Crossed Molecular Beam Studies of Scattering and DEFCOM Spectroscopy

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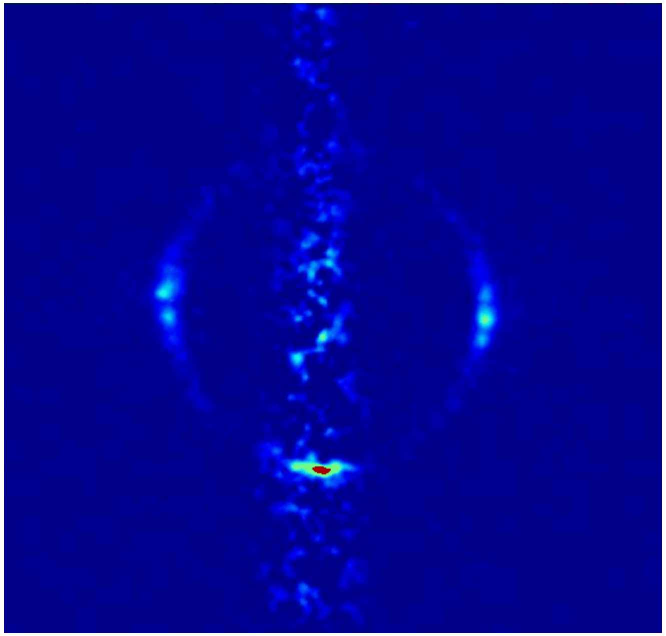

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Outline

- Short History of Collisional Energy Transfer studies

- Description of Ion Imaging with Velocity Mapping for Inelastic scattering as backdrop.

- Quantum-State-Selective Inelastic Scattering
  - Differential cross sections for single rotational states
  - Scattering of Electronically excited states.
  - Scattering of Kr atoms (μKelvin samples of atoms and molecules)
  - DEFCOM spectrometer: <u>D</u>ual-<u>E</u>talon <u>F</u>requency-<u>Com</u>b Spectrometer, A new way to do several sorts of spectroscopies.

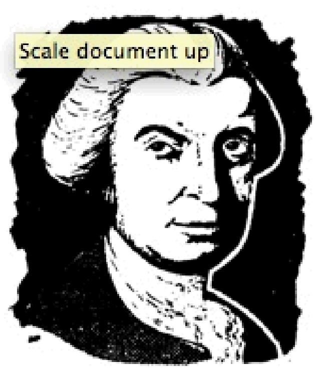
Short History of Collisional Energy Transfer

The modern concept of Potential Energy Surfaces came from thinking about collisional energy transfer. Roger Boscovich (1711-1787)

One of the great philosophical arguments at the time took place between the adherents of Descartes who—following Aristotle—thought that forces can only be the result of immediate contact and those who followed Newton and believed in his concept of force acting at a distance.

Imagine 2 equal bodies, one fast one (10m/s) gaining upon a slower one (5m/s). Upon collision the faster one will slow down and the slower one will speed up. How does this happen?

The change in speed can't be instantaneous Boscovich argued, as that would not be continuous and a body can't be going both faster and slower at same time. Therefore the change in speed must take some time but if the change only happens at contact then because they are moving at different speeds for a period of time, while in contact, then one would travel into the other, impossible. Therefor repulsive interaction must take place over a small space and time.



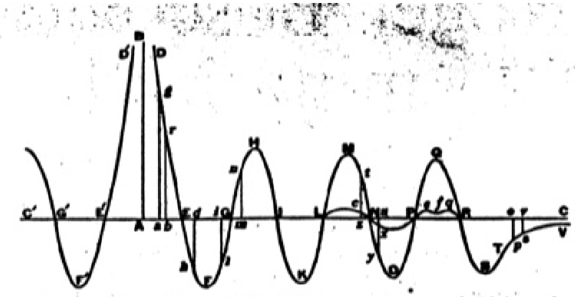
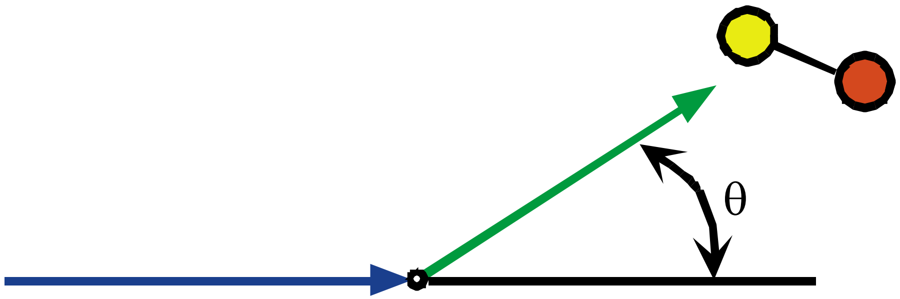


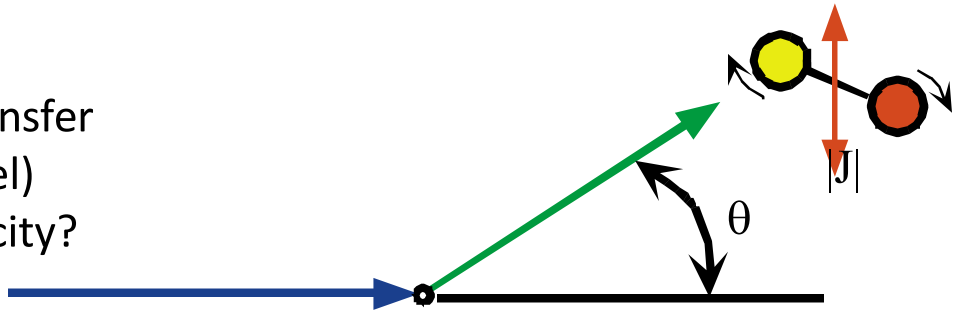
Diagram from Boscovich's "Theory of Natural Philosophy reduced to a single law of forces" showing the type of interaction between point atoms. There is a very large repulsion for close approach and an approximation to the inverse square law at large distances with several stable interatomic distances in between.

Fast Forward a Few Hundred Years: A Molecular Dynamics Approach to Rotational Energy Transfer Collisions

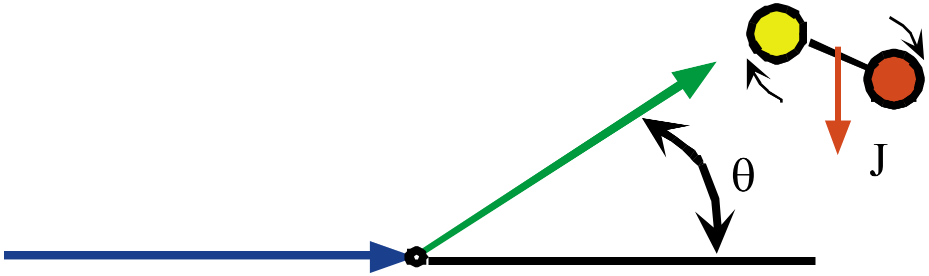
State-to-state Differential Cross Sections For NO+ Ar electronic and rotationally inelastic collisions (scattering angle)



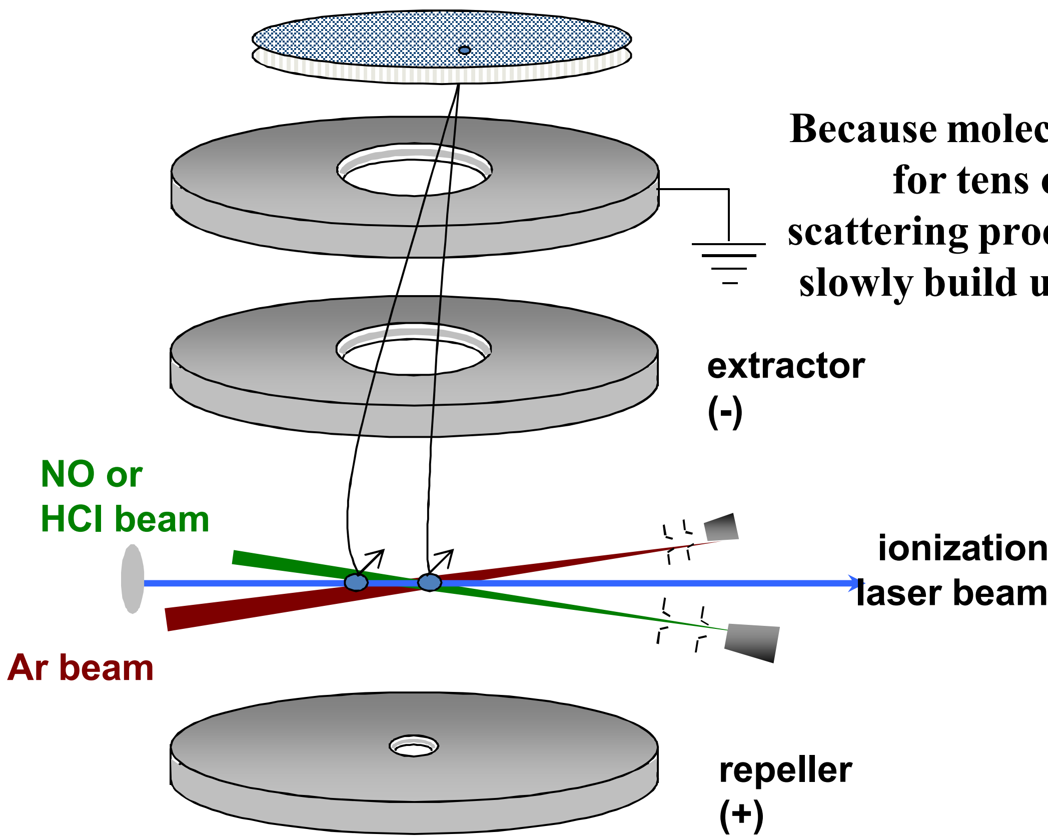
Rotational Alignment in Collisional Energy Transfer NO +Ar Products (Frisbee, propeller, cartwheel) How is J vector pointed relative to recoil velocity?



Rotational Orientation in NO +Ar Products (clockwise – counterclockwise) can also be measured, J vector up or down?

