Toying with molecules; Manipulating Neutral Molecules with Electric Fields

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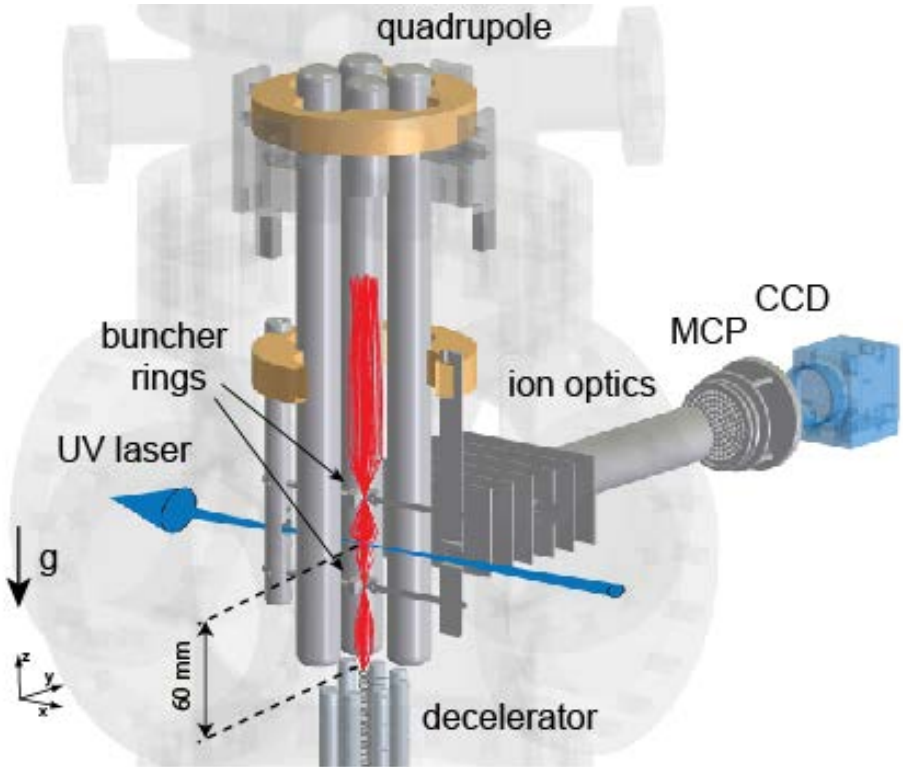

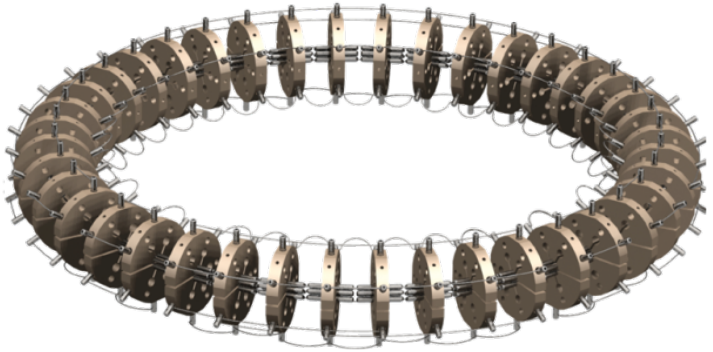

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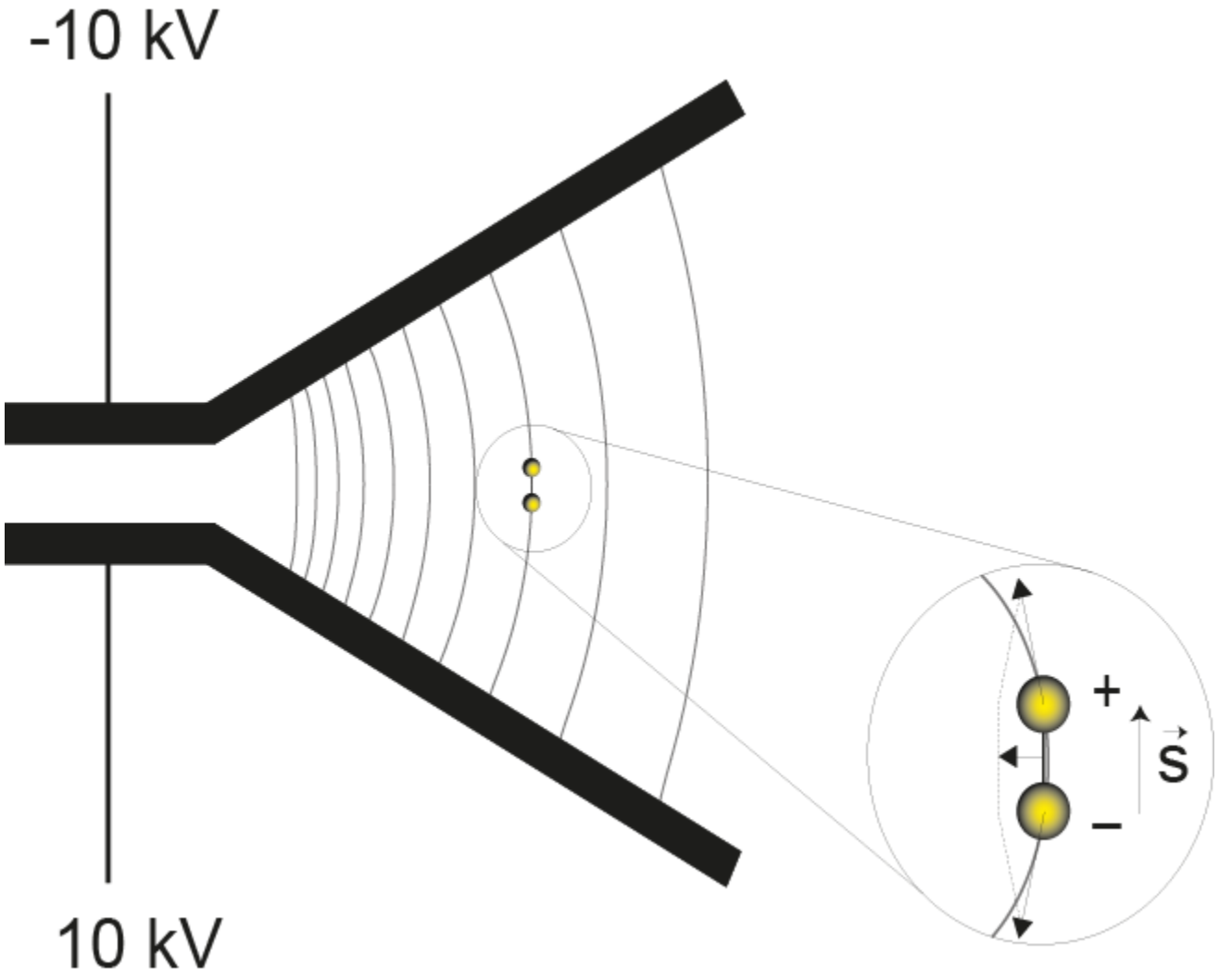
A dipole in an inhomogeneous E-field



Ions vs. Polar Molecules

- Force on a charged particle: $\vec{F} = -q\vec{\nabla}\Phi$
- Potential energy: $\mathrm{W} = q\Phi$
- Force on a polar molecule: $\vec{F} = \mu\cos\theta\ \vec{\nabla}E$
- Potential energy: $\mathrm{W} = -\mu\cos\theta\ E$

Thus, with a suitable translation, all techniques that are applied to charged particles can also be applied to polar molecules!!

Ions vs. Polar Molecules

But there are a number of caveats:

- The force on a polar molecules is 10^8 times smaller than the force on a charged particle
- The force depends [illegible] of the molecule in the [illegible]

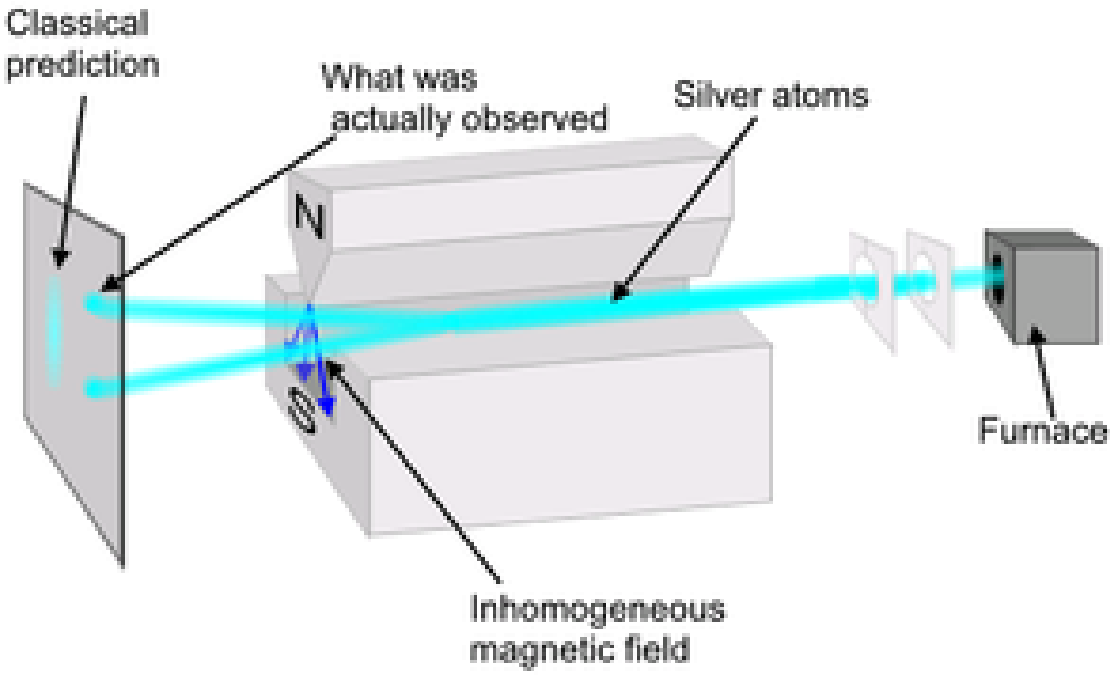
SPACE QUANTIZATION!

The Stern Gerlach Experiment

Stern Gerlach experiment

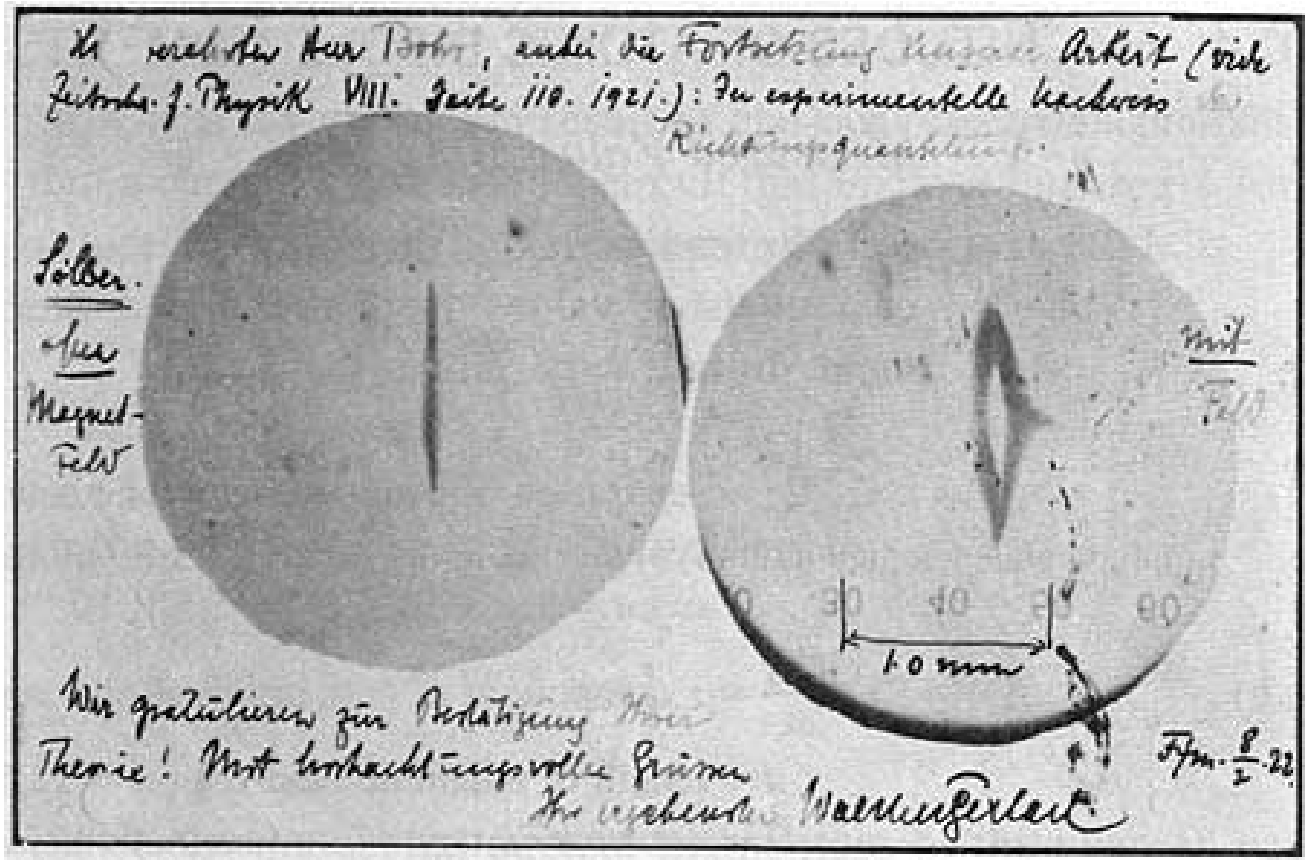
The concept of space quantization (i.e., the fact that the projection of the angular moment on the laboratory axis is quantized) was thought to be merely a mathematical model.

The deflection of a beam of silver atoms by **Stern** and **Gerlach** (1922) showed that it was real.



The Stern Gerlach Experiment

Postcard from Stern to Bohr, congratulating him with the experimental proof of his theory.



