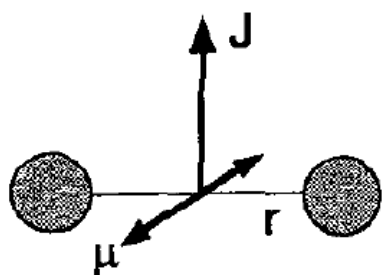
A molecular ensemble with $J = 0$ cannot show alignment or orientation, whereas for $J = 1/2$, an ensemble may possess a first-order orientation moment. For $J = 1$, the highest possible moments that can exist are $A_{\pm q}^{(2)}(J)$ or $\mathcal{A}_{\pm q}^{(2)}(J)$, whereas for $J = 2$, moments as high as $A_{\pm q}^{(4)}(J)$ or $\mathcal{A}_{\pm q}^{(4)}(J)$ can arise.



Parallel transition

$\Sigma - \Sigma$

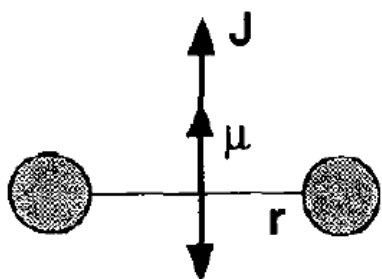
P or R branch



Perpendicular transition

$\Sigma - \Pi$

P or R branch



Perpendicular transition

$\Sigma - \Pi$

Q branch

Figure 4 The connection between the rotational angular momentum, $\mathbf{J}$, the transition-dipole moment, $\boldsymbol{\mu}$, and the molecular axis, $\mathbf{r}$, for a diatomic molecule in the high- J limit. The figure shows the relationship between $\mathbf{J}$, $\boldsymbol{\mu}$, and $\mathbf{r}$ for Q- and P, R-branches for parallel and perpendicular transitions.

The intensity of a probe process, whether 1-photon absorption or chemiluminescence, (1 + 1) LIF, (1 + 1) REMPI, or (2 + 1) REMPI with linearly, elliptically, or circularly polarized photons, can be expressed in a simple form in terms of alignment parameters (81, 89–91, 93, 108):

$$I = C (\text{det}) n(J_i) \sum_{k,q} P_q^{(k)}(J_i, \Lambda_i, J_e, \Lambda_e, J_f, \Lambda_f; \Omega) A_q^{(k)}(J_i).$$