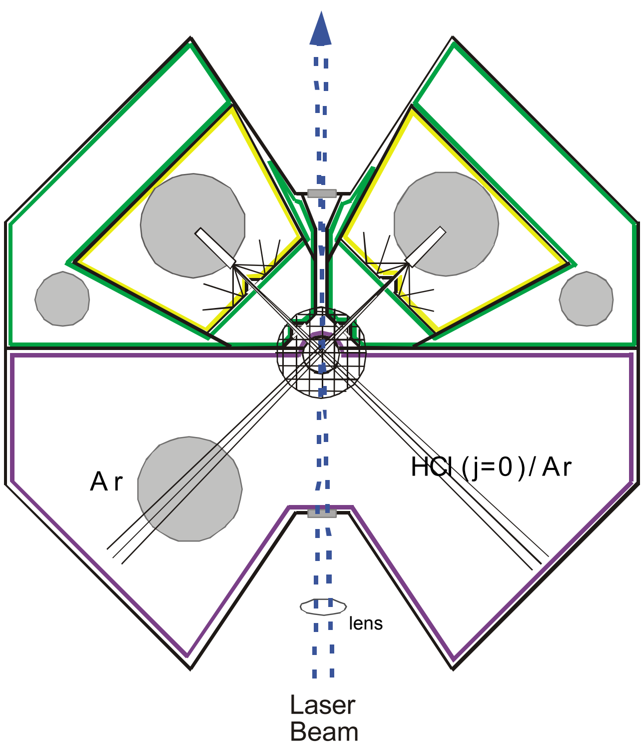


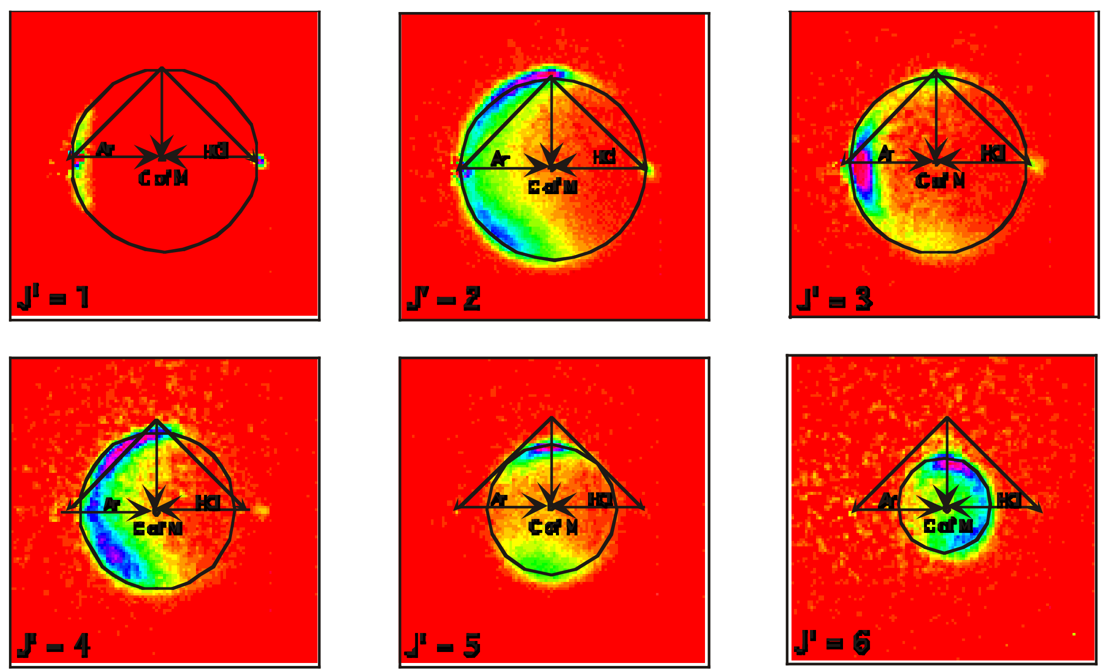
Velocity Mapping is Very Important for Studying Bimolecular Reactions in Crossed Beam Arrangement With Ion Imaging.

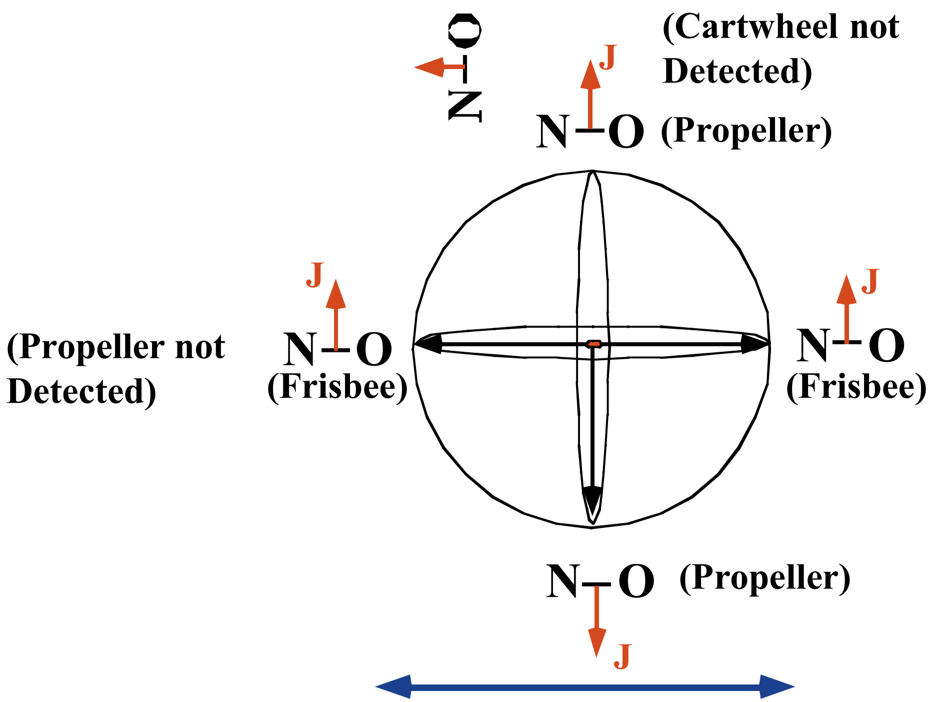


Because molecular beam pulses last for tens of microseconds scattering products that are moving slowly build up their concentration

A distorted view of the Differential Cross Section is directly measured.
This is because products with different lab-frame velocities
are detected with different efficiencies. Note even-odd alternation







Horizontal Polarization of Probe Laser on an R Branch Transition detects μ||ε.

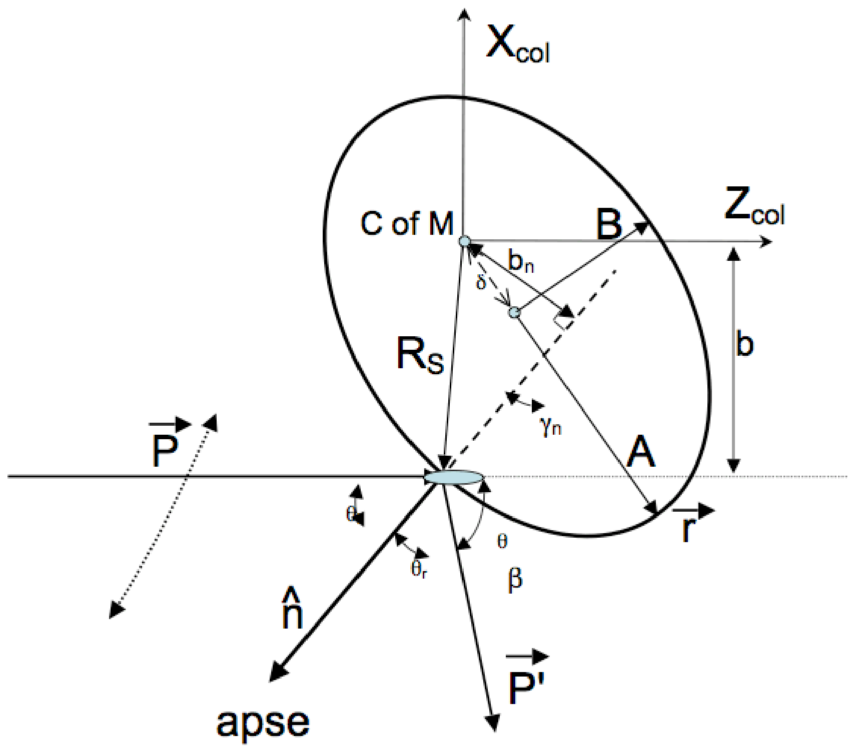
The alignment is described by moments…..(Thanks you Dick Zare et al….)

$A^2_0(j') = J'$ along z axis 1 to -1/2

$A^2_{2+}(j') = J'$ along X $(3/4)^{1/2}$ or Y $(-3/4)^{1/2}$

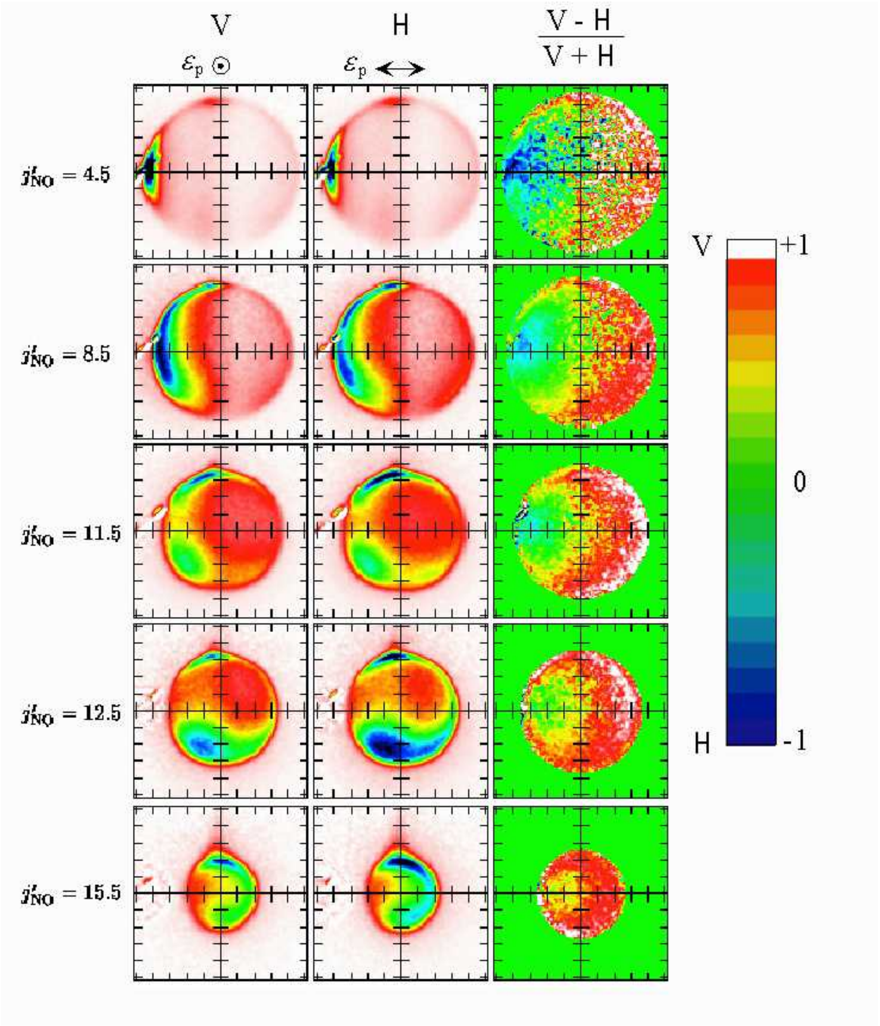
Collisions at high collision energy can be thought of as hard and sudden.

The classical dynamics associated with hard ellipse scattering can be analytically described. The Apse vector is the vector along which angular momentum is transferred



J cannot be transferred along the Apse angle.

- We take the difference between the vertical and horizontal images and normalize by the sum of the images to get and image we can fit using three alignment moments. We fit each line of data (top to bottom) with the moments. We can then plot the moments as a function of scattering angle.



Alignment Moments Were Measured for NO(X) + Ar and Compared to Quantum Calculations