Scanned at the American
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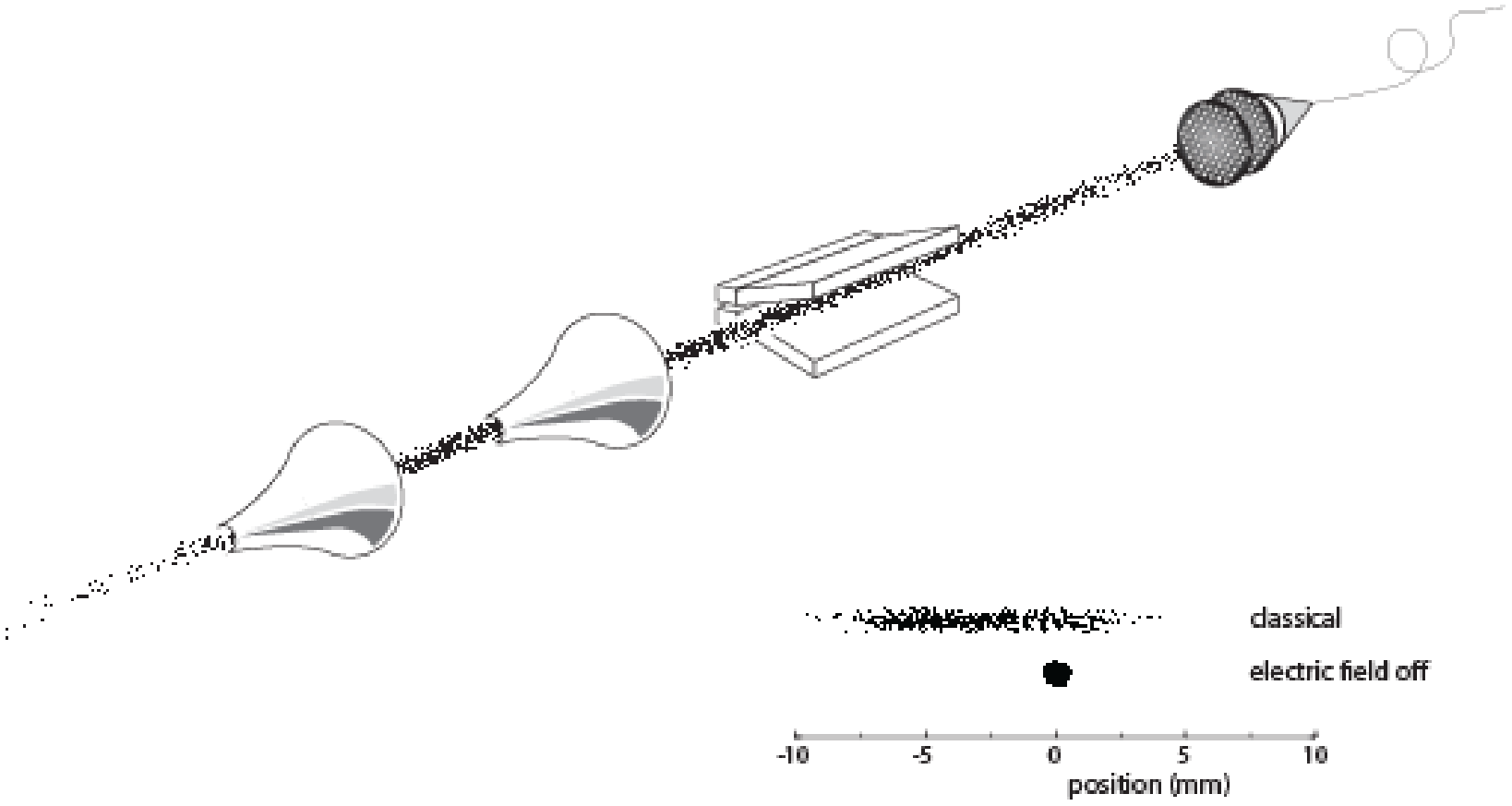
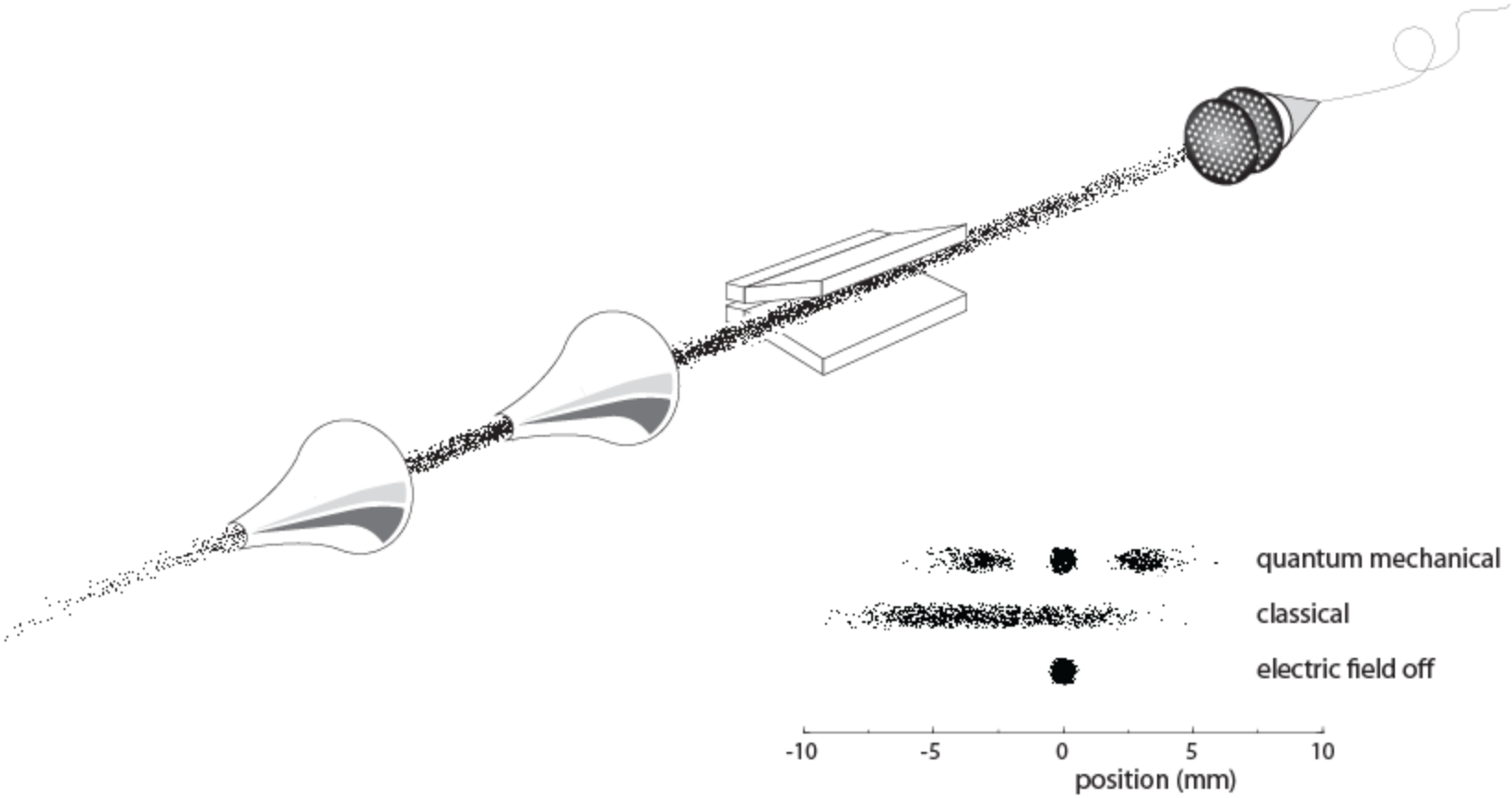
The Stern Gerlach Experiment

Deflection of a beam of triplet CO molecules (classical);



The Stern Gerlach Experiment

Deflection of a beam of triplet CO molecules (Quantum Mechanics);



molecules - Google zoeken

https://www.google.com/search?q=molecules&rlz=1C1NHXL_nlNL762NL762&source=lnms&tbm=isch&sa=X&ved=0ahUKEwjLqvPltvDiAhURL1AKHX

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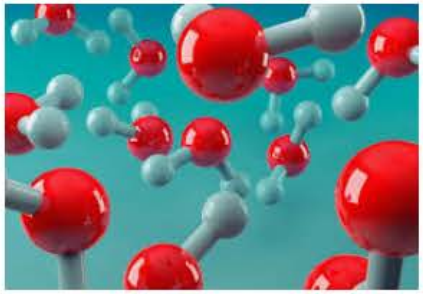

Definition and Examples of a Molecule
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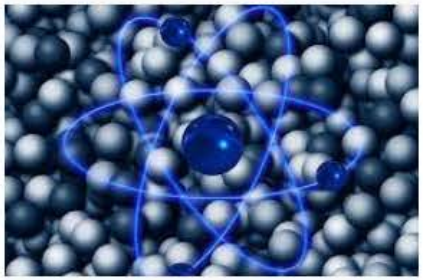

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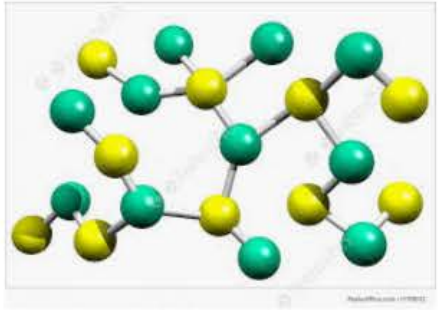

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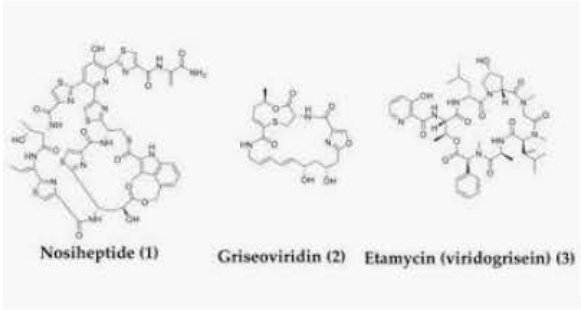

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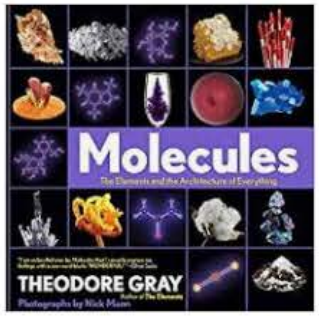

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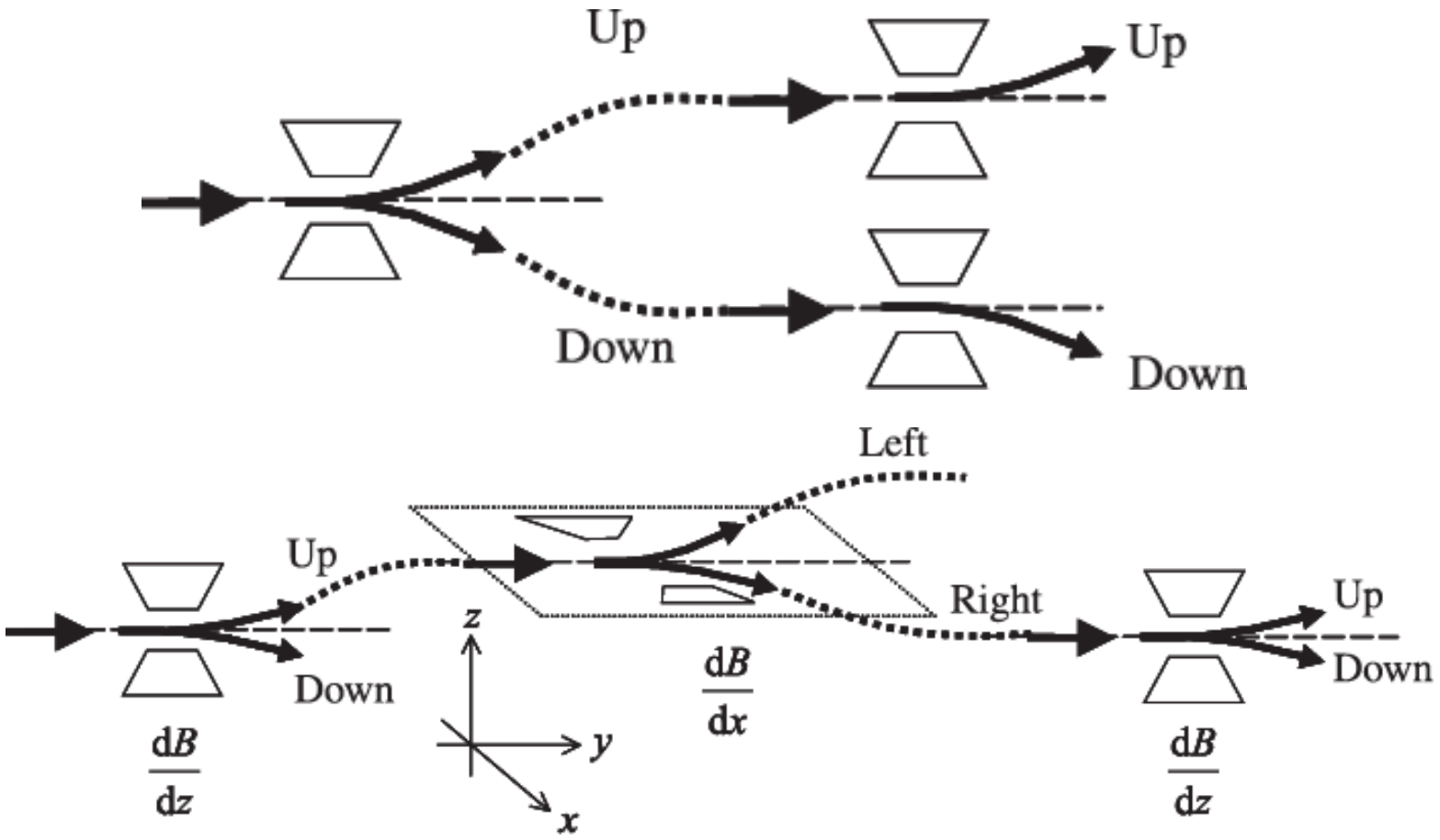
The Stern Gerlach Experiment

Multiple SG;



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Ions vs. Polar Molecules

But there are a number of caveats:

- The force on a polar molecules is 10^8 times smaller than the force on a charged particle

- The effective dipole moment is a function of the electric field and depends on the particular quantum state:
  - More non-linearities
  - Black body radiation and Majorana transitions limit the lifetime

Manipulating Molecules using E-Fields

- Stark effect
- Lenses, guides and deflectors for molecules in LFS states
- Decelerating molecules in LFS states using an array of inhomogeneous electric fields; **The Stark decelerator**
- Traps for molecules in LFS states
- A storage ring for molecules in LFS states
- What about molecules in HFS?