C is an experimental sensitivity constant

n(J) the state population in the initial state

indices i, e, f stand for initial, excited, final state in LIF or REMPI

2+1 REMPI

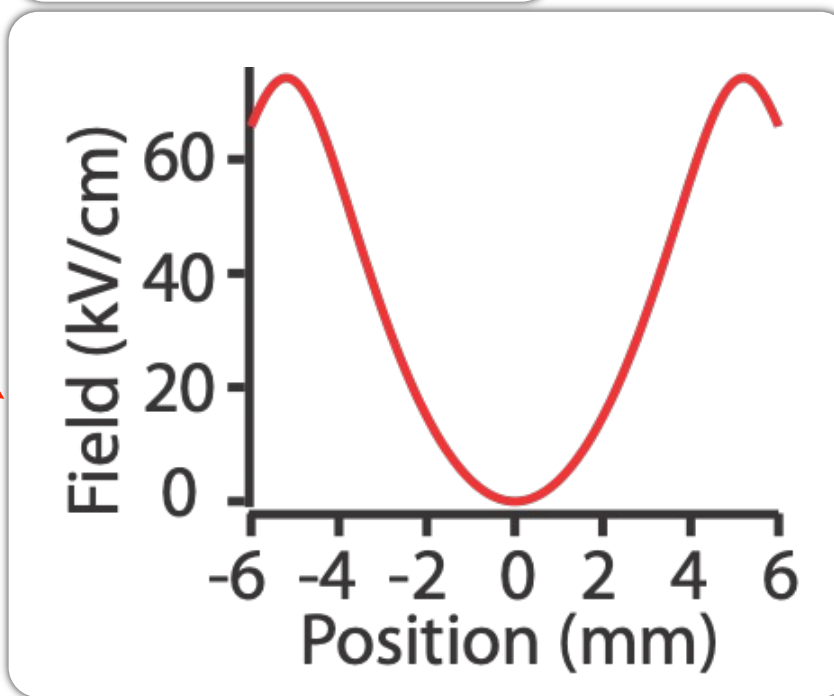
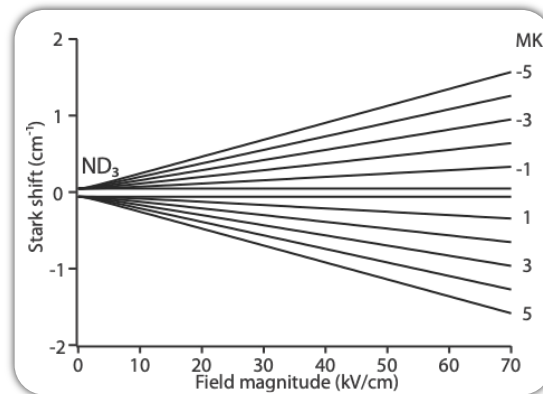
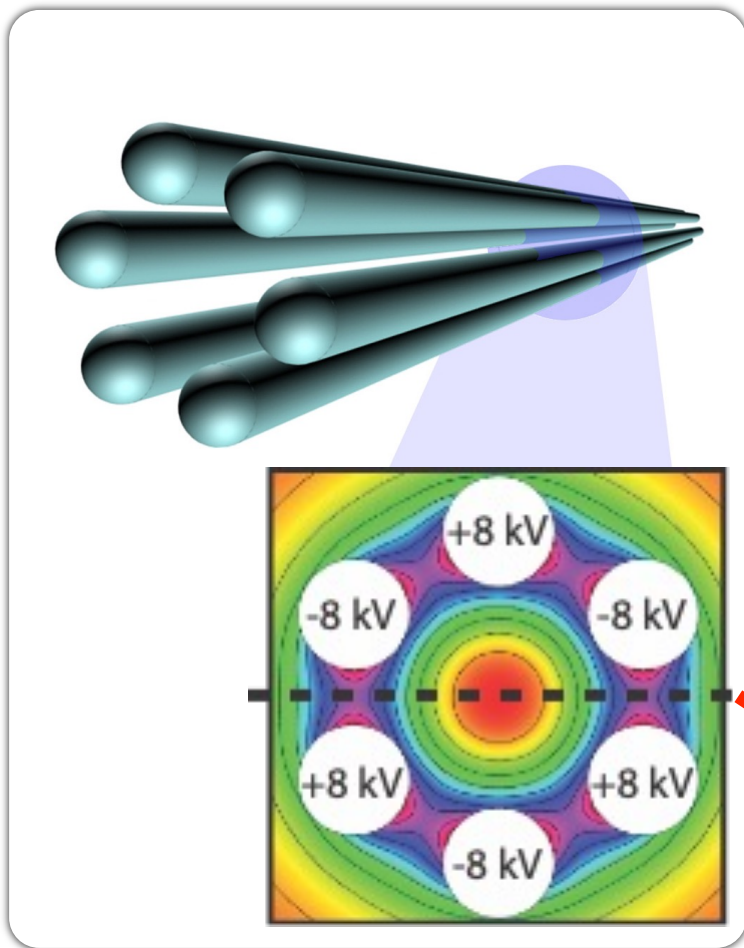
$$I[a_q^k(i)] = 1 + \sum_{k=1}^{2J} s_k \sum_{q=-k}^k a_q^k(i) C_q^k(p, \varphi_{dP}),$$