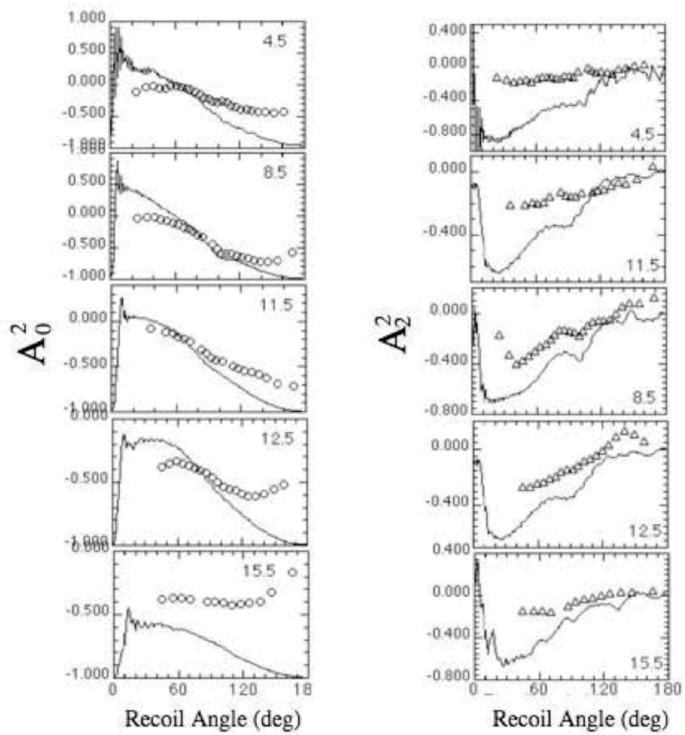
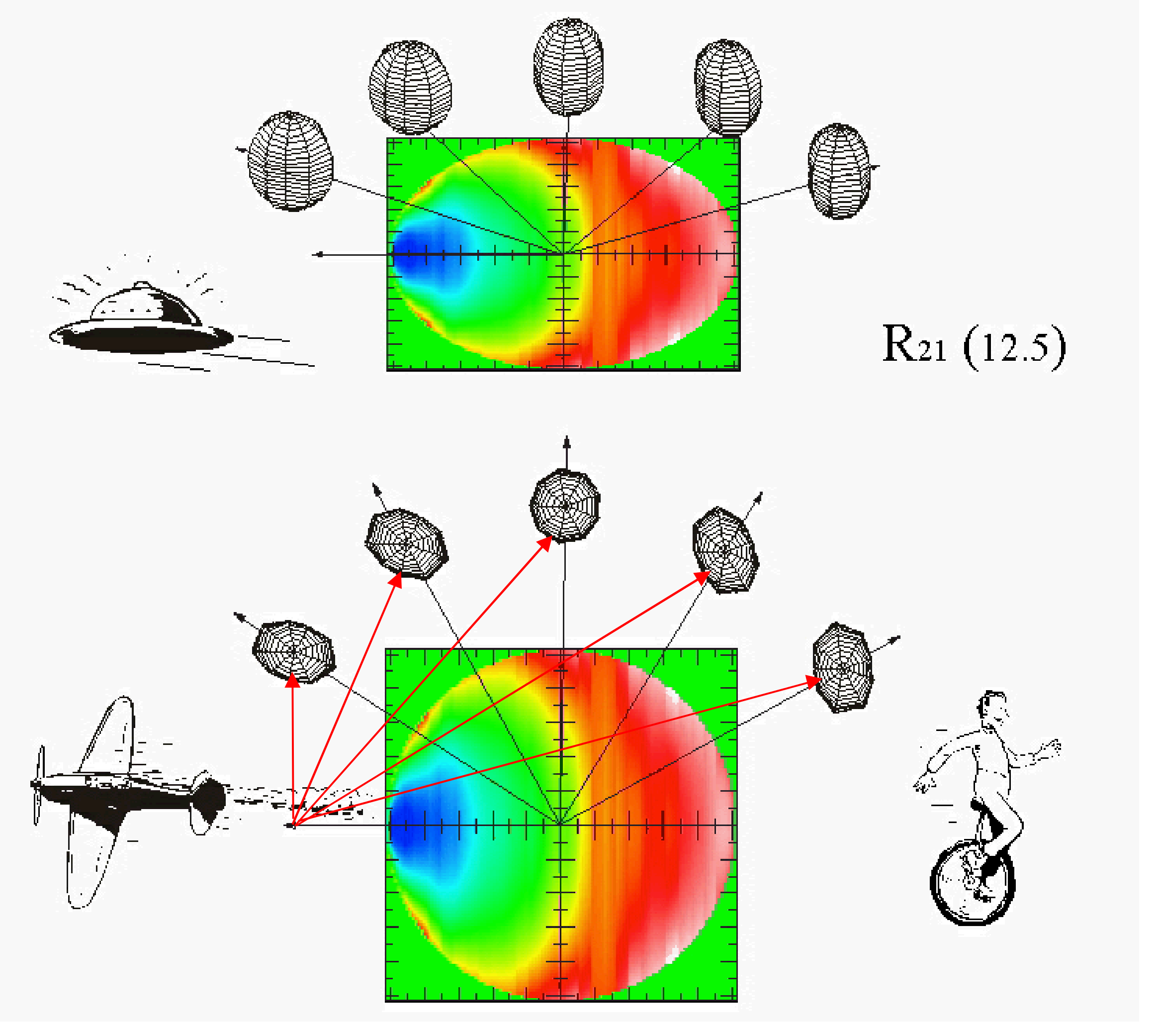


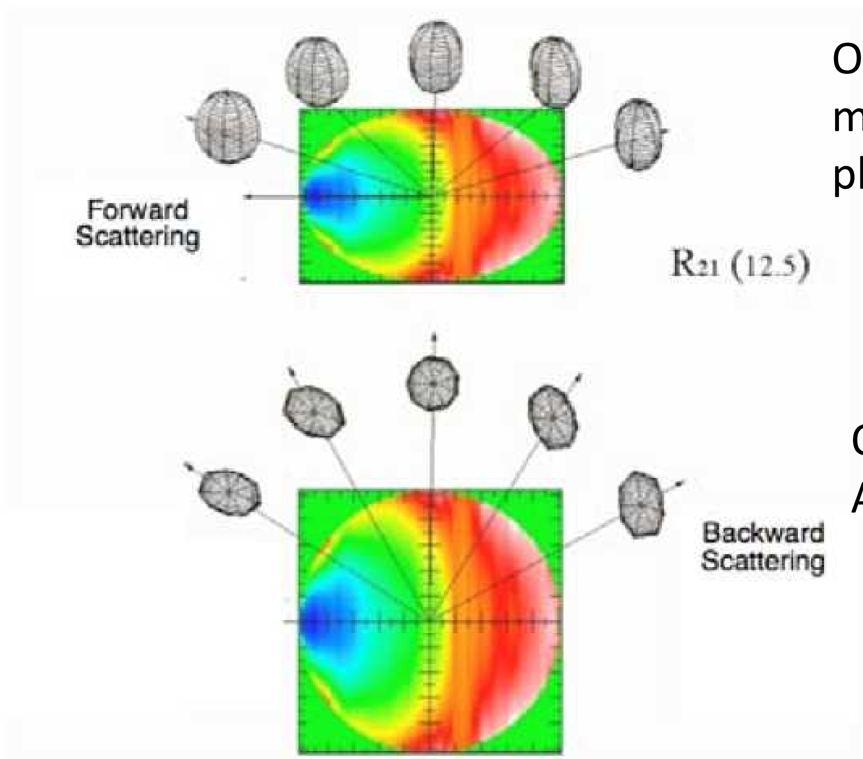
Figure 22. Alignment moments, A_0^2 and A_2^2 are obtained for many angles of recoil from the difference in images obtained between images recorded with horizontal and vertically polarized light for several final rotational states, see previous Fig.21. These aligment moments are compared to those expected from quantum close-coupling calculations on ab initio coupled-cluster CCSD(T) potential energy surfaces performed using the HIBRIDON 4.1 software for time-independent quantum calculations. (improved results Wade et al. 2004).

Alignment moments describe
The extent that the angular
momentum vector, J, lies parallel
the center-of-mass collision vector
or perpendicular to
the center-of-mass collision vector

- The Three Alignment moments define the 3-D distribution and they are drawn here for J=12.5
- Obloids represent the J distribution as a function of the final scattering velocity.
- Scattering products are dominantly aligned orthogonal to the scattering plane- as is predicted by a classical hard ellipse model.
- With short axis along Apse angle



Alignment of J 12.5 as function of scattering angle.

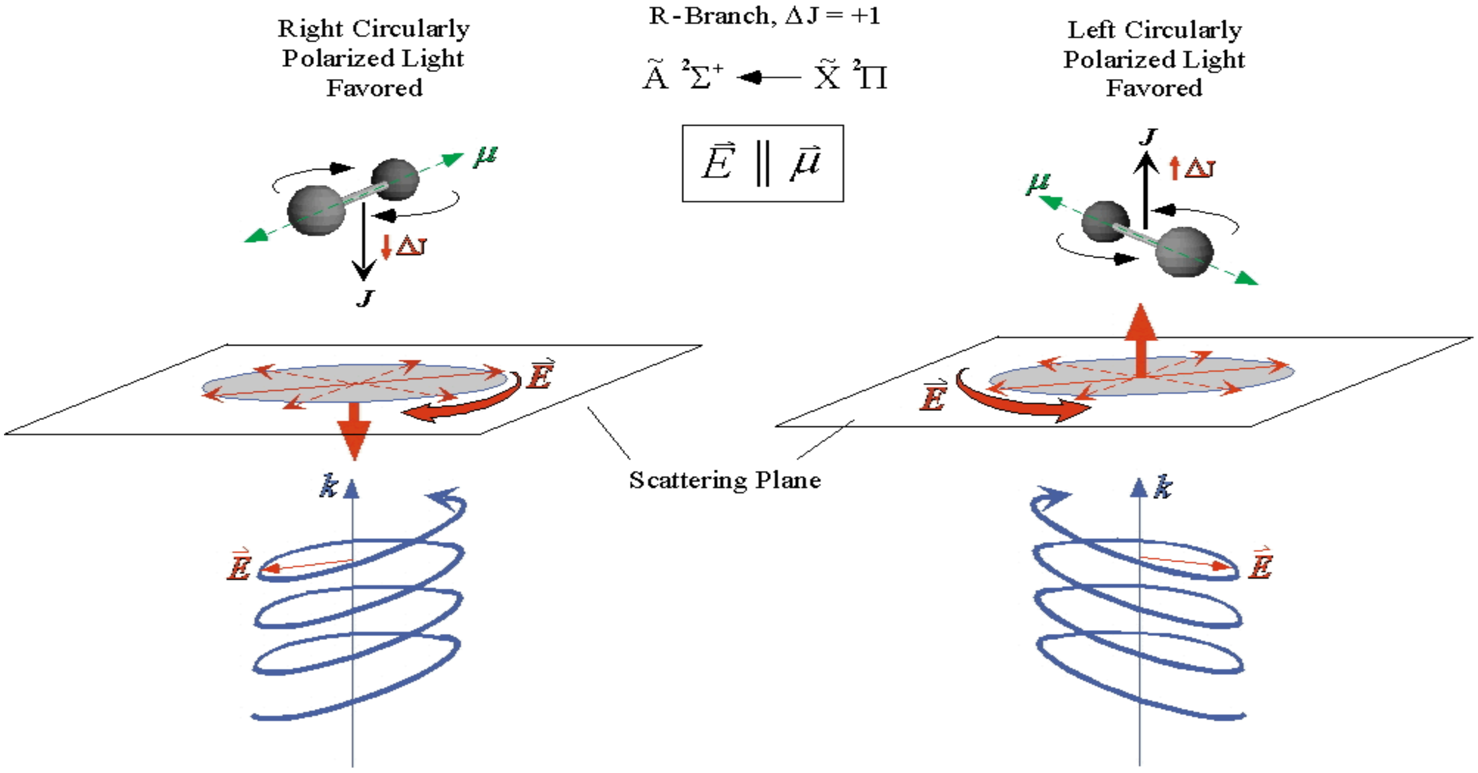


One can convert the Alignment moments of the Angular Momentum into plots of the angular momentum vector, J.

One sees a dimple in the J distribution Associated with the Apse Angle.