S.Y.T. van de Meerakker, H.L. Bethlem, N. Vanhaecke, G. Meijer, Chem Rev **112**, 4828 (2012)

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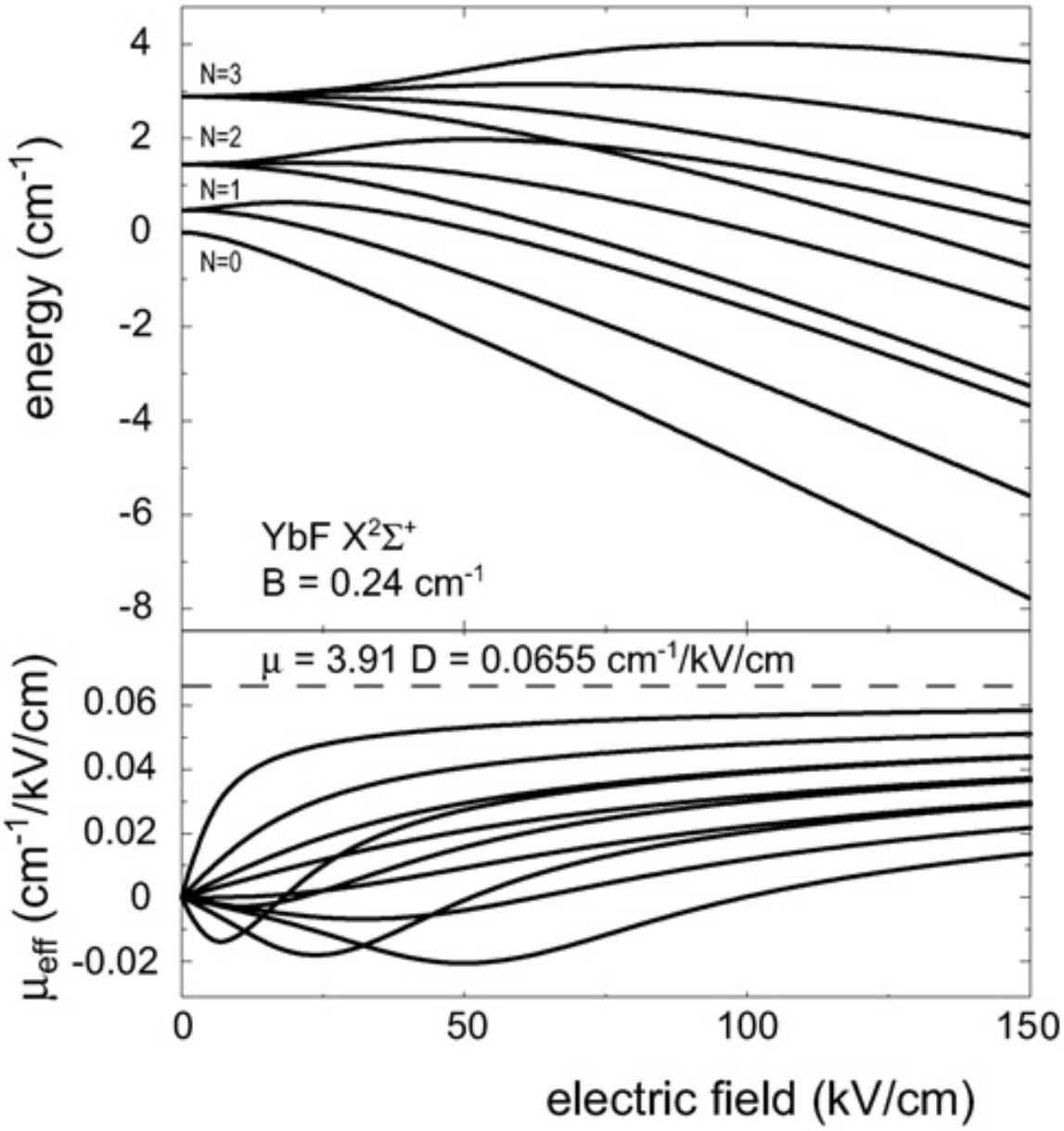
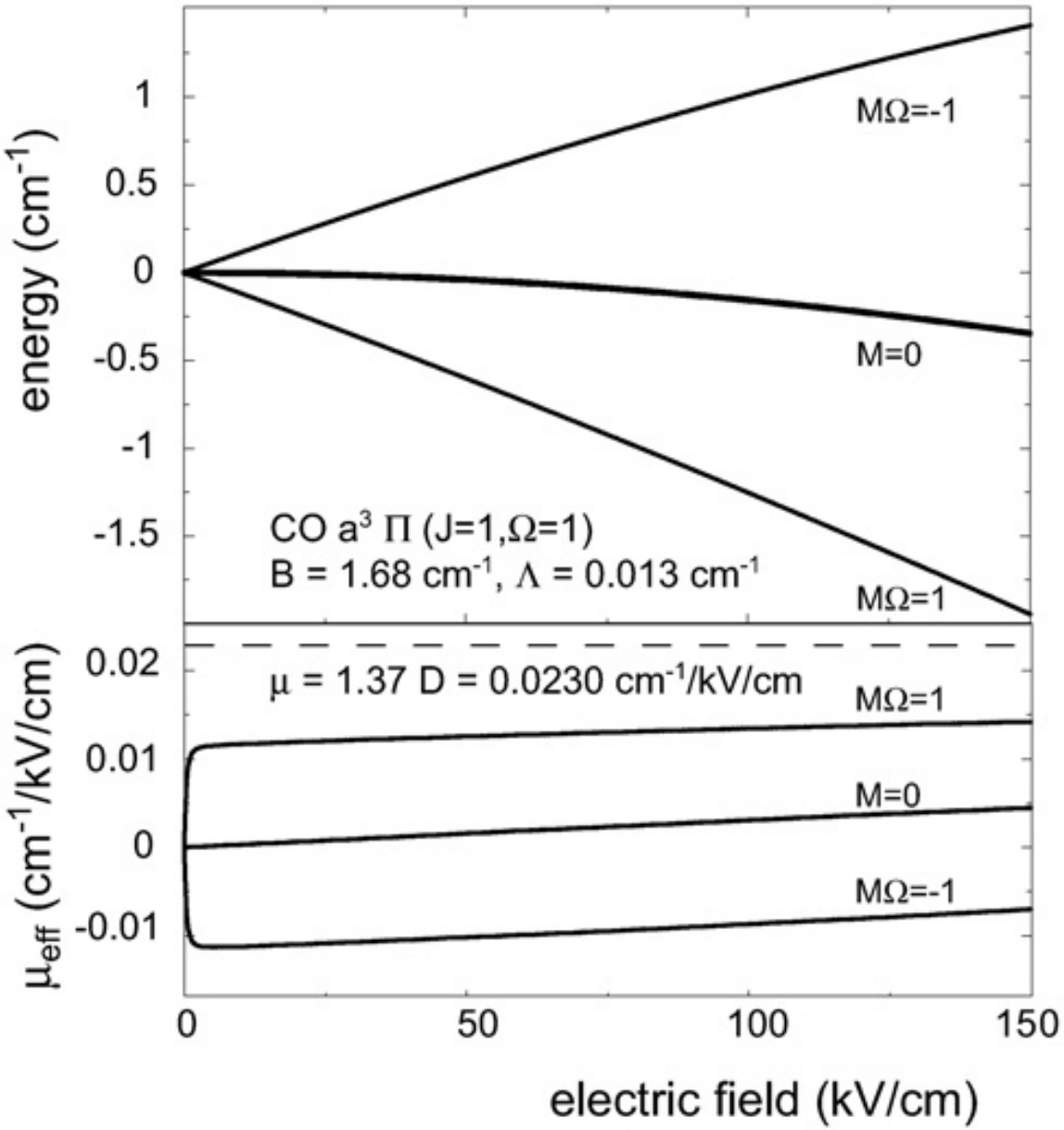
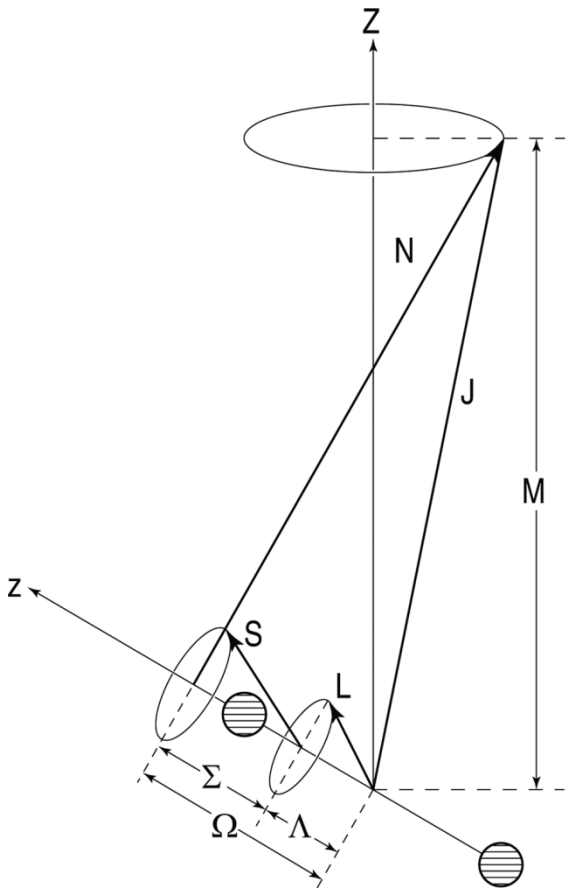
S.Y.T. van de Meerakker, H.L. Bethlem, N. Vanhaecke, G. Meijer Chem Rev **112**, 4828 (2012)