C are reduced spherical harmonics

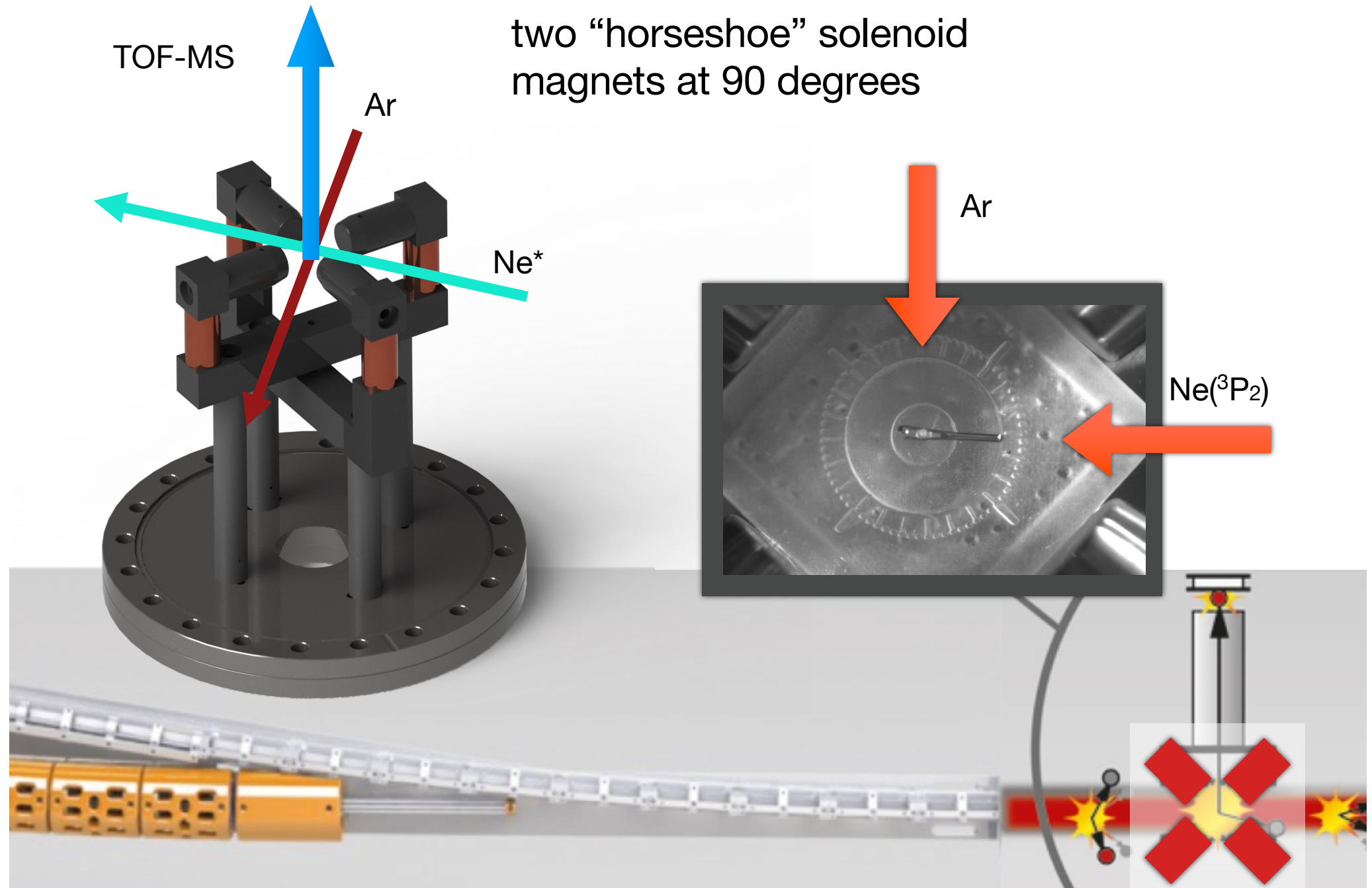
Sensitivity factors

$$s_k = P_k \frac{[J(J+1)]^{k/2} \sqrt{2k+1} \sqrt{2J+1}}{c(k) \langle J || J^{(k)} || J \rangle}$$