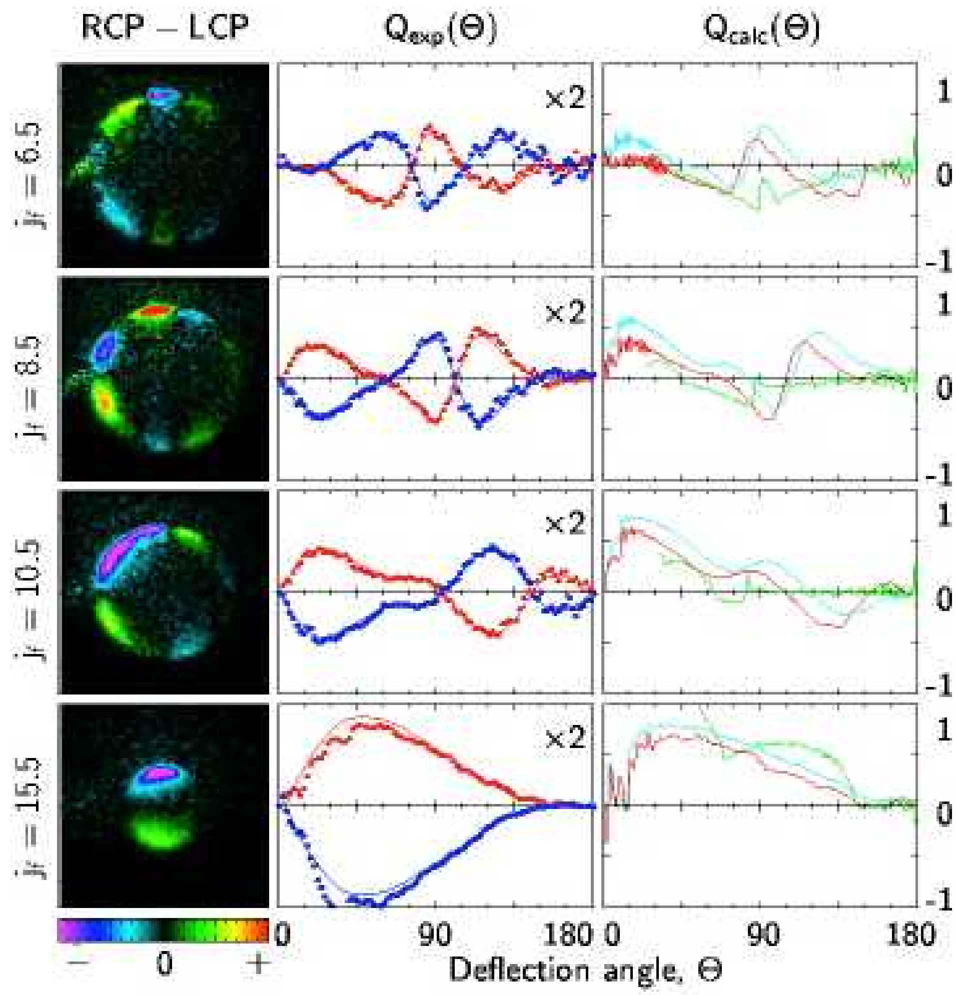
We were not able to measure the very forward scattered molecules. New predictions about alignment moments for the most forward scattering are "interesting"

The Absolute Sense of Rotation of the NO Collision Products Can Be Probed Using Circularly Polarized Light

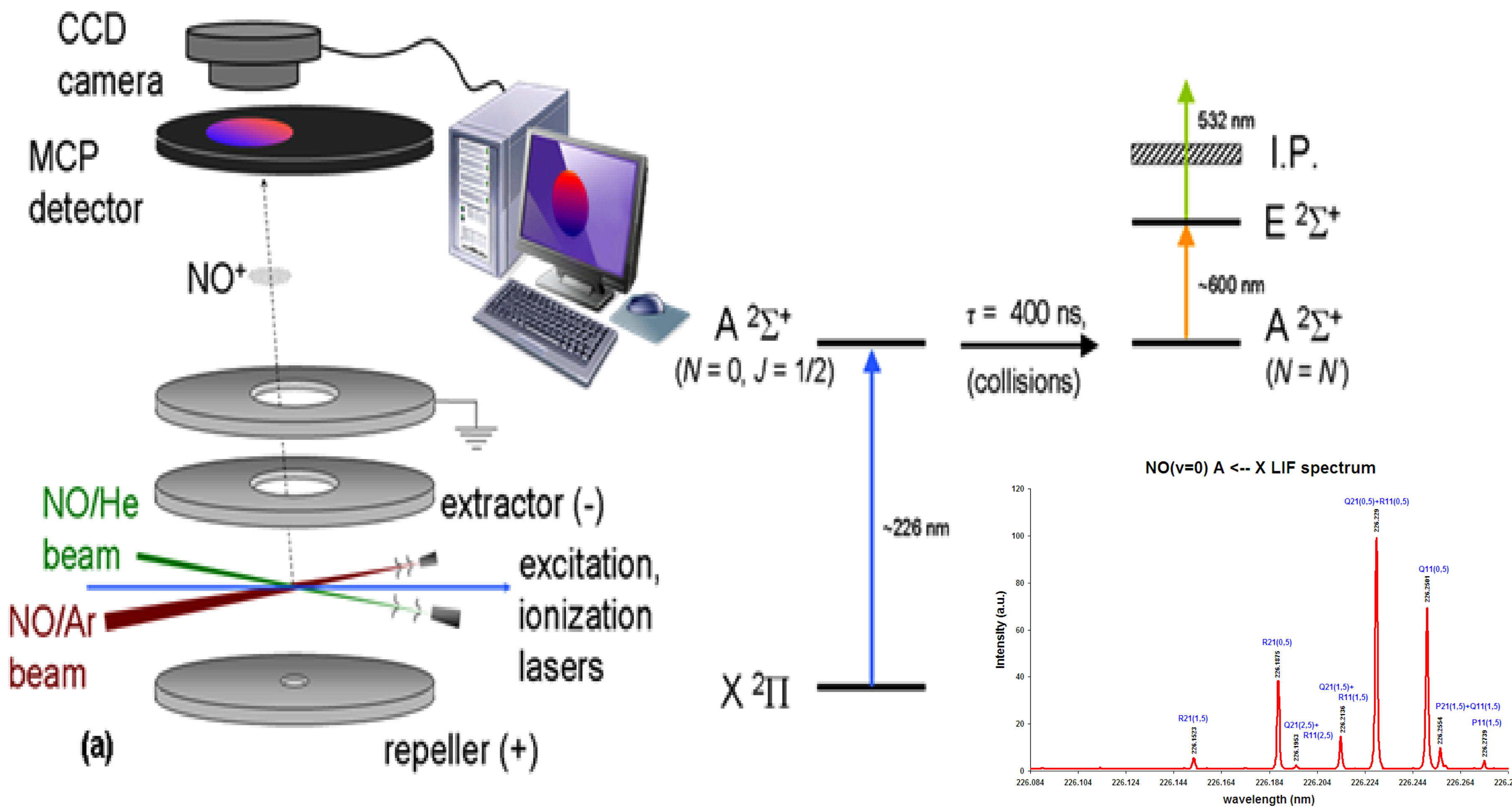


Difference Images With Perimeter Plots and Calculated A^{1}_{-1} Moments.

- Calculations are done using full close-coupled quantum calculations using two recent ab initio NO-Ar potentials of Alexander and the Hybridon scattering package.

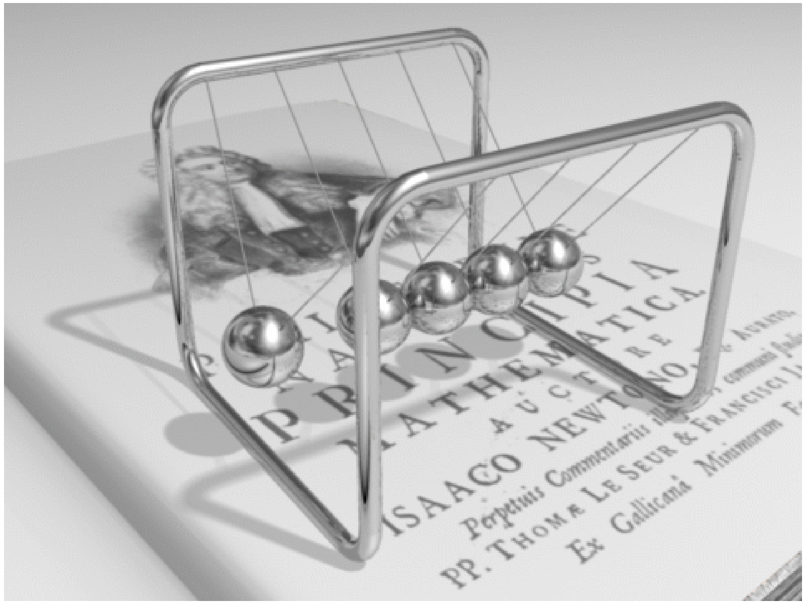


Apparatus and Detection Mode for measuring DCS and Alignment of Electronically Excited State Molecules.



Collisions are Subject to Conservation of Energy and Momentum!

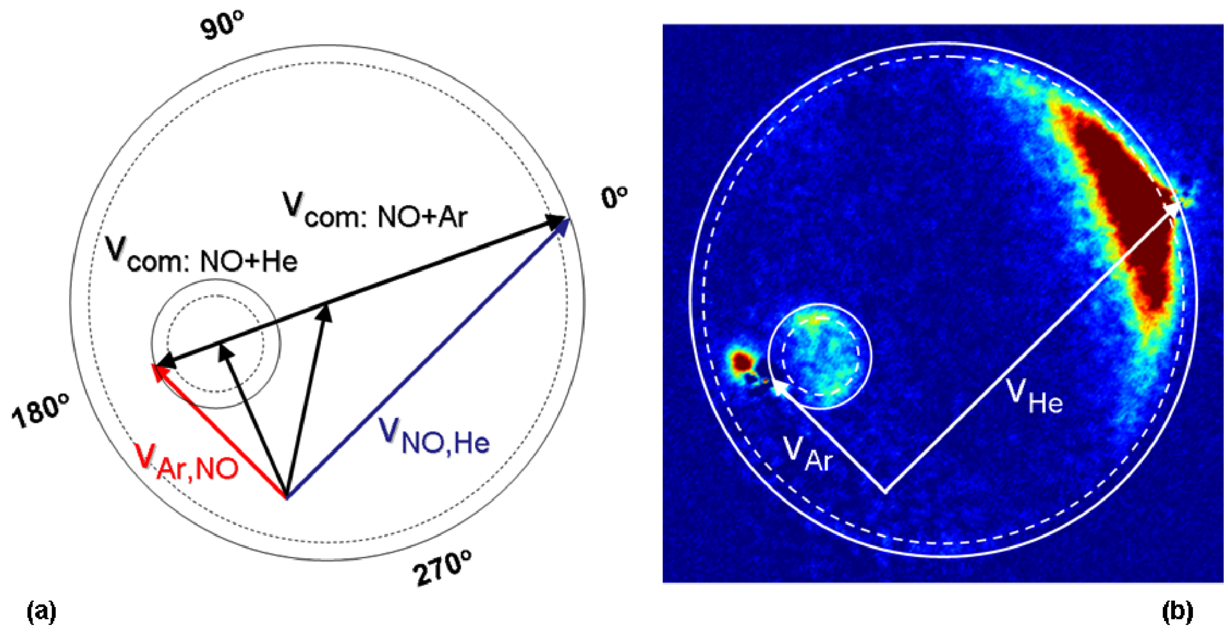
Think of it as a Newton's cradle



Particles with equal mass. One has initial momentum, The other does not. The collision transfers "all" the energy from the moving particle leaving it stationary.

Only one way to conserve both momentum and energy simultaneously

Expected Collision Dynamics From NO/Ar Beam Scattering From NO/He beam



Three dimensional scattering of unequal mass particles capable of inelastic processes are Also constrained by conservation of energy and momentum, The Newton Sphere

Background Subtracted Scattering Data and the Differential Cross Sections Obtained from Data.