Stark effect of YbF

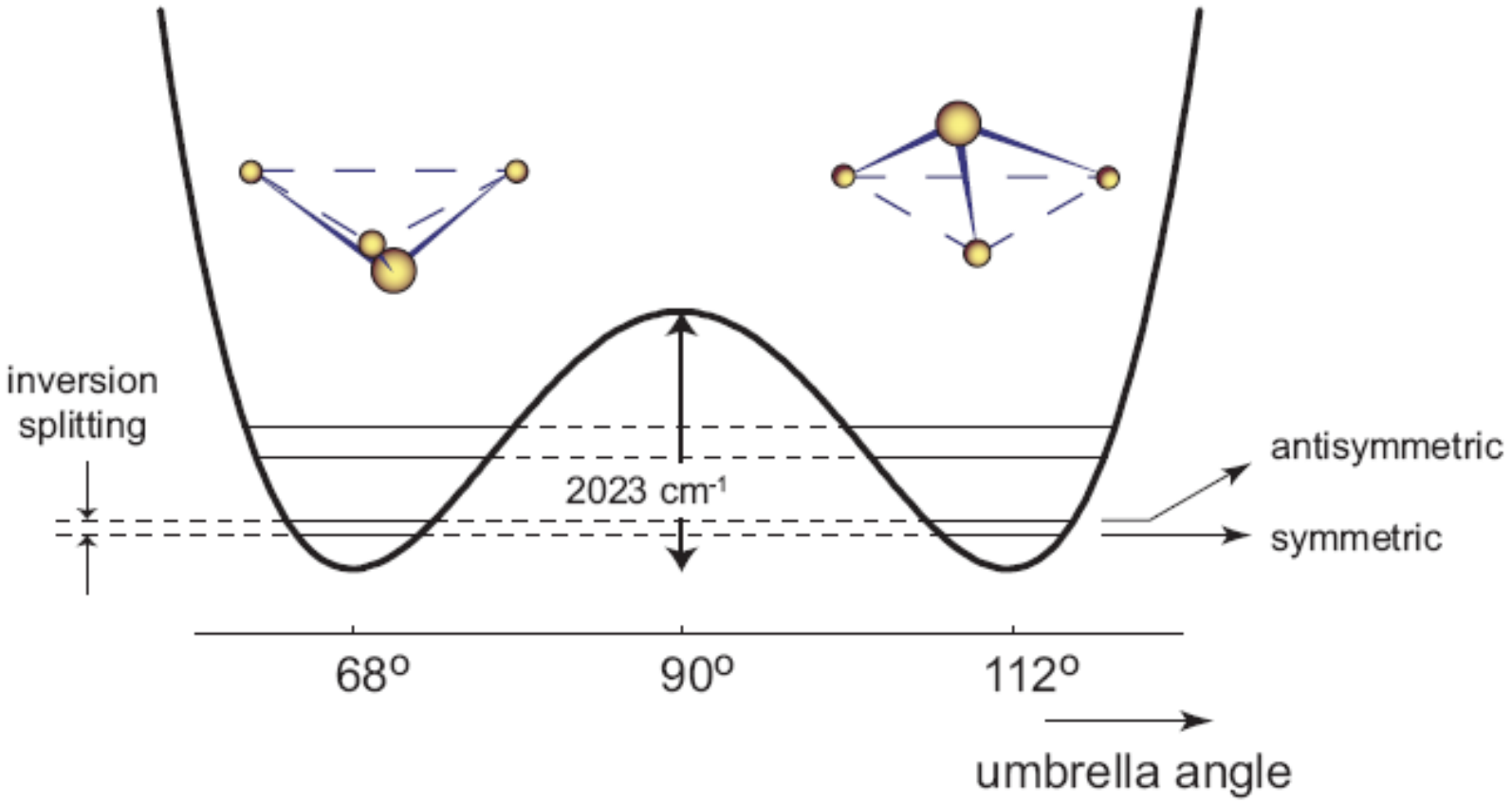


Stark effect of CO $a^3\Pi$

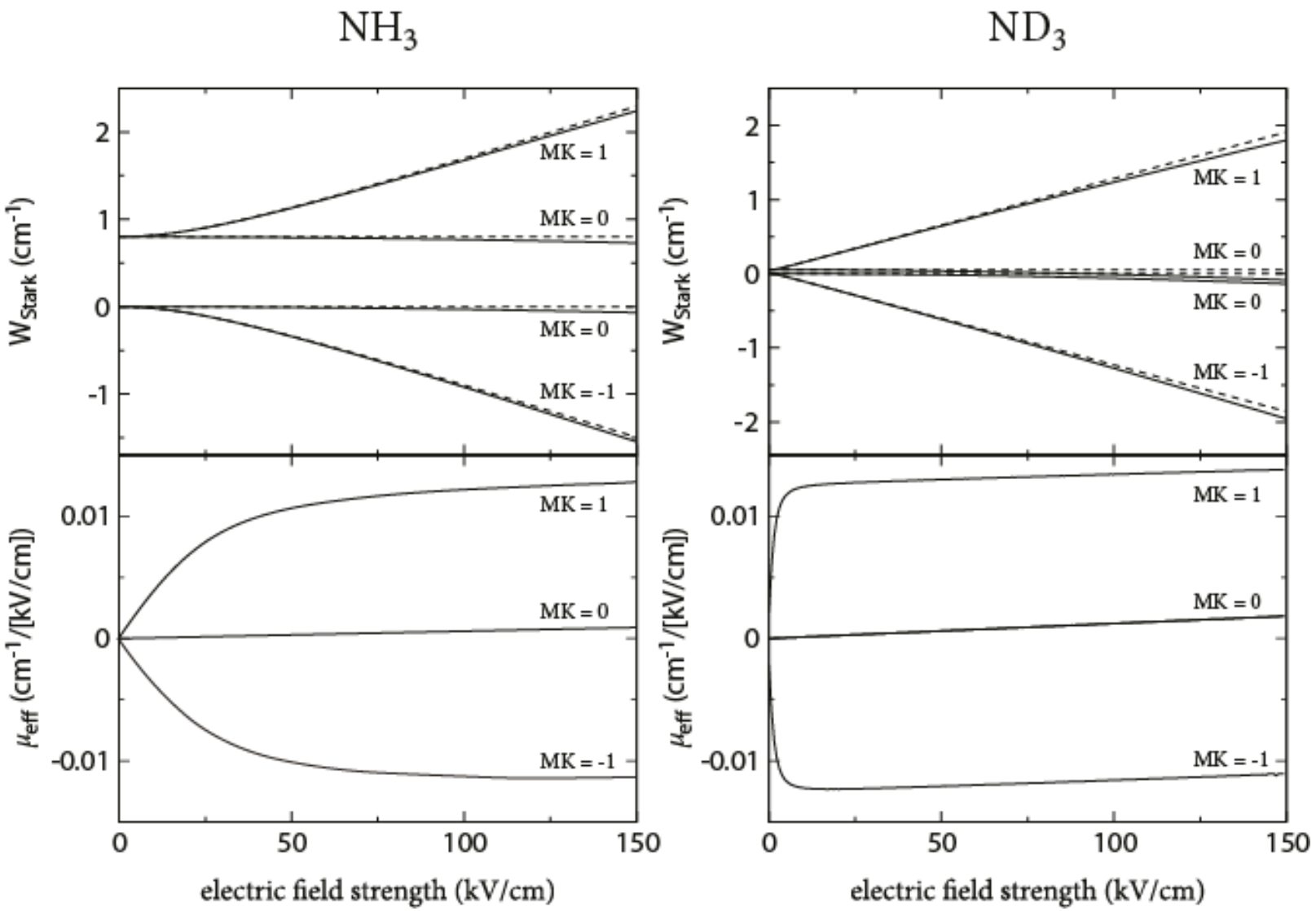




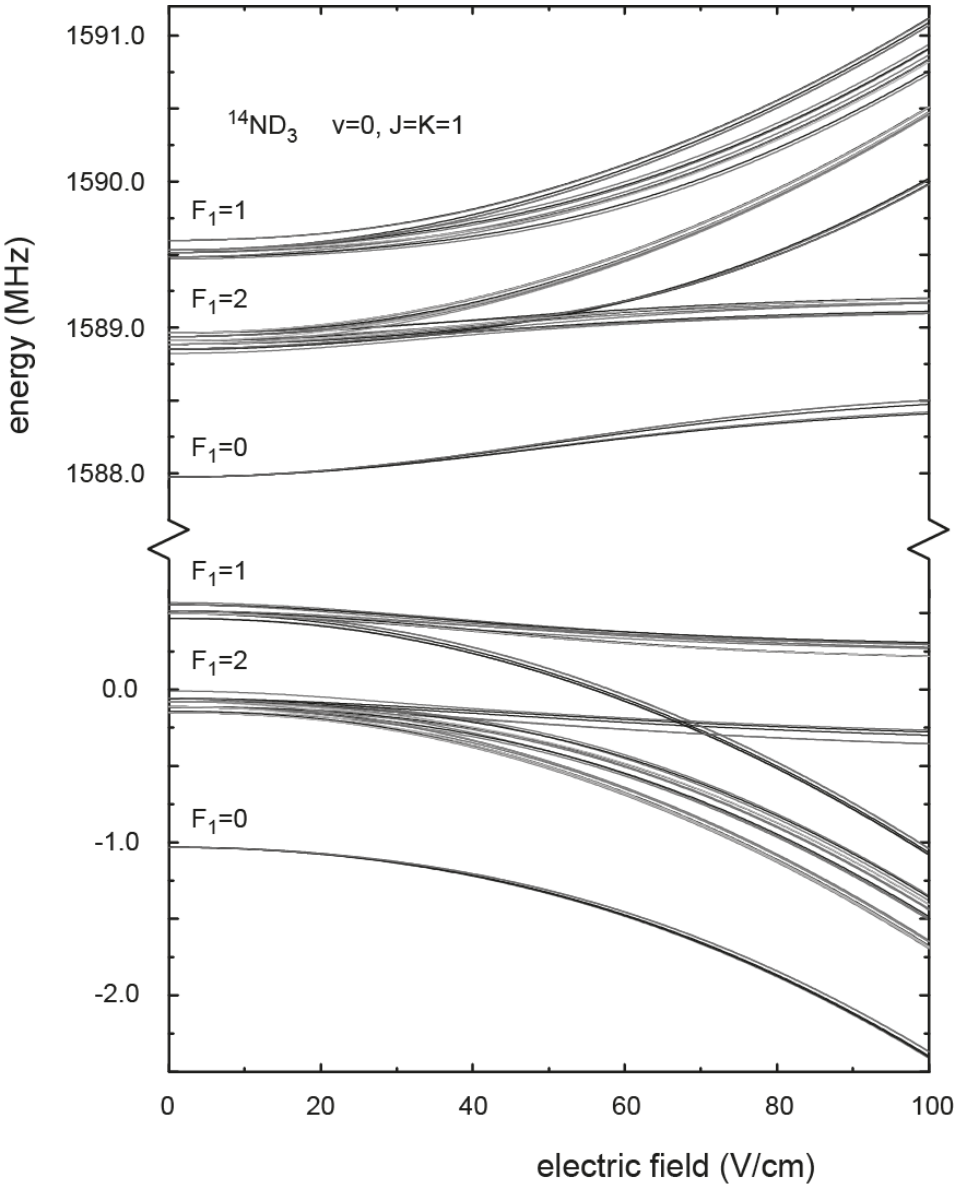
Stark effect of ammonia (inversion)



Stark effect of ammonia



Stark effect of ammonia (hyperfine structure)



Precision Measurement of Time-Reversal Symmetry Violation with Laser-Cooled Polyatomic Molecules

Ivan Kozyryev[1,*] and Nicholas R. Hutzler[2,1,†]

[1]*Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA*

[2]*Division of Physics, Mathematics, and Astronomy, California Institute of Technology, Pasadena, California 91125, USA*

(Received 1 June 2017; published 28 September 2017)

Precision searches for time-reversal symmetry violating interactions in polar molecules are extremely sensitive probes of high energy physics beyond the standard model. To extend the reach of these probes into the PeV regime, long coherence times and large count rates are necessary. Recent advances in laser cooling of polar molecules offer one important tool—optical trapping. However, the types of molecules that have been laser cooled so far do not have the highly desirable combination of features for new physics searches,

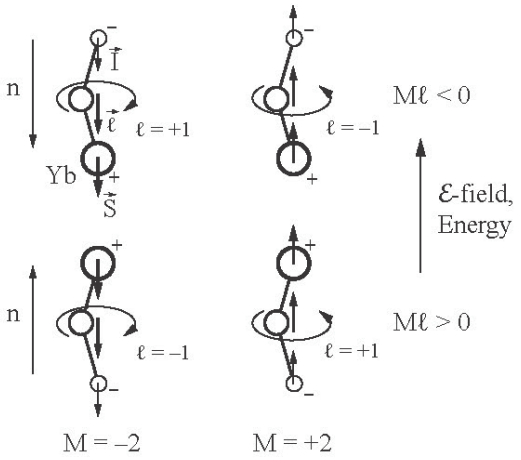


FIG. 1. Angular momentum in the fully-polarized stretched states $F = |M| = 2$, in which each of the component angular momenta are stretched as well. The quantum numbers S, ℓ, and I are indicated at the top-left. The internuclear axis points from the negative to the positive ion, meaning that the dipole moment lies along the internuclear axis. Compare the very similar figure for a $^3\Delta_1$ state like WC X [26] or ThO H [27]. Like Ω, ℓ is quantized in the molecule frame, which is why the direction of the vector $\vec{\ell}$ on the figure and the value of ℓ may differ. Since the EDM shift is $\propto \vec{S} \cdot n \propto \ell$, we can see that this interaction is reversed in the upper/lower Stark shifted states.

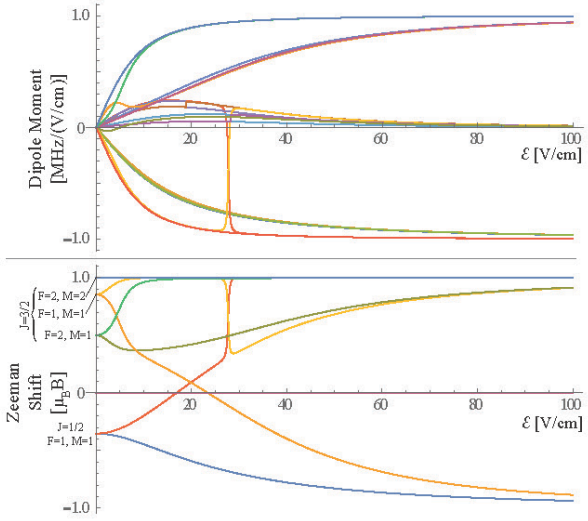


FIG. 2. Electric dipole moments (top) and Zeeman shifts (bottom) with γ =30 MHz, $q = -10$ MHz, $b = 2$ MHz, and $d = 4$ D, representative of YbOH. The Zeeman shift is in units of $\mu_B \mathcal{B}$ in a small magnetic field. The dipole moment is also signed polarization, as described in the text. The jumps indicate avoided crossings. The labels on the left side correspond to the zero-field eigenstates. The colors in both plots correspond to the same states.

Manipulating Molecules using E-Fields

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Multipole Expansion of the E-field

In free space, the electric potential can be written as:

$$\vec{E} = -\vec{\nabla}\Phi \qquad \nabla^2\Phi = 0$$

$$\Phi = \sum_{L,M} a^{LM} r^L Y^{LM}$$

Most interesting to us are terms with M=L; 'planar' symmetry

$$\Phi = U_0 + U_1 x + U_2(x^2 - y^2) + U_3(x^3 - 3xy^2)\ldots$$

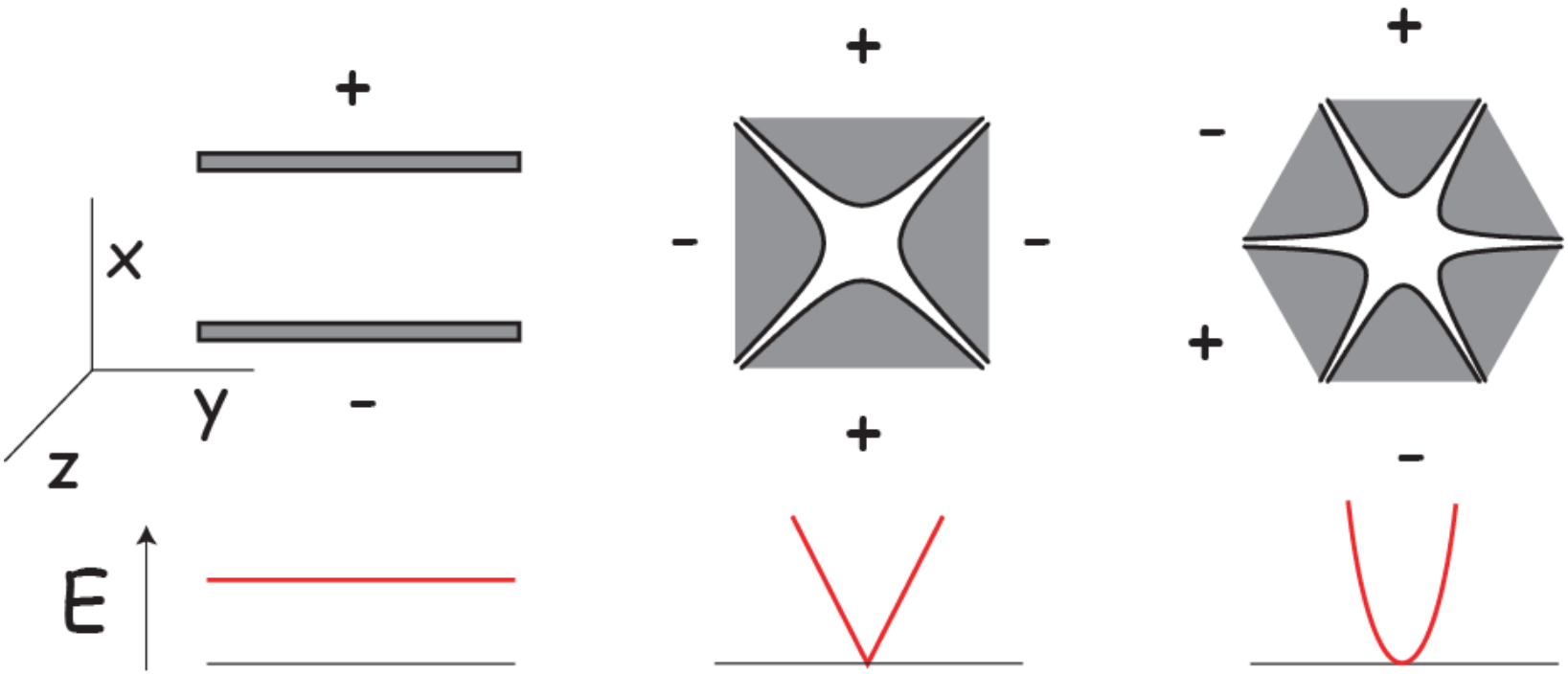
And terms with M=0; 'cylindrical' symmetry