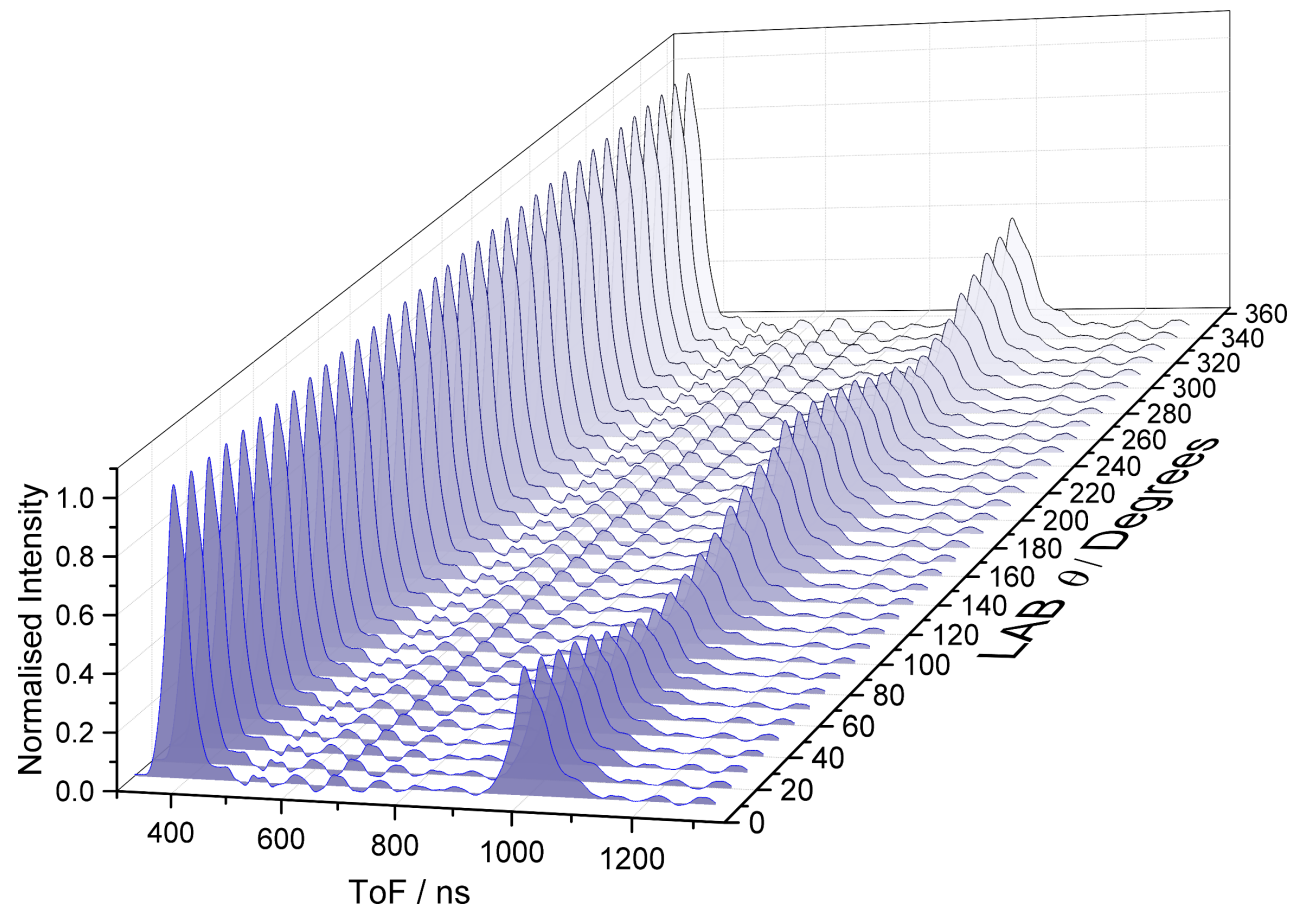
Guide: 2D trap



Ne(3P_2)+Ar (1S) Stereodynamics

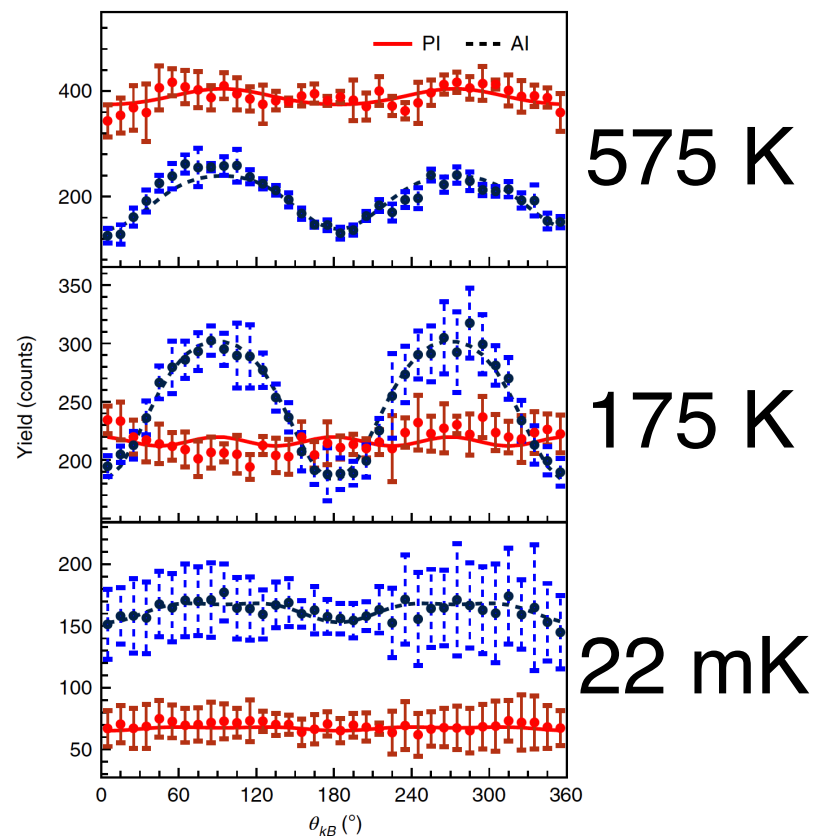
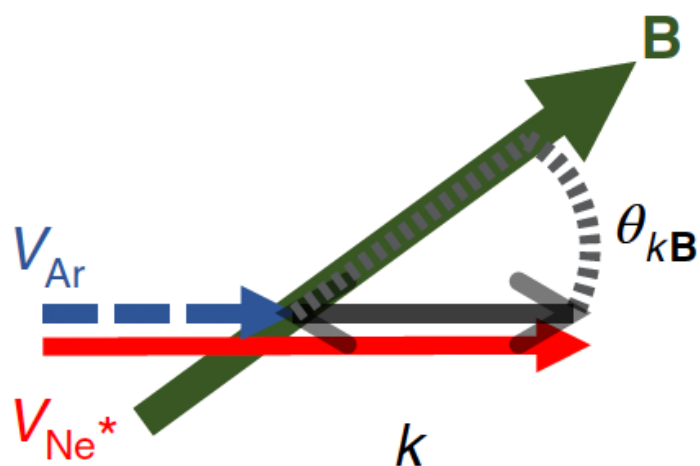