NO scattering from He

NO scattering from Ar

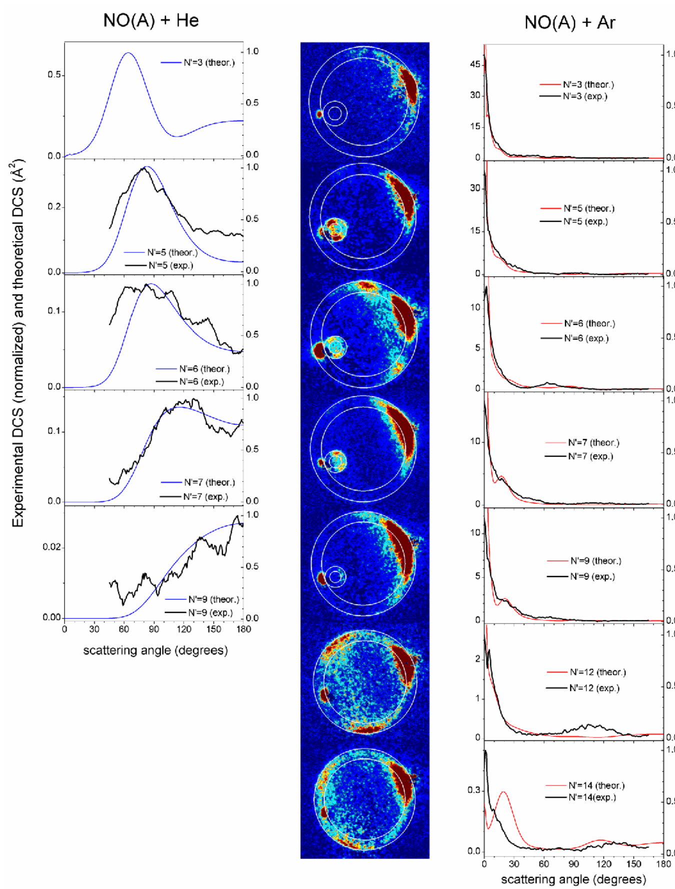
N=3

N=5

N=6

N=7

N=9



N=3

N=5

N=6

N=7

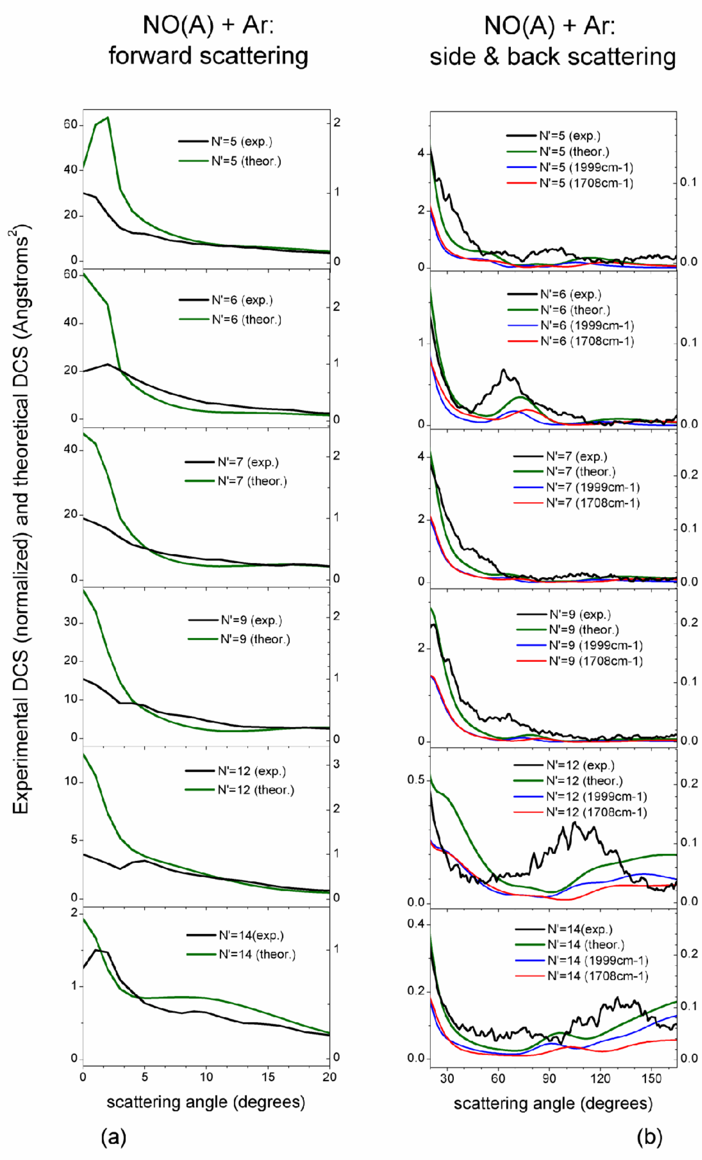
N=9

N=12

N=14

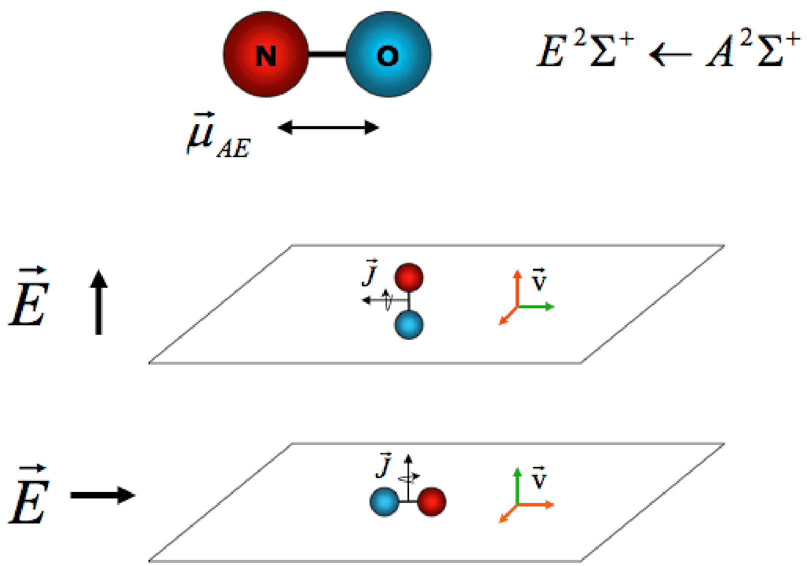
Expanded view of Differential Cross Sections

Experiment under Estimates the forward scattering due background subtraction procedure



Theory to predict the position of the Rainbow Scattering at too large and angle.

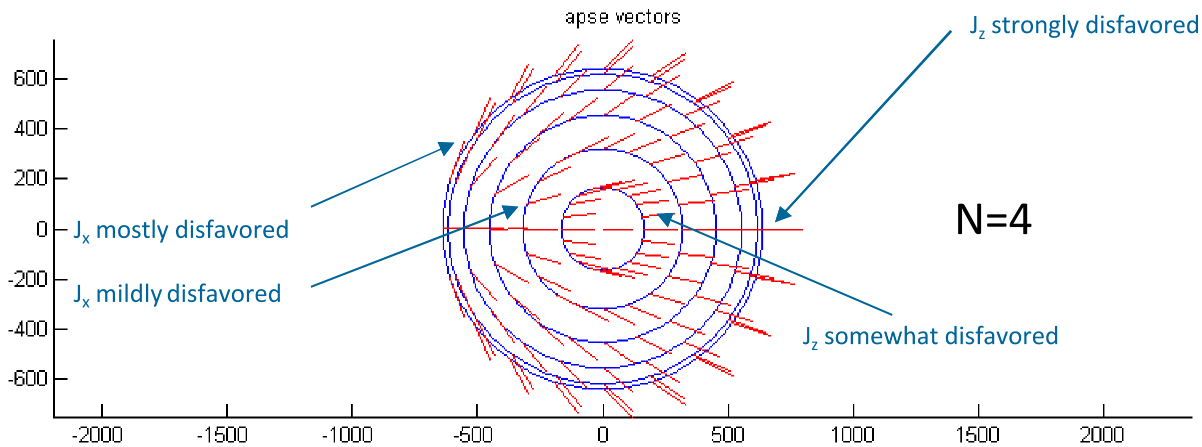
Is the scattering is polarization dependent? Can we alignment of electronically excited state scattering?

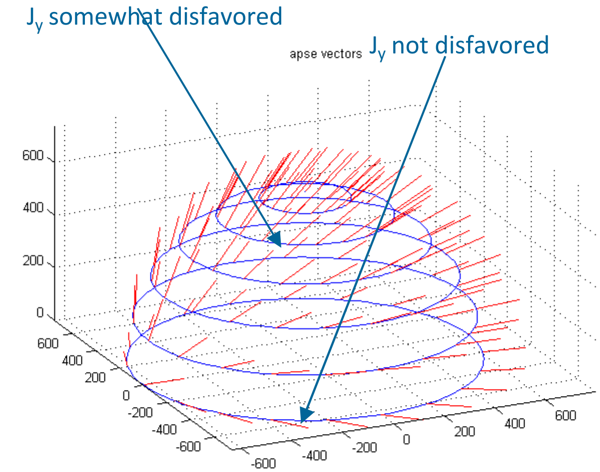


For NO traveling toward or away from laser beam perpendicular polarization is sensitive to cartwheel and propeller rotation.

For NO traveling toward or away from laser beam horizontal polarization is sensitive to Frisbee or propeller motion.

Classical 'Apse' model: Apse vectors



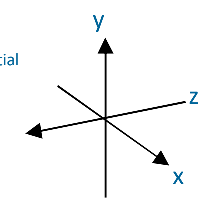


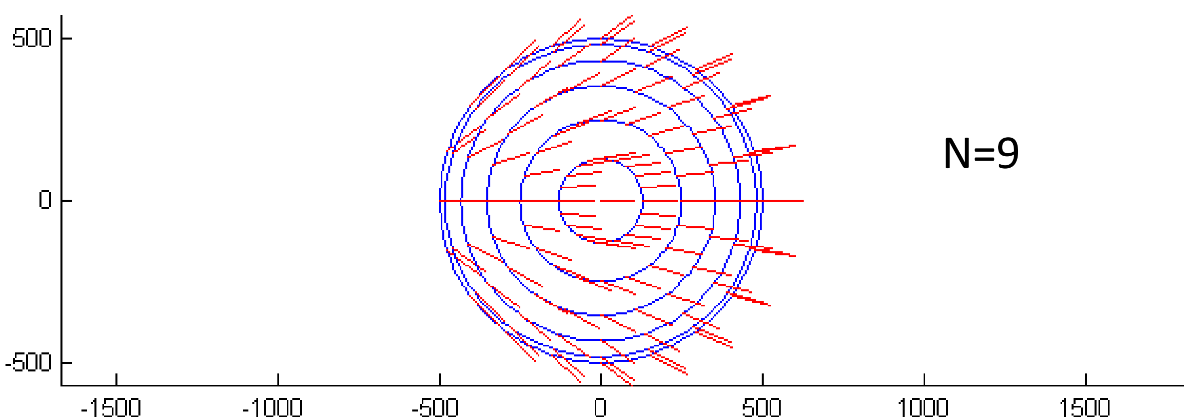
x–axis = k vector of probe laser

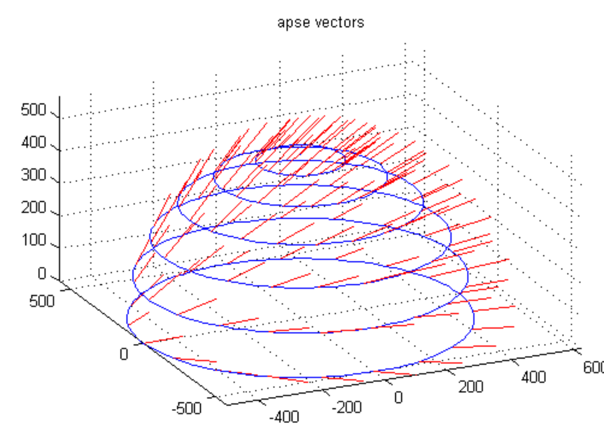
z-axis defined as COM $v_{initial}$

x-axis is laser vector

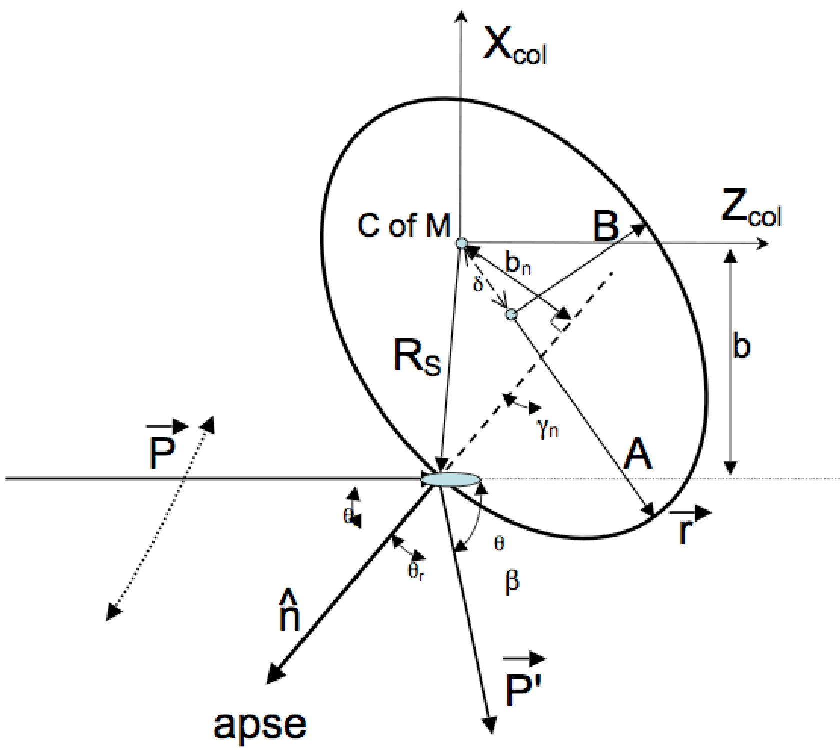
y-axis is m/z detection



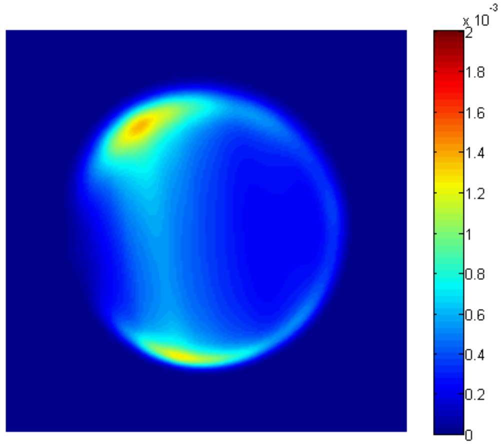




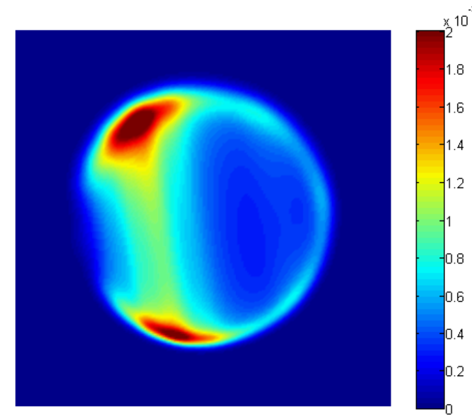
The classical dynamics associated with hard ellipse scattering can be analytically described. The Apse vector is the vector along which angular momentum is transferred