$$\Phi = U_0 + U_1 z + U_2(z^2 - \rho^2/2) + U_3(z^3 - 3z\rho^2/2)\ldots$$

Expansion of the Electric field in 2D

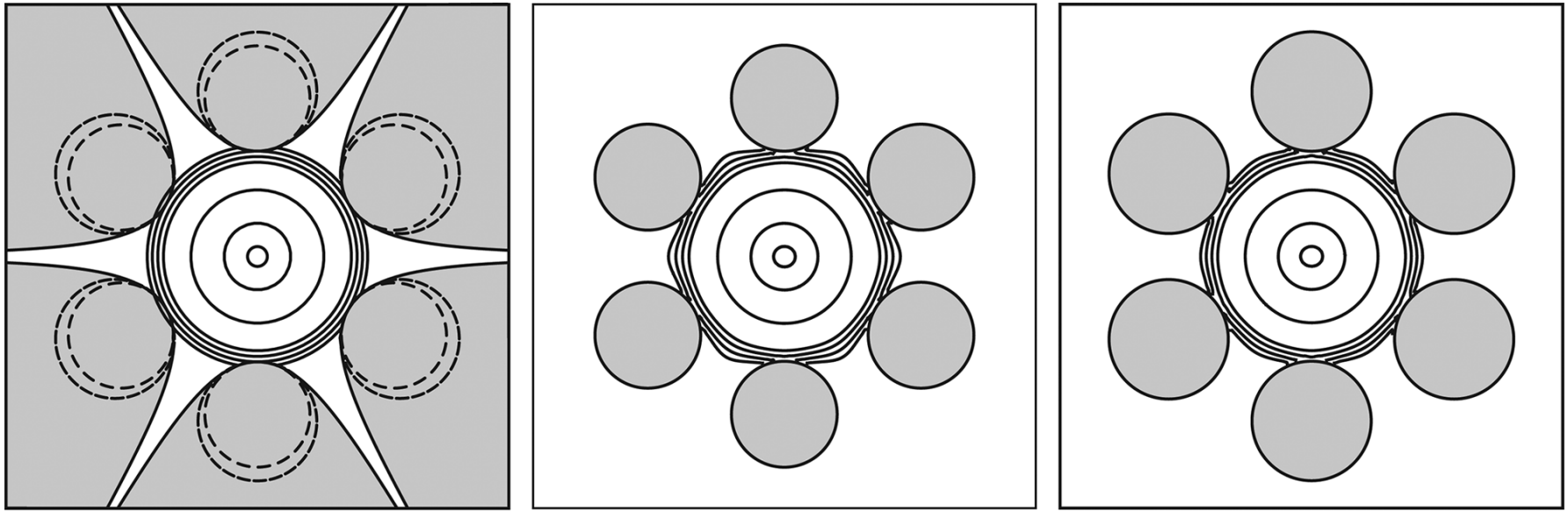
terms with M=L ‘planar’ symmetry

$$\Phi = U_0 + U_1 x + U_2 (x^2 - y^2) + U_3 (x^3 - 3xy^2) \ldots$$



Making an actual hexapole

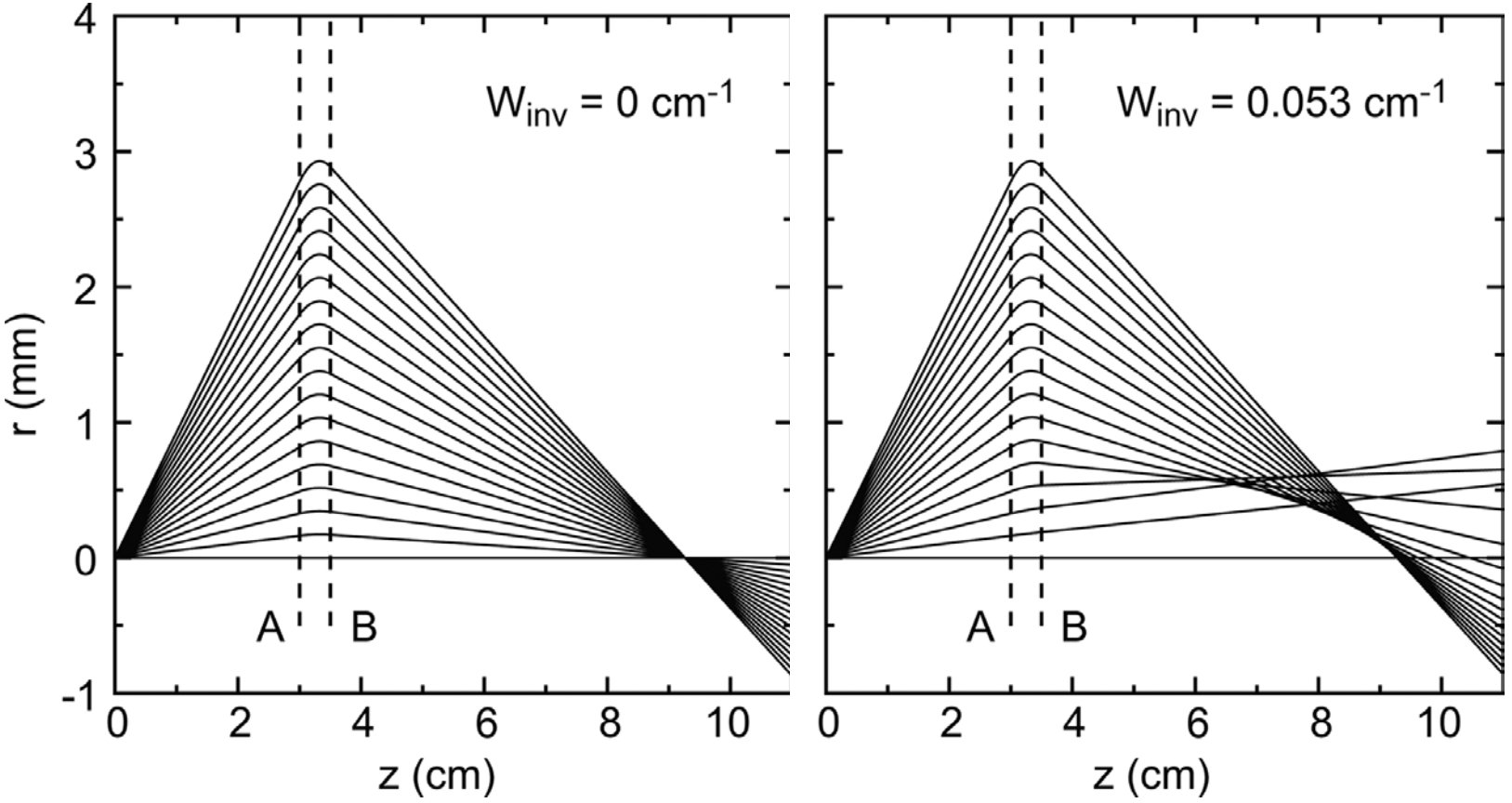
The electric field is uniquely defined by (1) Laplace equation and (2) the boundary conditions.



(a) Ideal hexapole (b) Rod radius: *R/2* (c) Rod radius: *0.565R*

Focusing Polar Molecules with a Hexapole

Trajectories of ammonia (ND3) molecules through a hexapole lens.



Limitation due to Laplace

Focusing fields are limited to those that can be obtained from the series expansion

Makes it impossible to generate;

-guide for LFS with non-zero offset

-guide for LFS (with maximum on the axis)

-lens that compensates for non-ideal Stark shift

-deflection field that deflects in one direction and does nothing in the other direction.

-linear AG lens

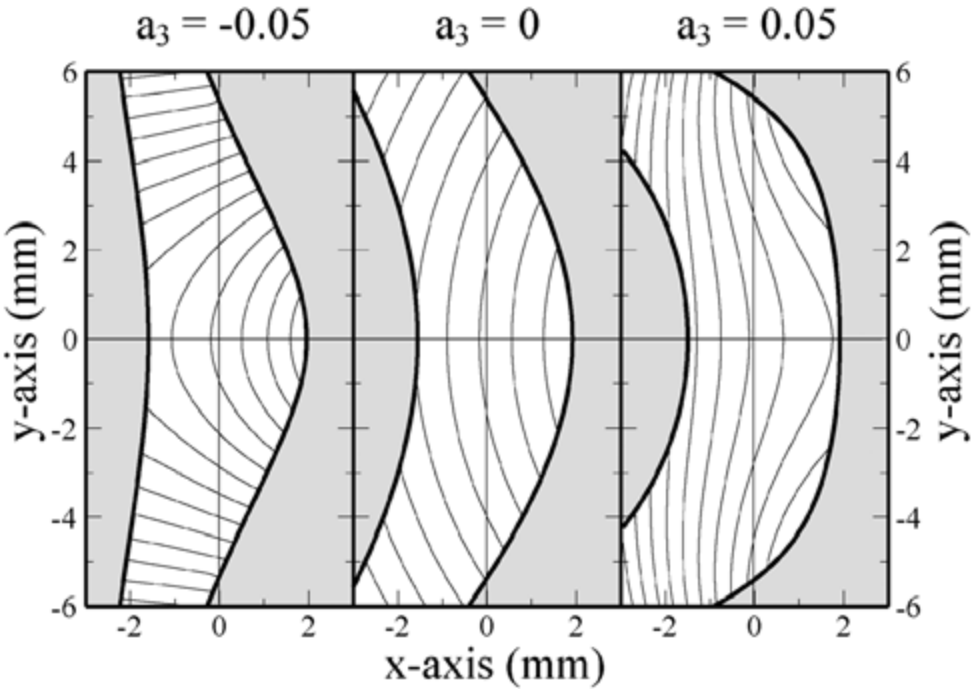
An ‘ideal’ deflector

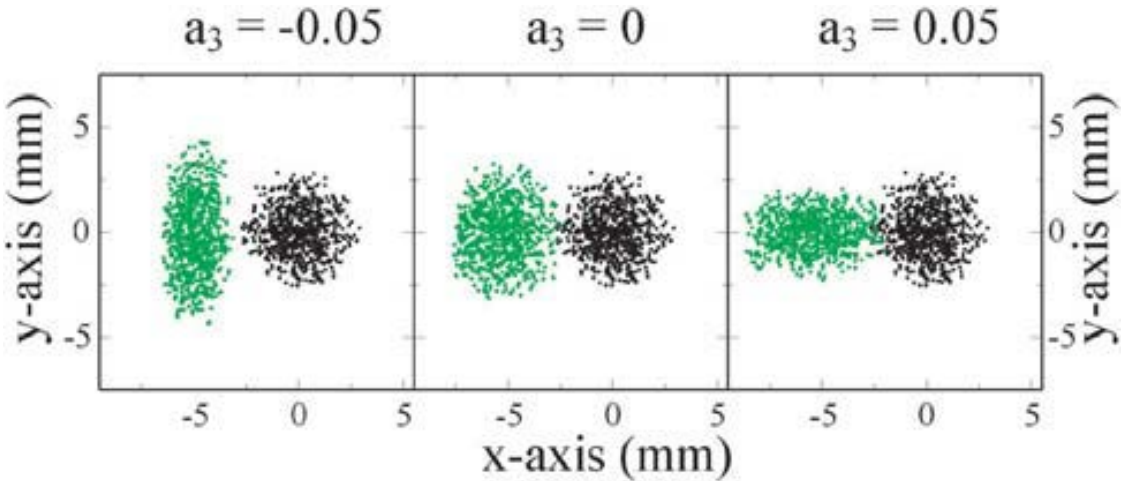
$$F_{Stark,x} = \mu_{eff} E_0 \left(\frac{a_2}{a_1} \frac{1}{r_0} + 2 \frac{a_3}{a_1} \frac{x}{r_0^2} - \left(\frac{1}{2} \left(\frac{a_2}{a_1} \right)^3 - 2 \frac{a_2}{a_1} \frac{a_3}{a_1} \right) \frac{y^2}{r_0^3} + \cdots \right)$$

$$F_{Stark,y} = \mu_{eff} E_0 \left(\left(\left(\frac{a_2}{a_1} \right)^2 - 2 \frac{a_3}{a_1} \right) \frac{y}{r_0^2} - \left(\left(\frac{a_2}{a_1} \right)^3 - 4 \frac{a_2}{a_1} \frac{a_3}{a_1} \right) \frac{xy}{r_0^3} + \cdots \right)$$