Results: $\text{Ne}(^3\text{P}_2)+\text{Ar}$



Merged beams

Angle between beams is zero
Combine with orientation of reactants

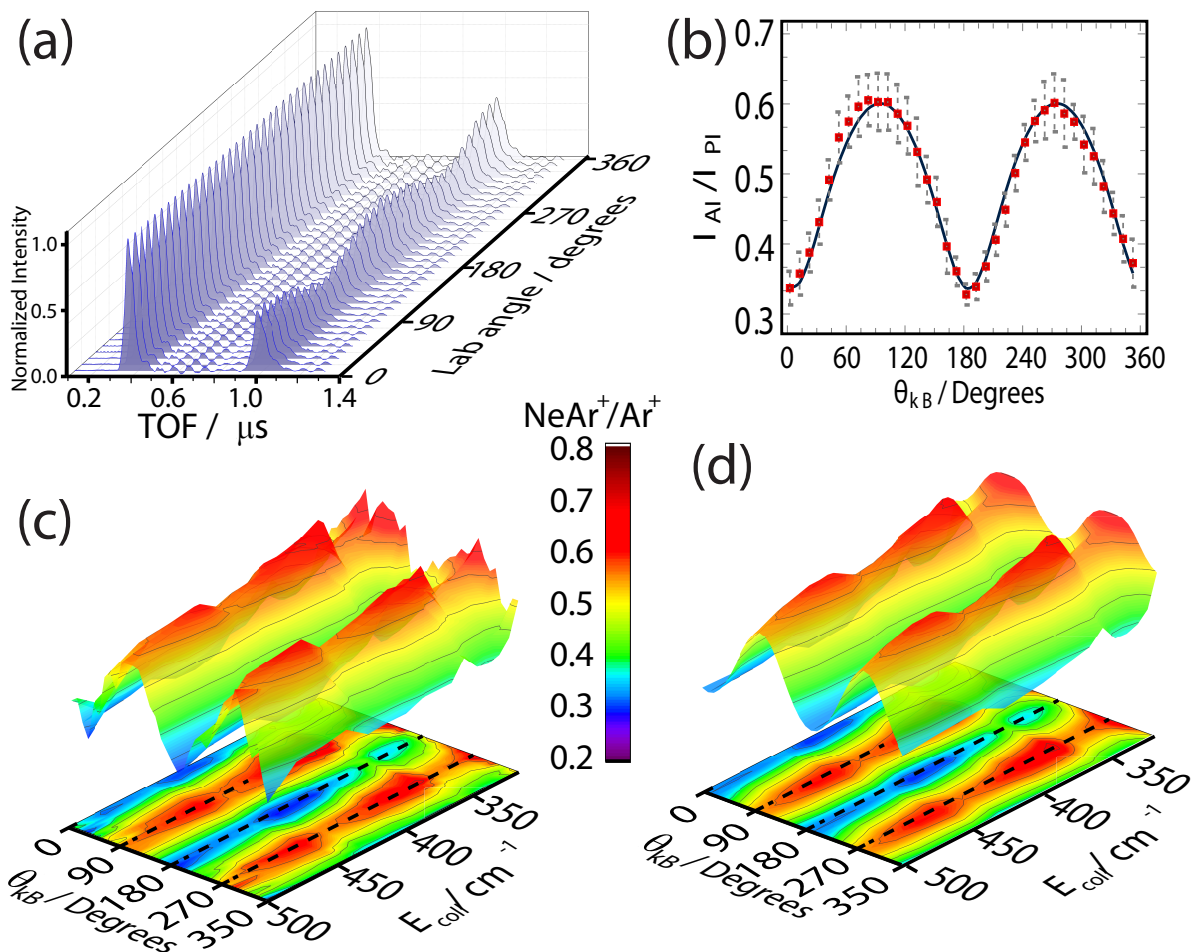


Gordon, Omiste, Zou, Tanteri, Brumer, and Osterwalder,
Nature Chem **43**, 7279 (2018).