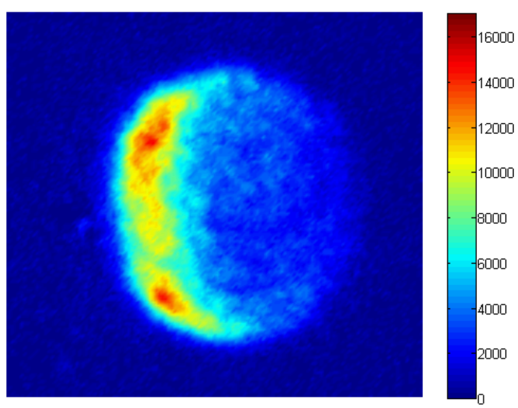
J cannot be transferred along the Apse angle.



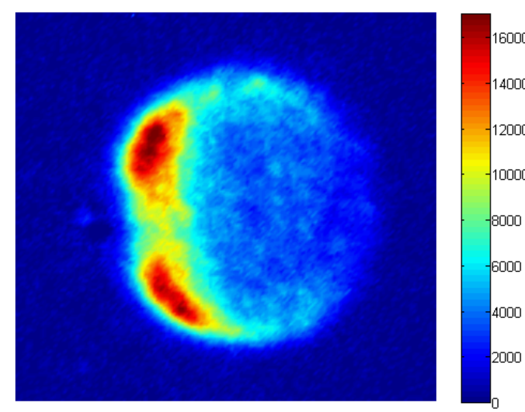
Exact model: V



Exact Model: H



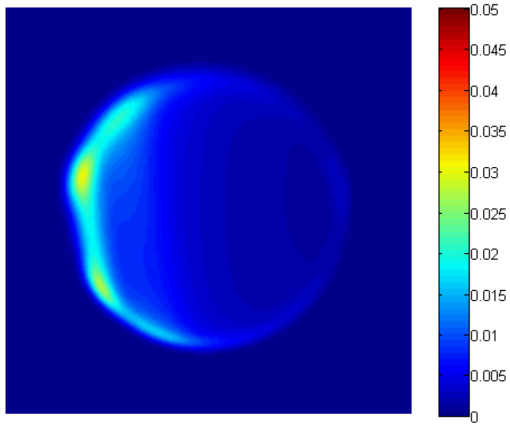
Experiment: V



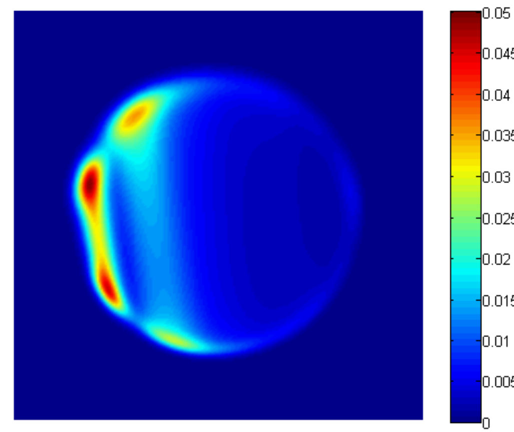
Experiment: H

Images of NO (N' = 5) for Vertical and Horizontal polarization of Ionization beams