An ‘ideal’ deflector

a1 = 1
a2 = 0.2





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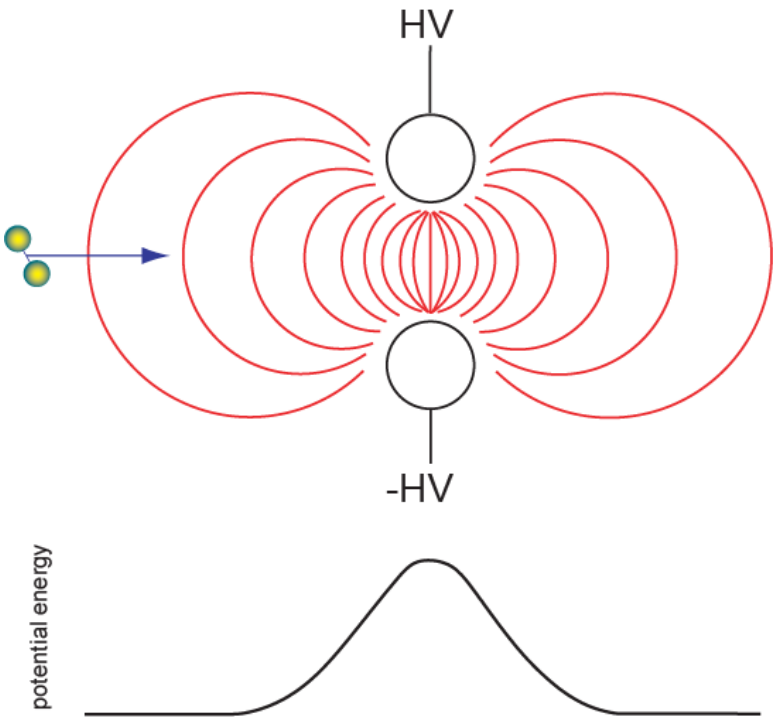
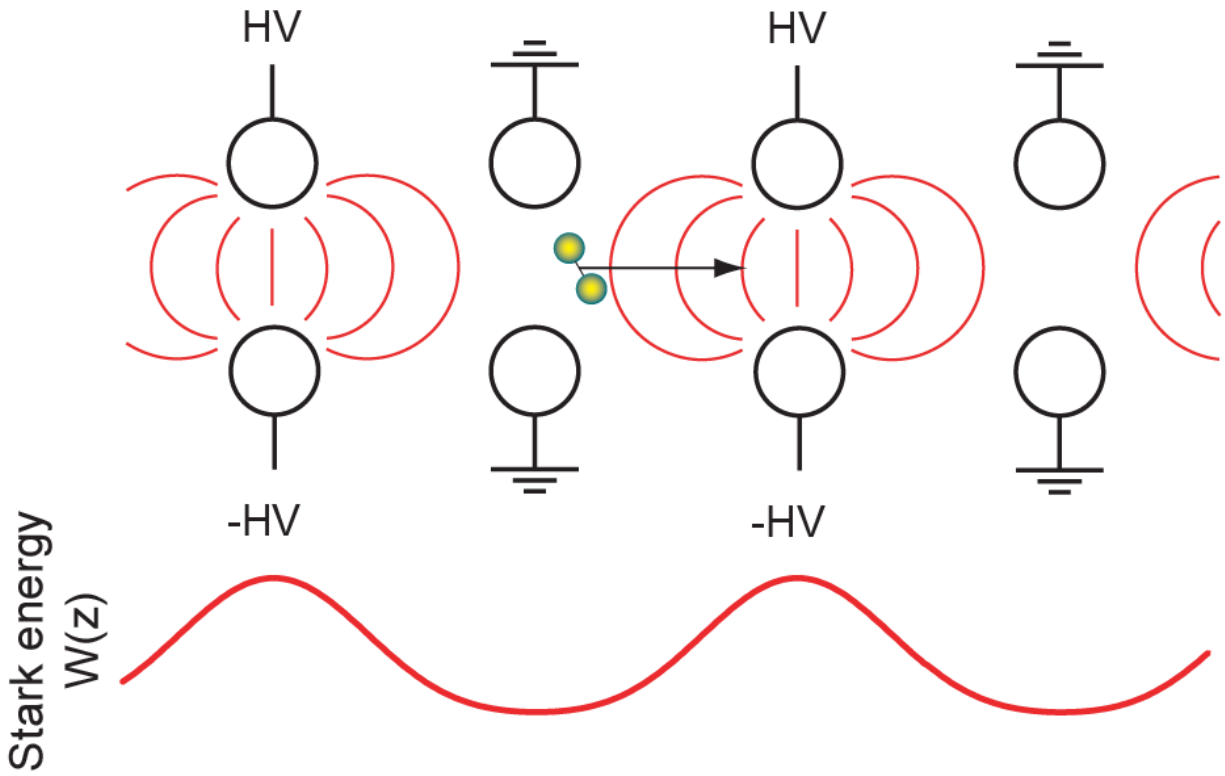
A molecule in an inhomogeneous E-field

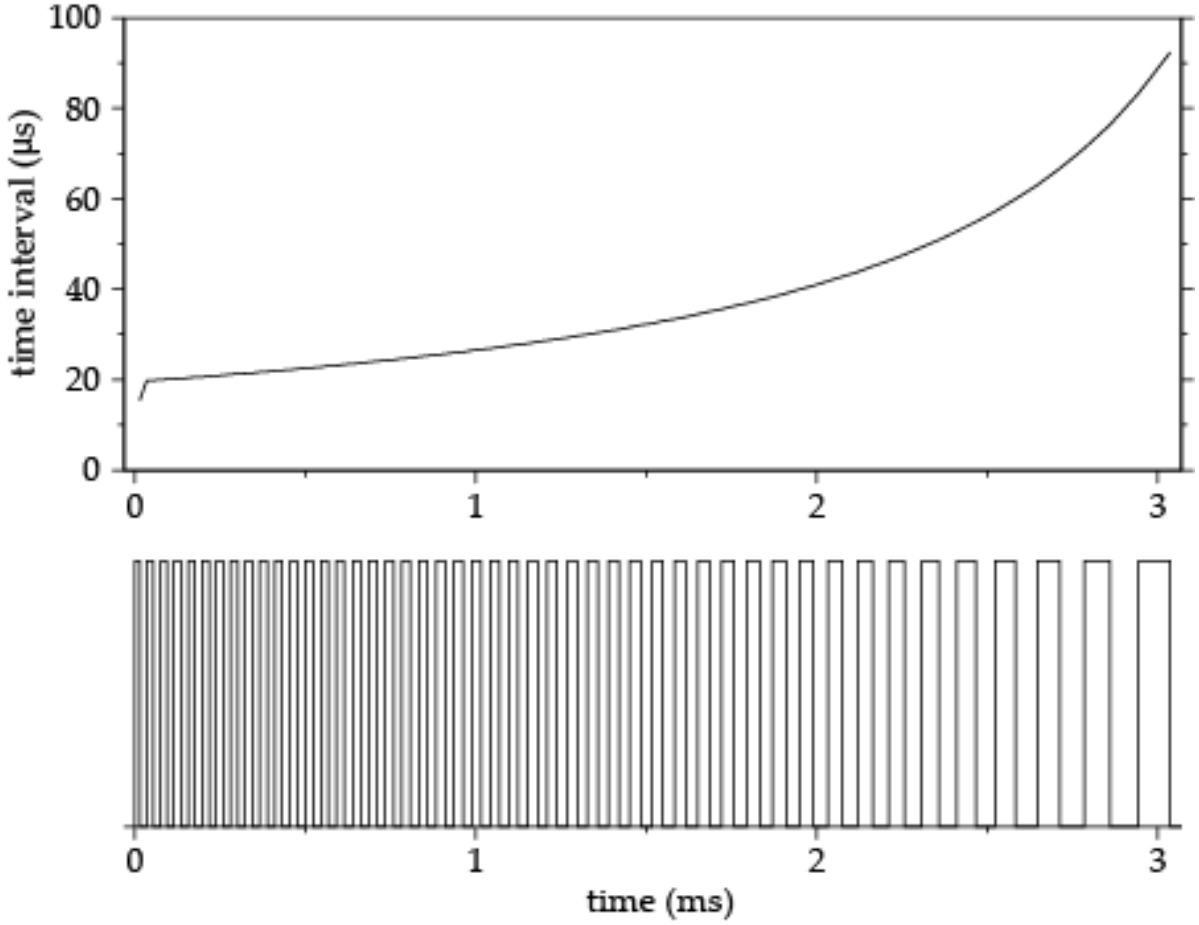


Energy loss, typically 1 cm-1 (~1.4 K) in an electric field of 100 kV/cm -- Need many stages.

An array of inhomogeneous E-fields

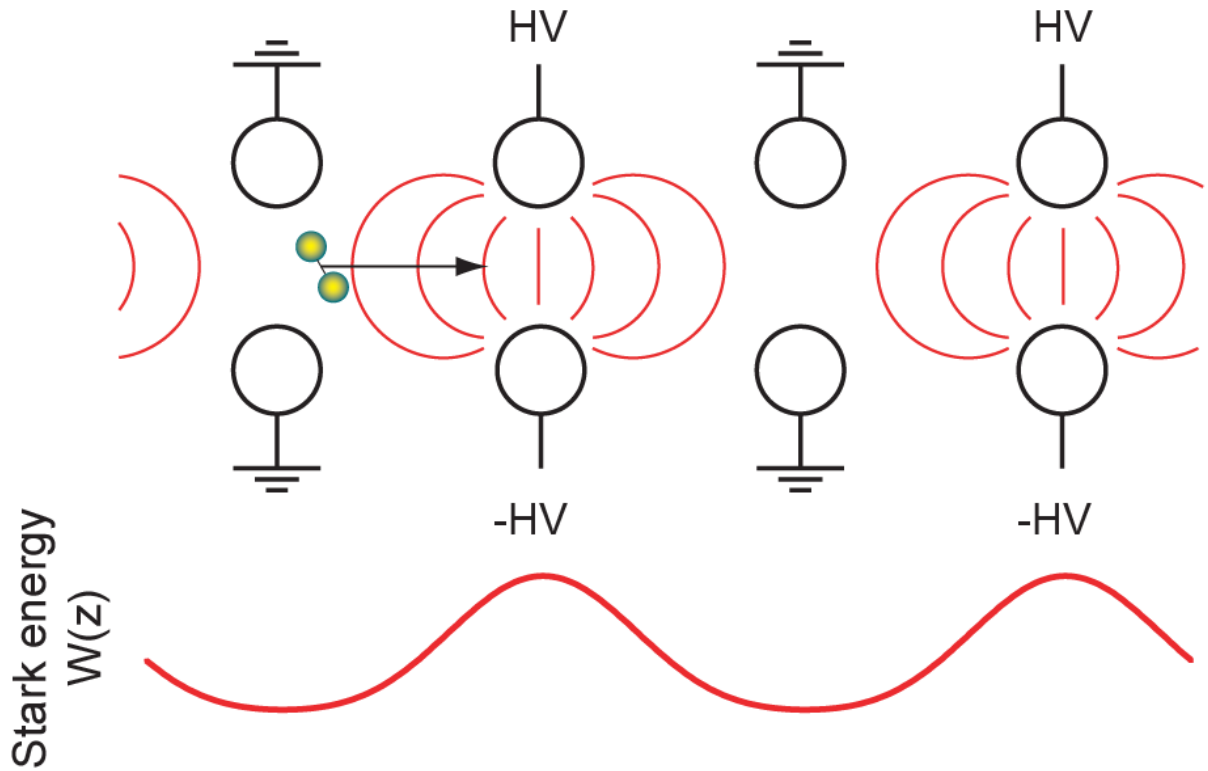


Time sequence applied to decelerator



Typical burst sequence used to decelerate ammonia molecules from 280 to 50 m/s.

An array of inhomogeneous E-fields



Dynamics in the decelerator; Phase Stability

The energy loss of the synchronous molecule per stage can be written as:

$$\Delta W(\varphi_0) = W(\varphi_0 + \pi) - W(\varphi_0) = 2a_1 \sin\varphi_0$$

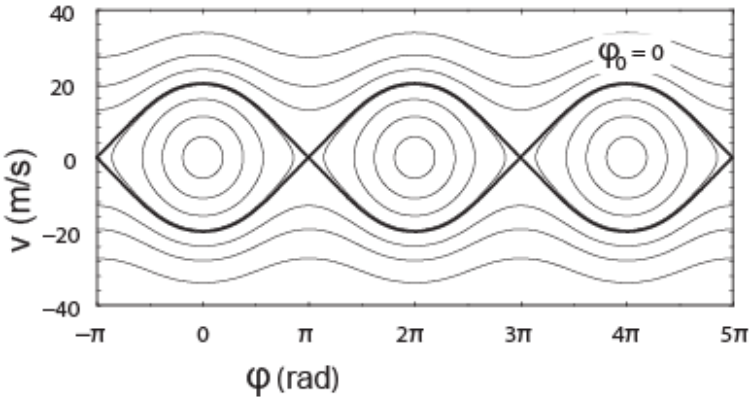
The average force on the synchronous molecules then is:

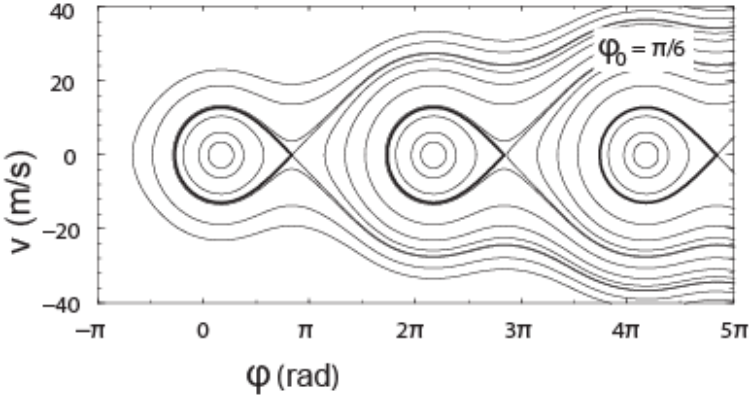
$$\overline{F}(\varphi_0) = \frac{-\Delta W(\varphi_0)}{L} = -\frac{2a_1}{L}\sin\varphi_0$$

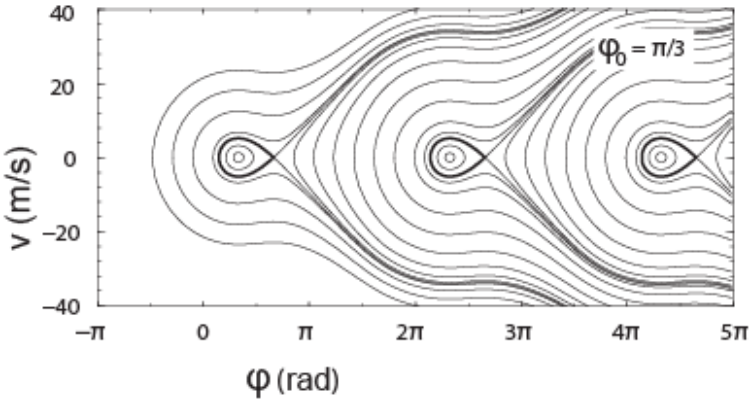
The equation of motion for molecules that are close to the synchronous molecule and have a slightly different velocity:

$$\frac{mL}{\pi}\frac{d^2\varphi}{dt^2} + \frac{2a_1}{L}(\sin(\varphi_0 + \Delta\varphi) - \sin(\varphi_0)) = 0$$

Dynamics in the decelerator; Phase Stability







Trajectories of molecules in phase space for different choice of the synchronous phase.