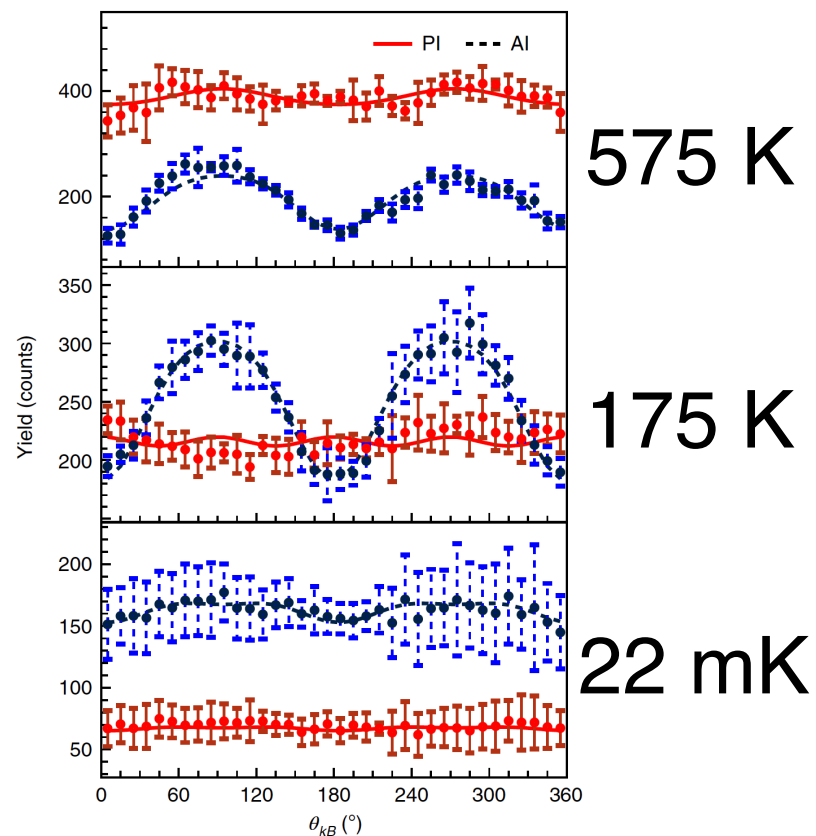
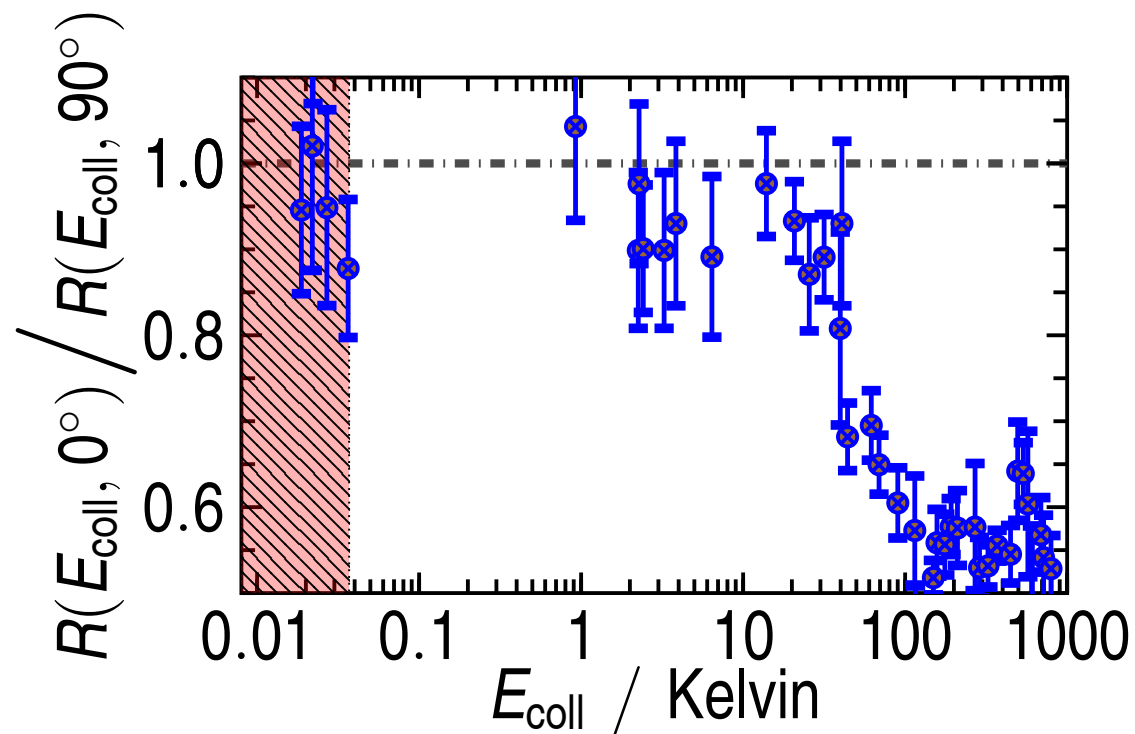
Merged beams