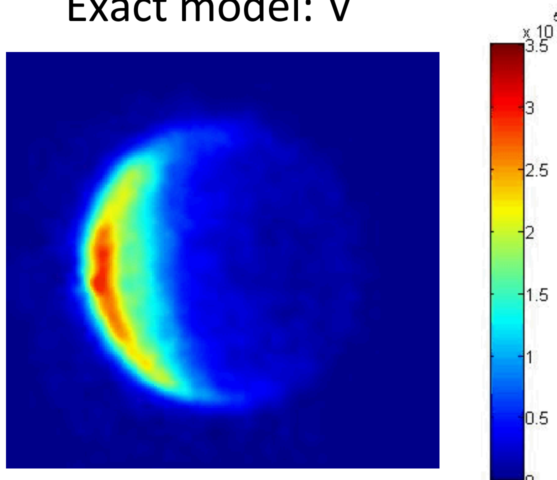
More forward scattering in experiment



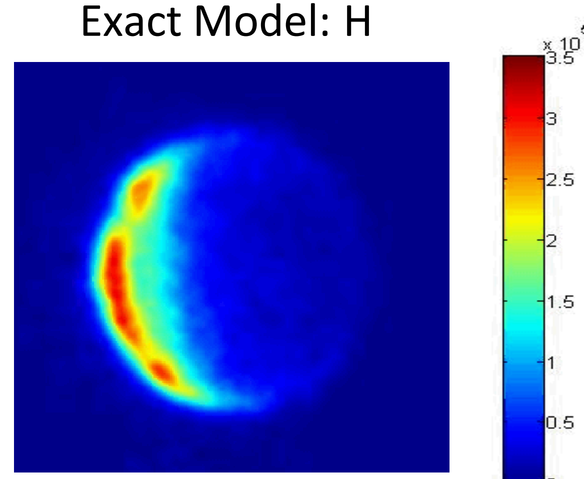
Exact model: V



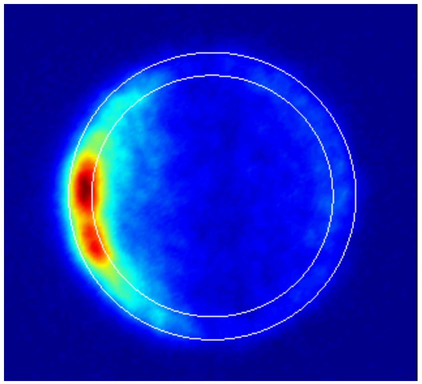
Exact Model: H

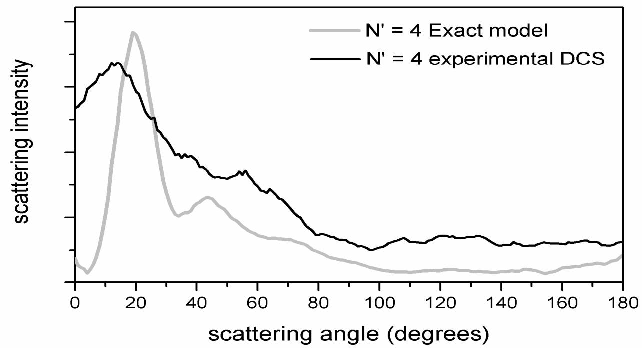


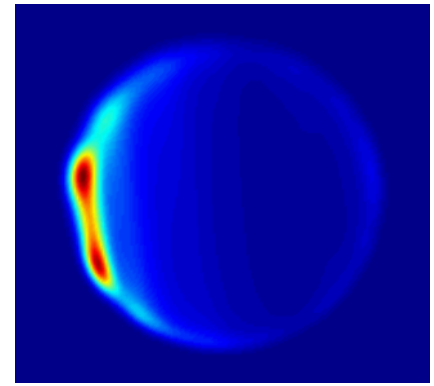
Experiment: V



Experiment: H



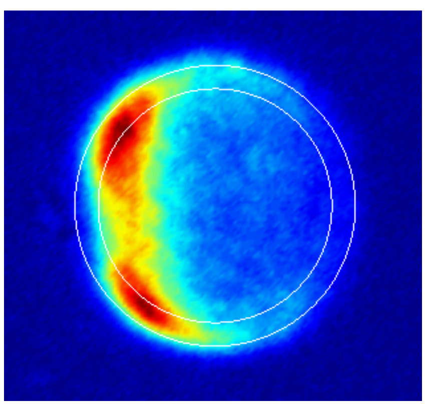


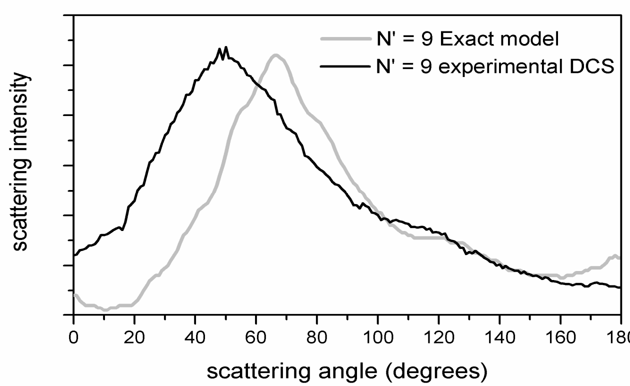


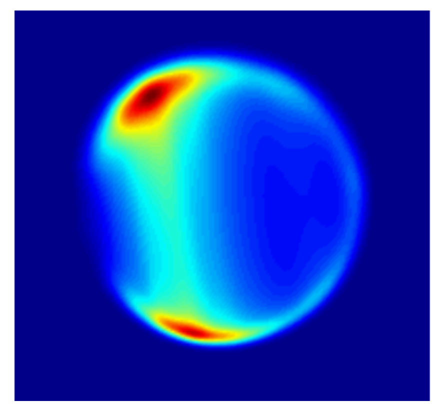
Experimental images

Annular profile comparison

Exact model

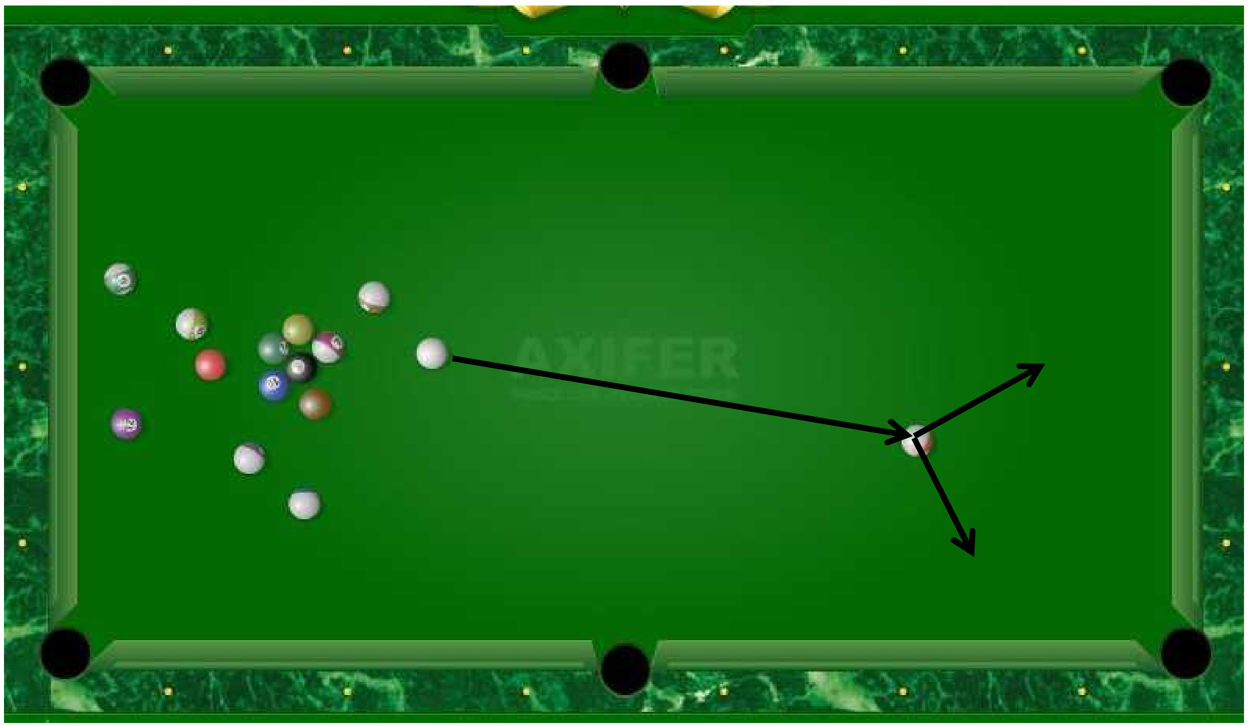






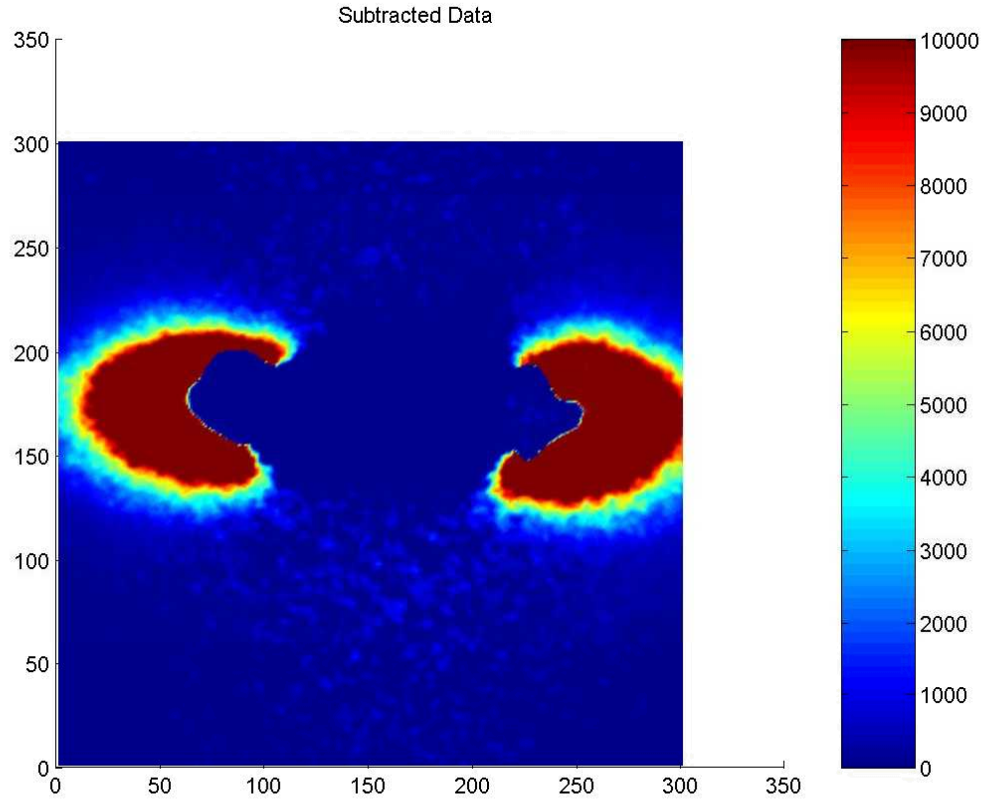
Elastic and Inelastic Scattering in Crossed Molecular Beams at 90° is One Techniques for Making milliKelvin Samples of Molecules.

Pool balls "always" scatter at 90°.