One needs to make a compromise between the energy loss per stage and the phase space acceptance

Liouville's Theorem

"In a system that is only acted upon by forces that can be derived from a potential, the number of particles per unit volume in six dimensional phase-space is conserved."

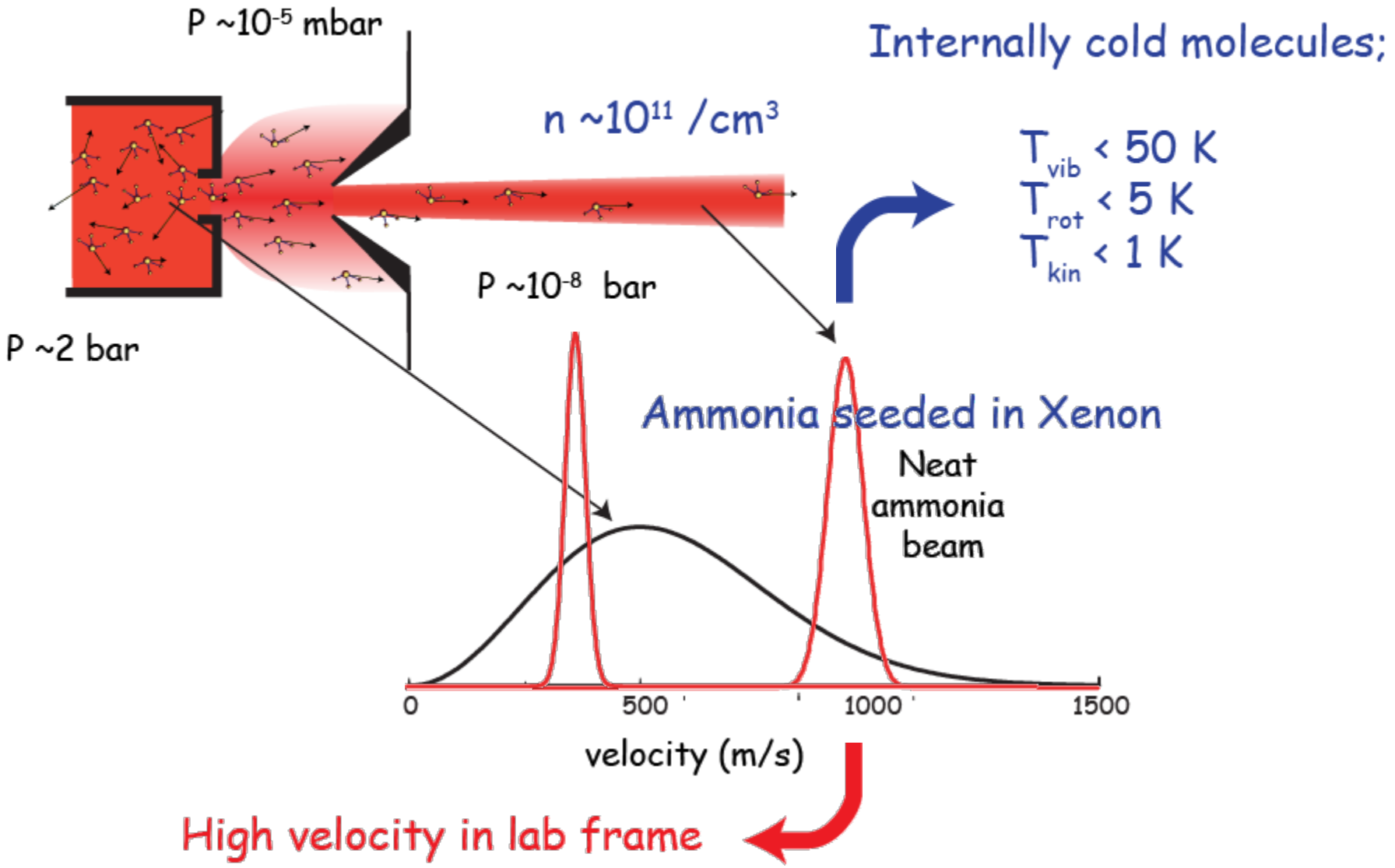
This theorem also applies to particles in time-varying electric or magnetic fields.
Ketterle and Pritchard, Phys. Rev. A **46**, 4051 (1992).

As a consequence:

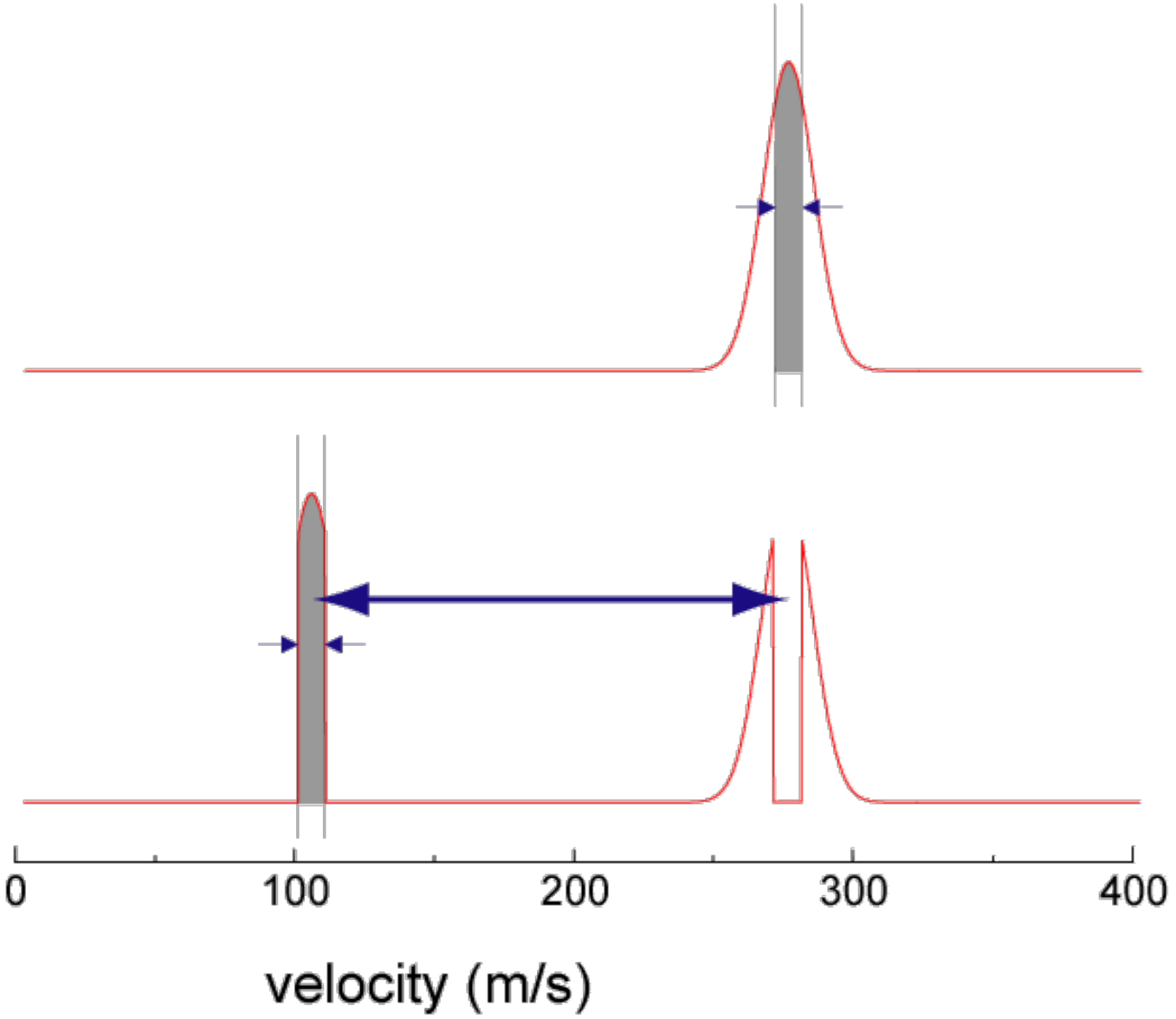
(1) different trajectories in phase-space do not intersect at any given instant of time.

(2) a boundary C_1 in phase-space, which bounds a group of particles at time t_1, will transform into a boundary C_2 at time t_2, which bounds the same group of particles.