Angle between beams is zero

Combine with orientation of reactants



Loss of orientation at low energies

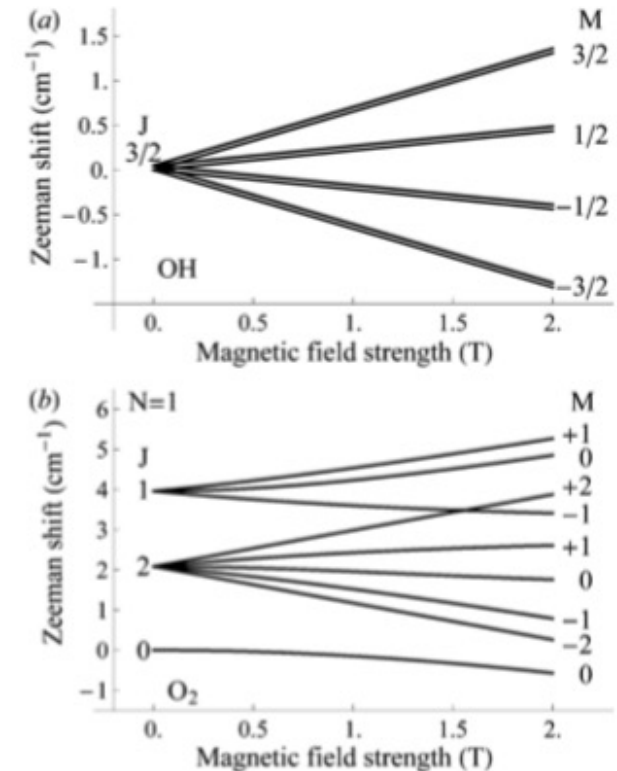
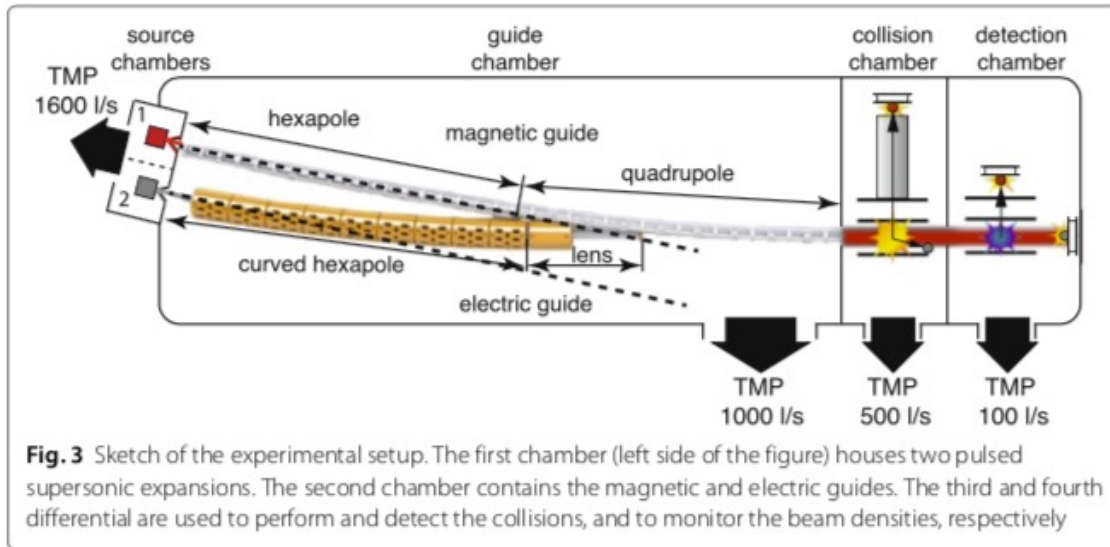
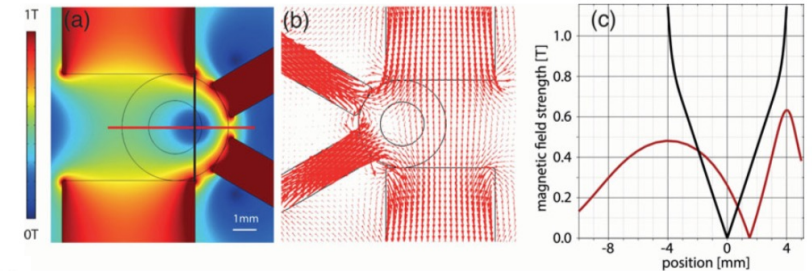