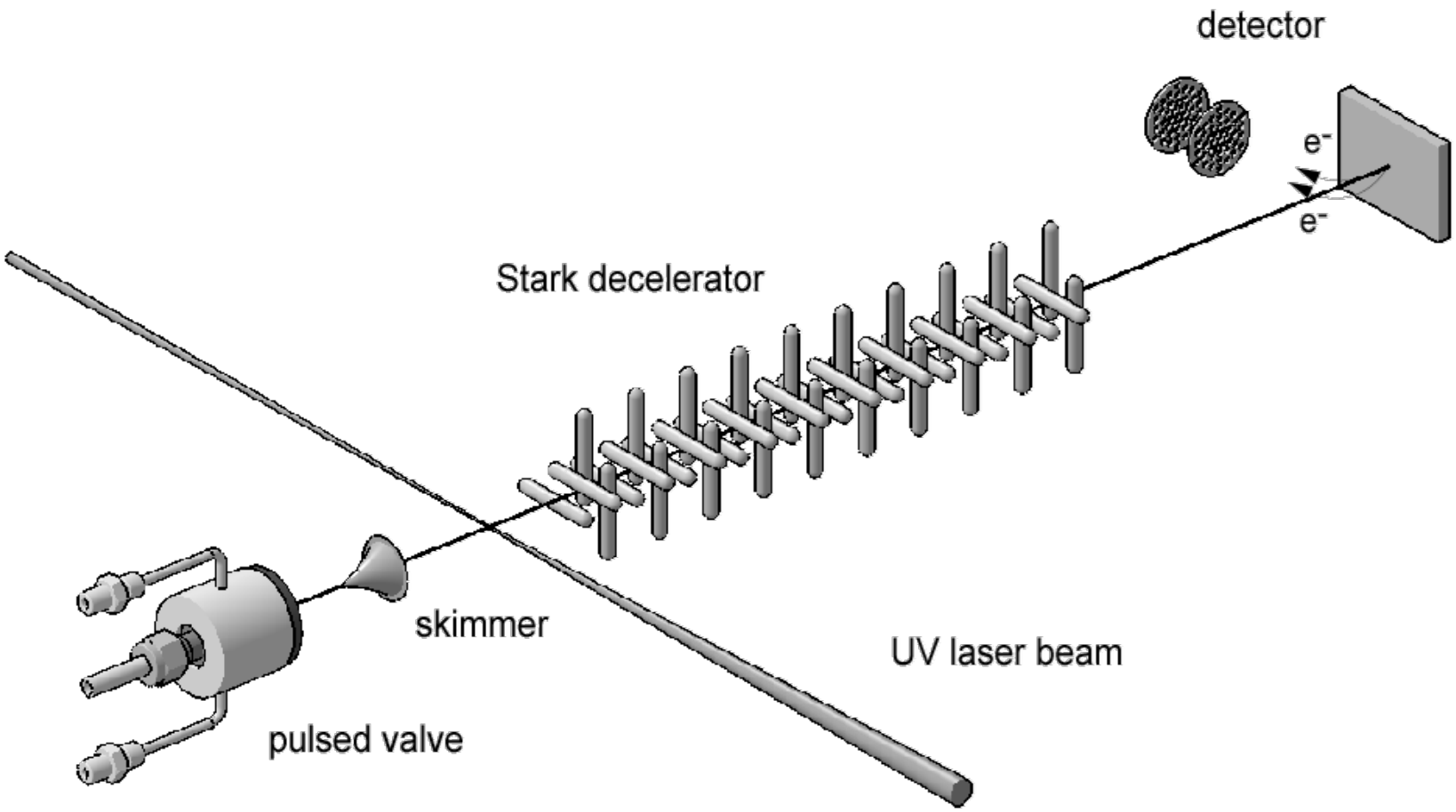
A (pulsed) molecular beam

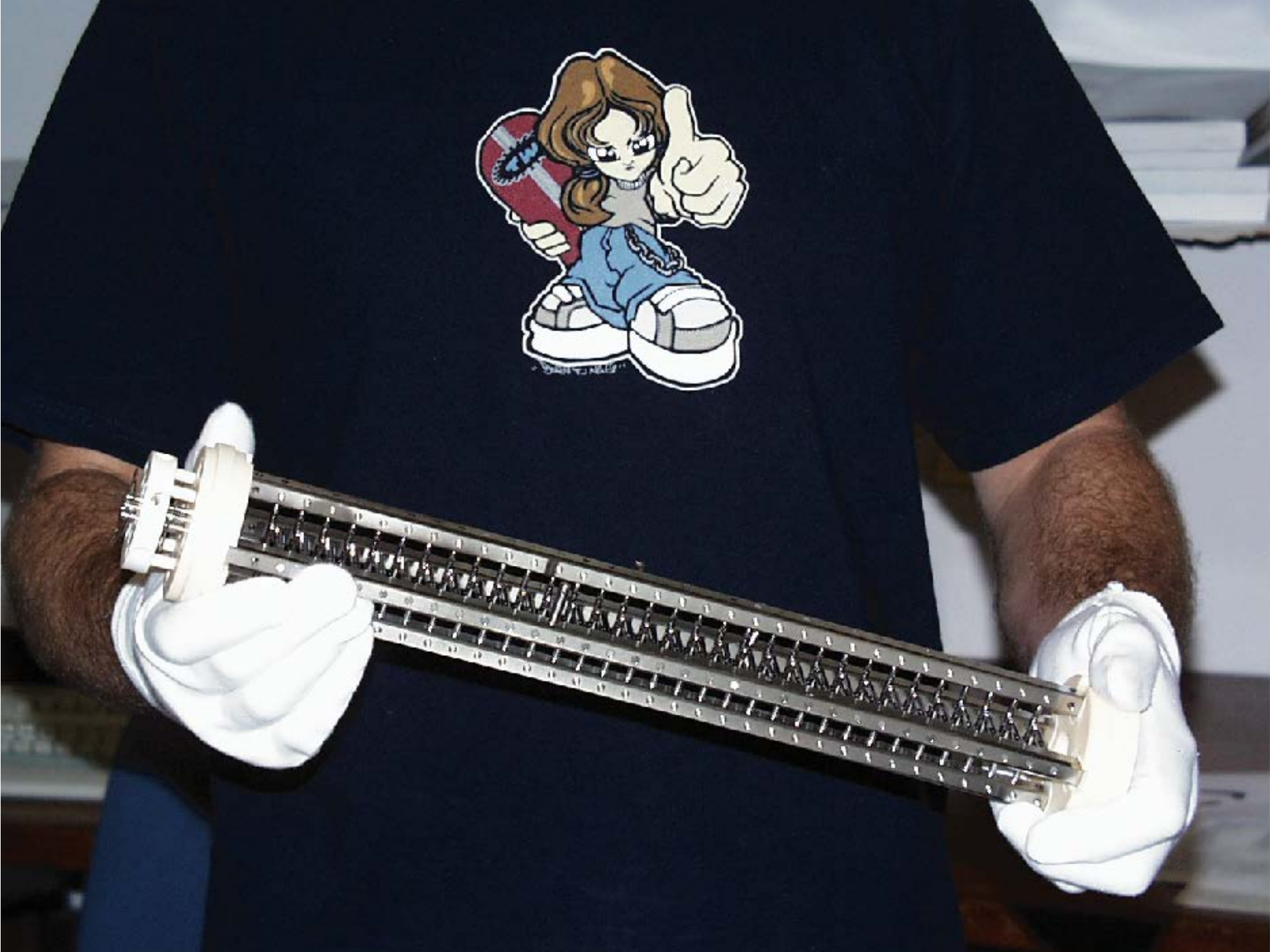


Velocity distribution of decelerated molecules



Decelerating Metastable CO Molecules





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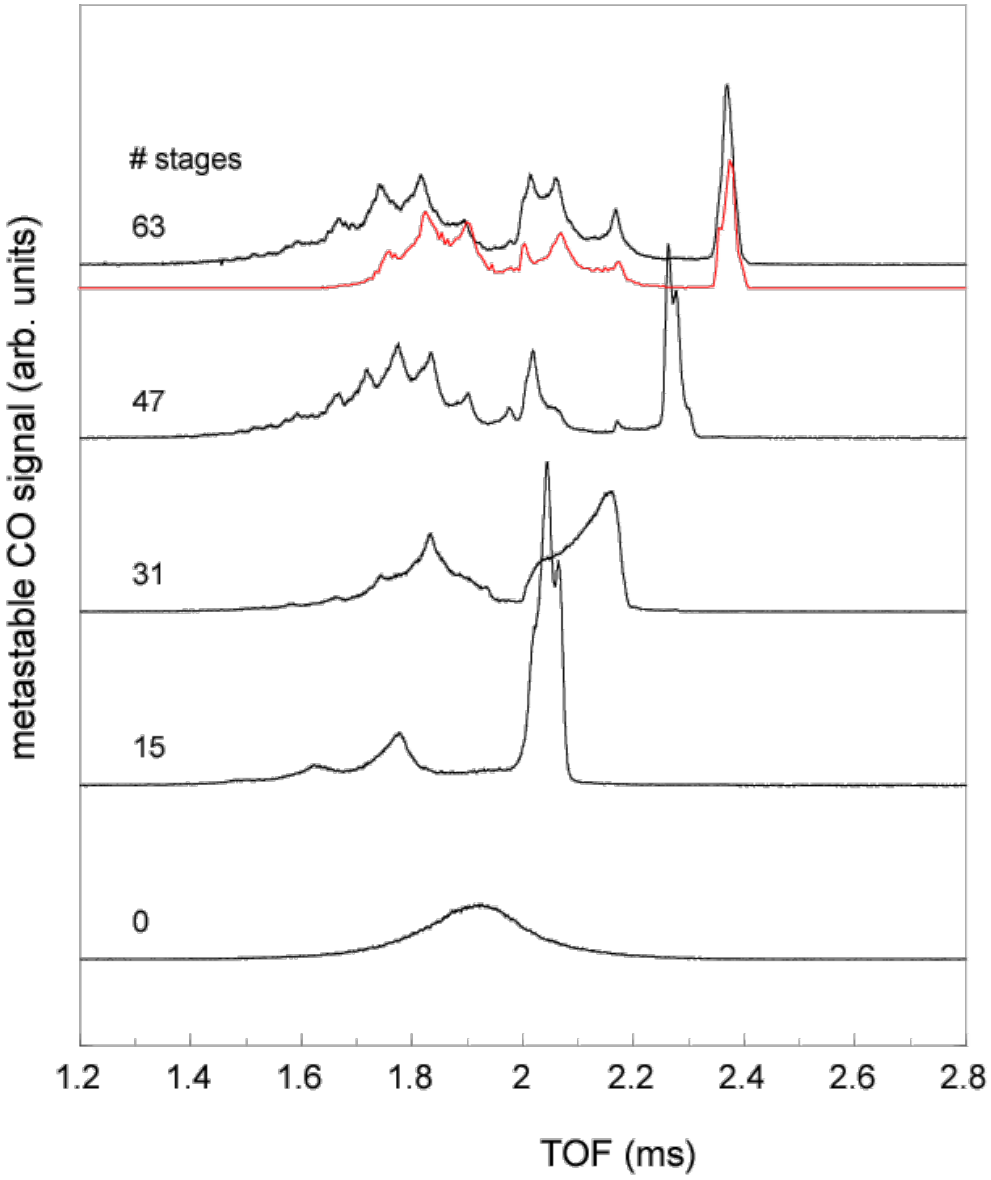
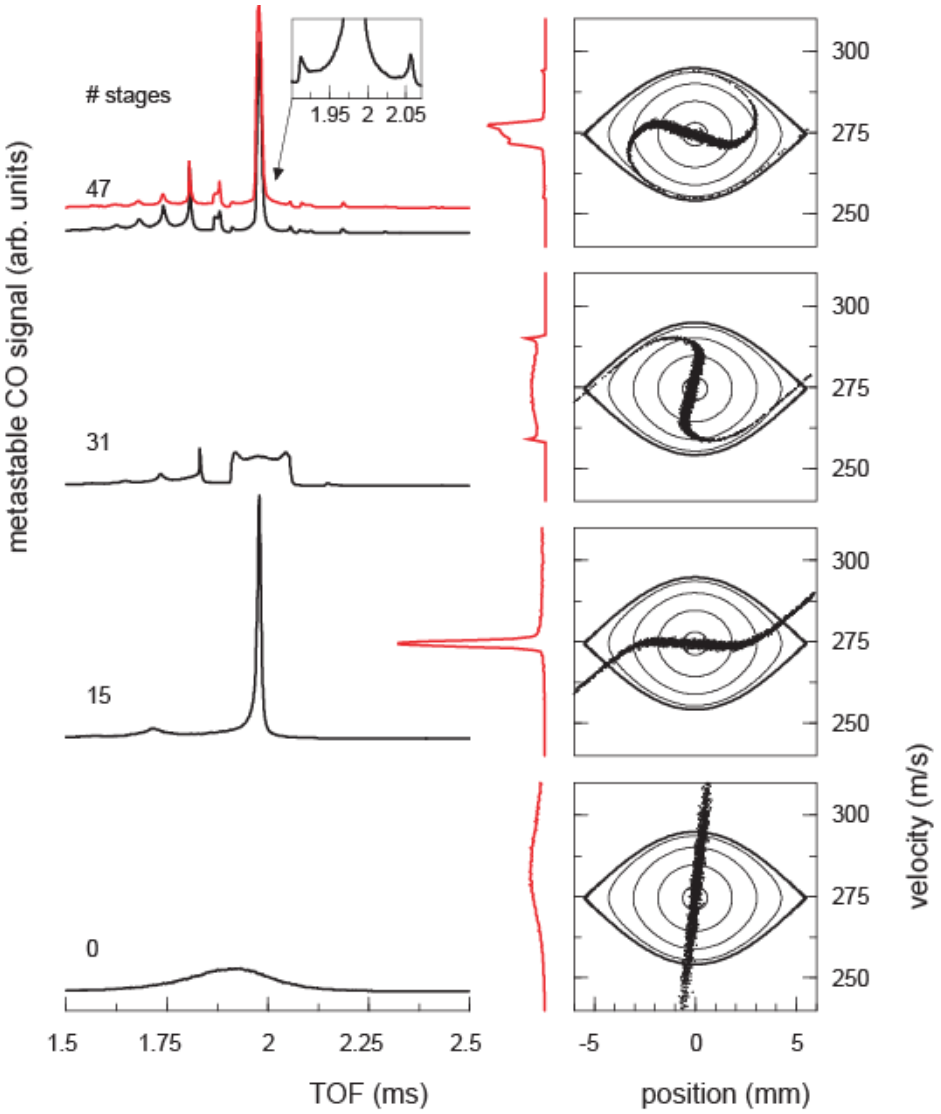
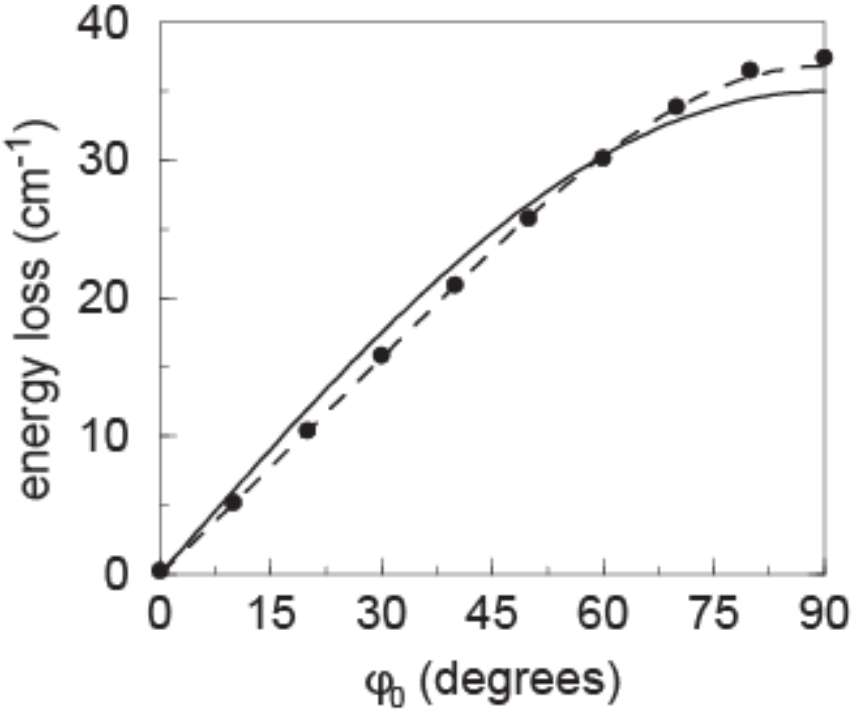
Experimental TOF profiles; 60^{o}

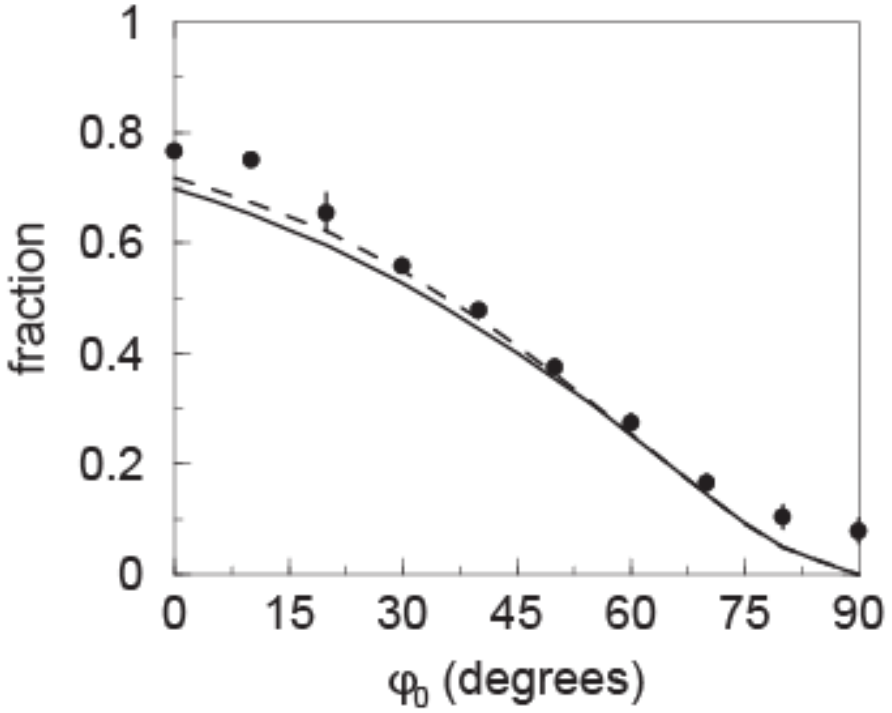


Experimental TOF profiles; 0º (guiding)



Energy loss and decelerated fraction





List of Decelerated Molecules (2019)

Light Molecules

CO^*	(Nijmegen/Berlin)
ND_3	(Nijmegen/Berlin/Amsterdam/JILA/Shanghai)
NH_3	(Nijmegen/Berlin/Amsterdam)
OH	(Berlin/JILA)
OD	(Berlin)
NH	(Berlin/JILA)
CH_3F	(Amsterdam)
H_2CO	(Berlin/JILA)
SO_2	(Hannover)
CH	(Oxford)
LiH	(London)

Heavy Molecules

YbF	(London)
CaF	(London)

Benzonitrile (Berlin)

SrF, BaF (Groningen)