Gordon, Omiste, Zou, Tanteri, Brumer, and Osterwalder,
Nature Chem **43**, 7279 (2018).

$$\langle J_q^{(k)} \rangle = \langle (J | J_q^{(k)} | J) \rangle = \sum \rho_{M'M} \langle JM | J_q^{(k)} | JM' \rangle,$$

$$A_q^{(k)}(J) = \frac{c(k)}{\langle JM | \mathbf{J}^2 | JM \rangle^{k/2}} \text{Re} \langle J_q^{(k)} \rangle.$$

An anisotropic distribution (orientation or alignment) necessitates different populations for the different M-states (the ρ_{MM} need to be different)



$$I(\Theta_{QR}) = I_0 \left[1 + \sum_{k=1}^{2J} s_k(J, J', \lambda) P_k(\cos \Theta_{QR}) A_0^{(k)}(J) \right]$$

Table 2. Detection sensitivity parameters for $O(^3P_2)$ and $Ne(^3P_2)$ as used in the present calculations. λ designates the laser polarisation, with $\lambda = 0$ and ± 1 for linearly and circularly polarised light, respectively.

λ	$O(^3P_2)$ 0	$O(^3P_2)$ ± 1	$Ne(^3P_2)$ 0	$Ne(^3P_2)$ ± 1
s_1	0	$\mp \frac{5}{\sqrt{6}}$	0	$\pm \frac{3}{4}\sqrt{6}$
s_2	$-5/7$	$5/7$	-1	$1/2$
s_3	0	0	0	0
s_4	$-48/7$	$-8/7$	0	0

$$A_0^{(1)} = \frac{(1+p)}{\sqrt{6}}$$

$$A_0^{(2)} = \frac{(3p-1)}{2}$$

$$A_0^{(3)} = \frac{7(1-p) + 3\sqrt{2}}{12\sqrt{3}}$$

$$A_0^{(4)} = \frac{(5p-4)}{24}.$$

For $\rho_{22}=p$, $\rho_{11}=(1-p)$, $\rho_{00}=0$

Oriented $O(^3P_2)$, $Ne(^3P_2)$, and $He(^3S_1)$ atoms emerging from a bent magnetic guide

Justin Jankunas^a, Kevin S. Reisman^a, T. Peter Rakitzis^b and Andreas Osterwalder^{a,*}

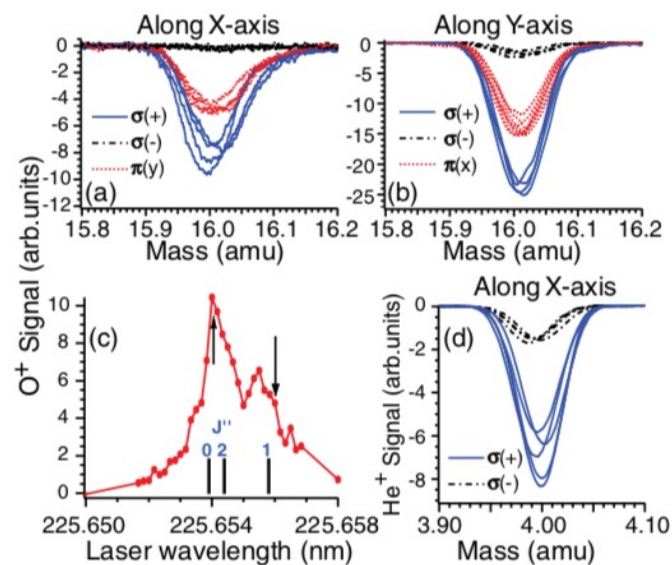


Figure 3. Typical O^+ signal as a function of laser polarisation when the laser beam is propagated along (a) X and (b) Y directions in the laboratory frame. A scan of the REMPI laser wavelength for $O(^3P_2)$ detection is shown in panel (c). The $J'' = 0$ and 2 upper states are not resolved (and not used for the present analysis), whereas the $J'' = 1$ intermediate level is. Solid bars indicate the theoretically predicted line positions. Arrows indicate the wavelengths used to detect $O(^3P_2)$ atoms. (d) Typical He^+ signal as a function of laser polarisation suggesting that the atomic angular momentum $J = 1$ of $He(^3S_1)$ is oriented.

Attosecond Dynamics