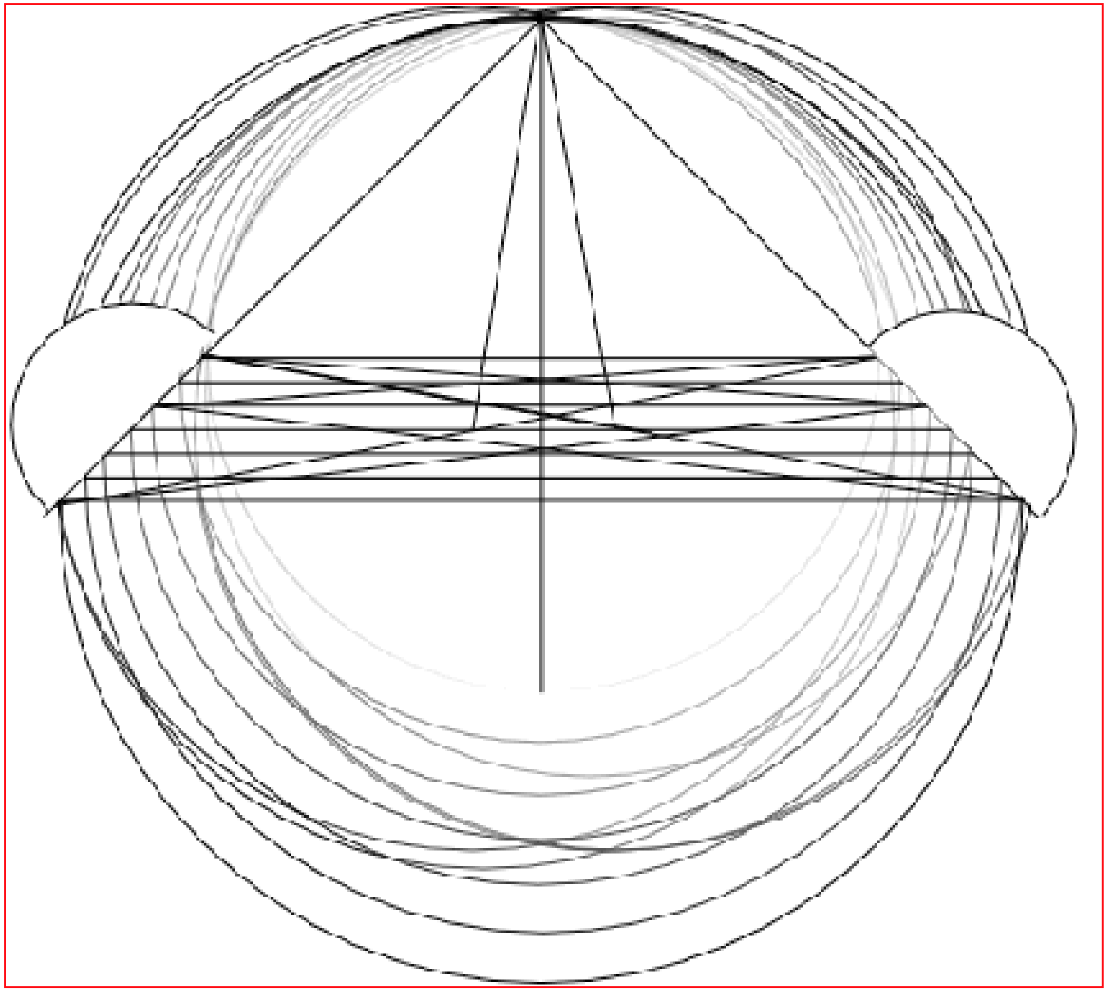


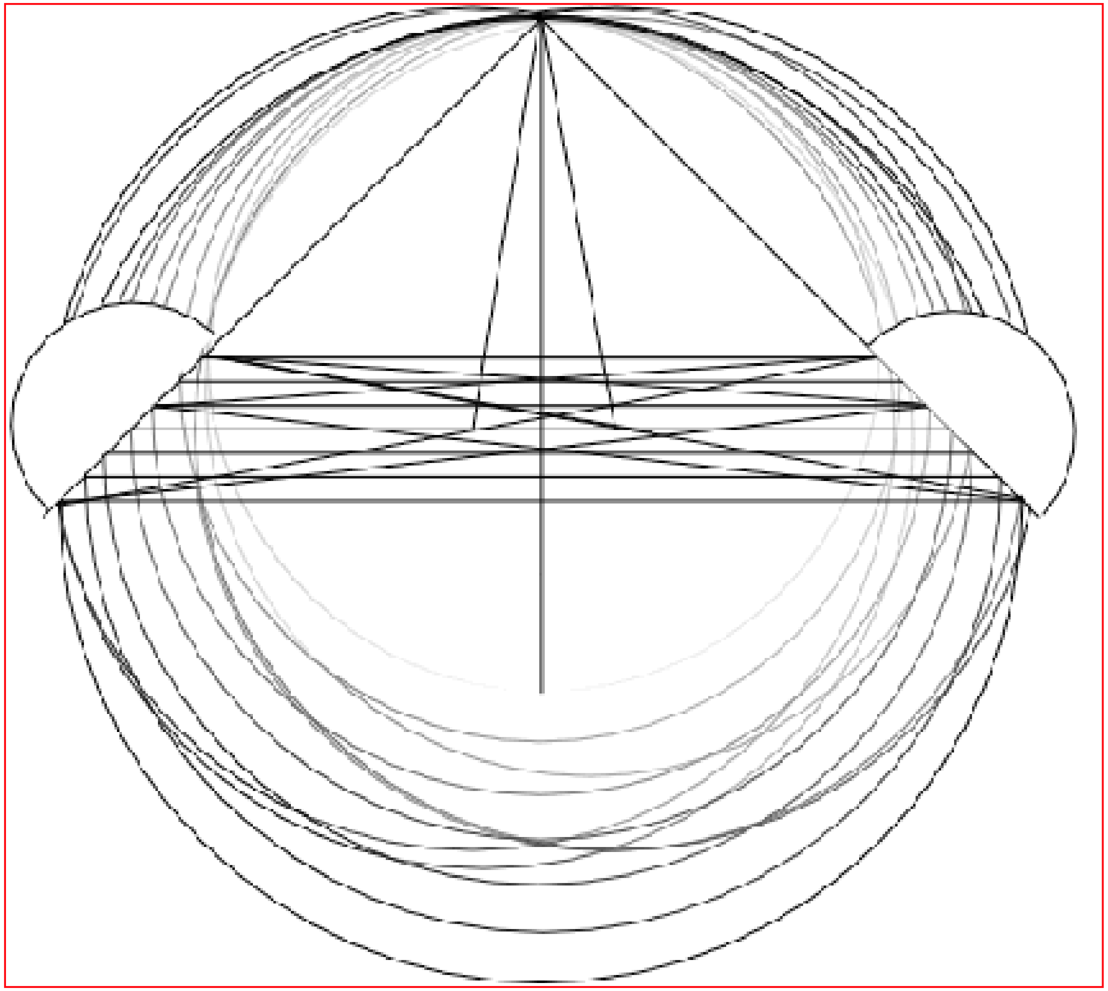
Run the classical trajectory backwards

Not so easy as REMPI on Kr creates charge explosion of Atomic Beams

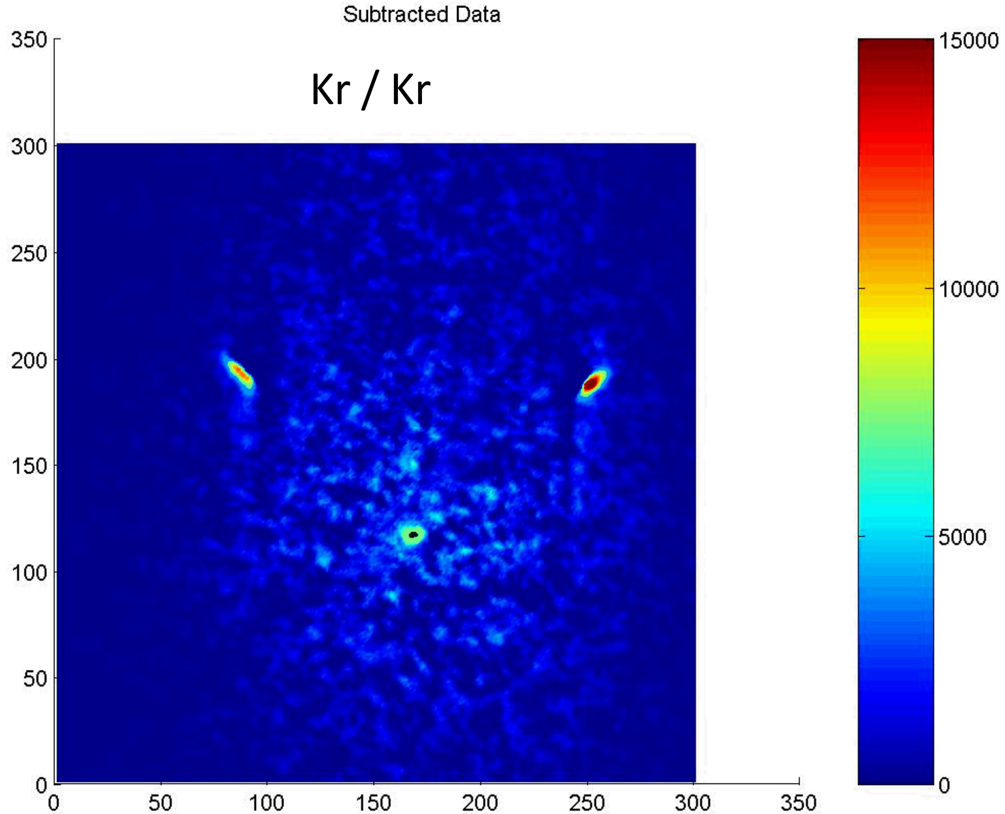


For molecular beams at 90° and of equal mass then the scattered molecules that have 0 lab frame velocity (elastically scattered) have no spread in velocity. Unfortunately J=0 is forward scattered not side!?



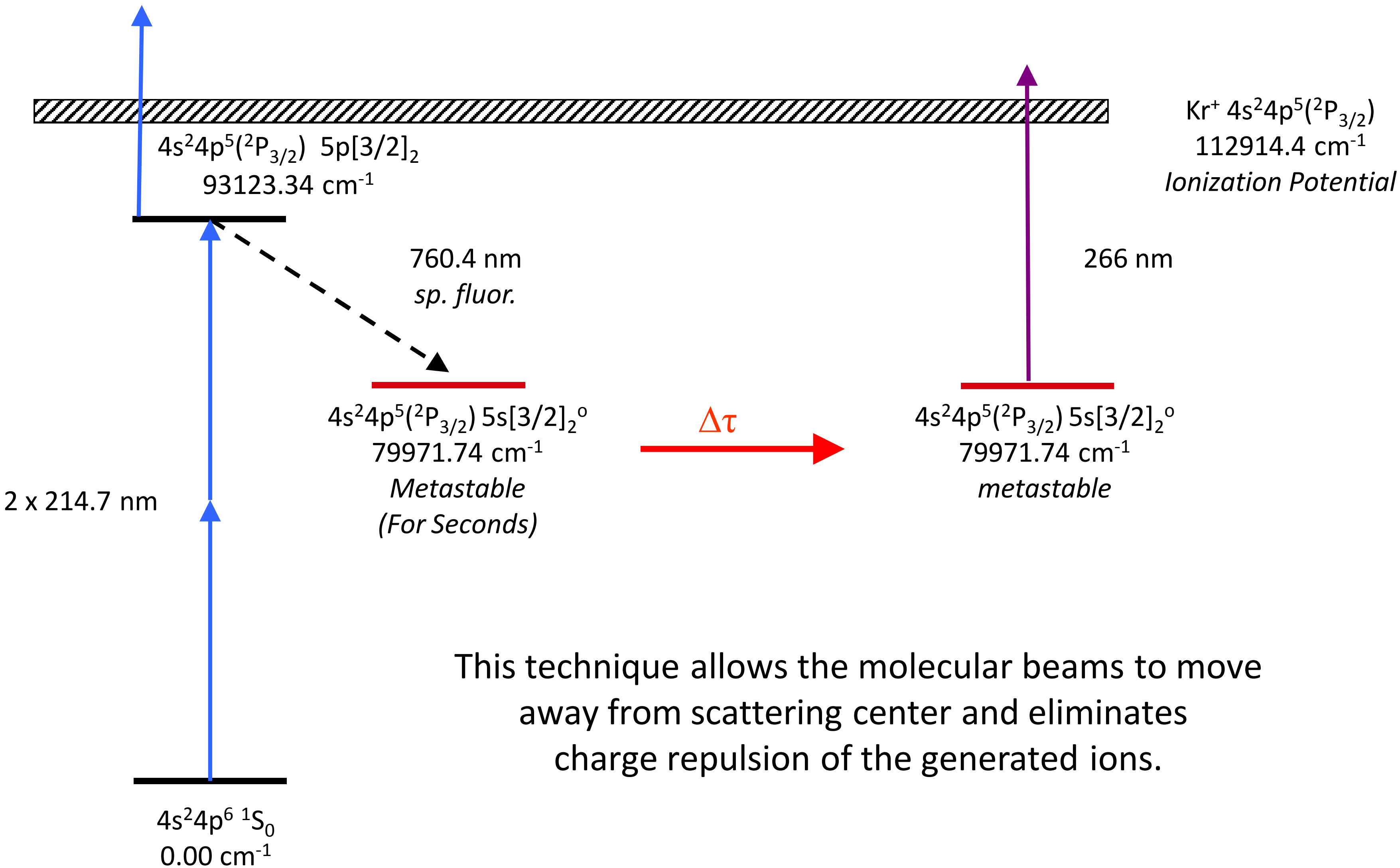


Elastic Atom - Atom scattering allows us to optimize the Apparatus and Conditions for Trapping.



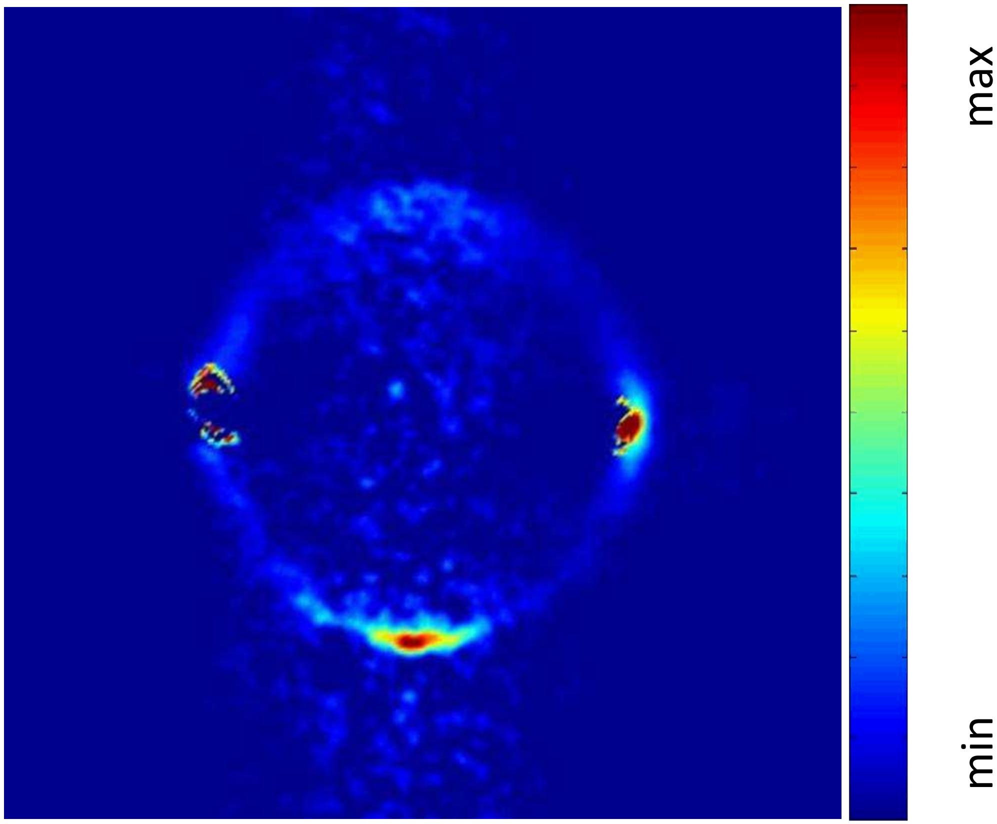
$$\Delta v'_{Kr} = \left(\frac{v_{Kr}}{v_{cm}}\right)\left(\frac{{m_{Kr}}^2 - {m_{Kr}}^2}{(m_{Kr} + m_{Kr})^2}\right)\Delta v_{Kr} = 0!$$

How do we Eliminate Charge explosion of the Atomic Beams and Monitor cold Kr? Create Metastable Kr and Use Delayed Ionization and Ion Imaging of Cold Kr After Beams are Gone.



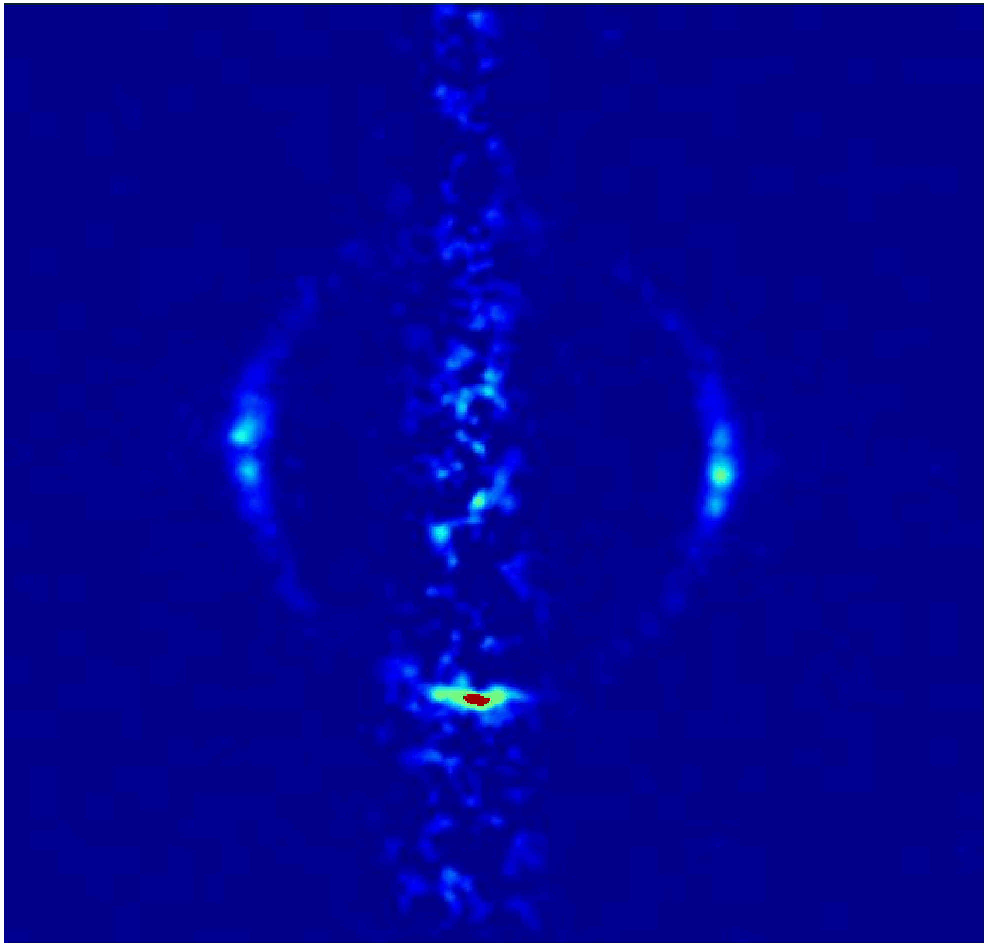
This technique allows the molecular beams to move away from scattering center and eliminates charge repulsion of the generated ions.

We have detected Cold Kr Atoms (500 nsec delay)



We observe not only cold atoms but the entire elastic scattering
differential cross section by letting the fast molecular beam mainly travel from our observation region.

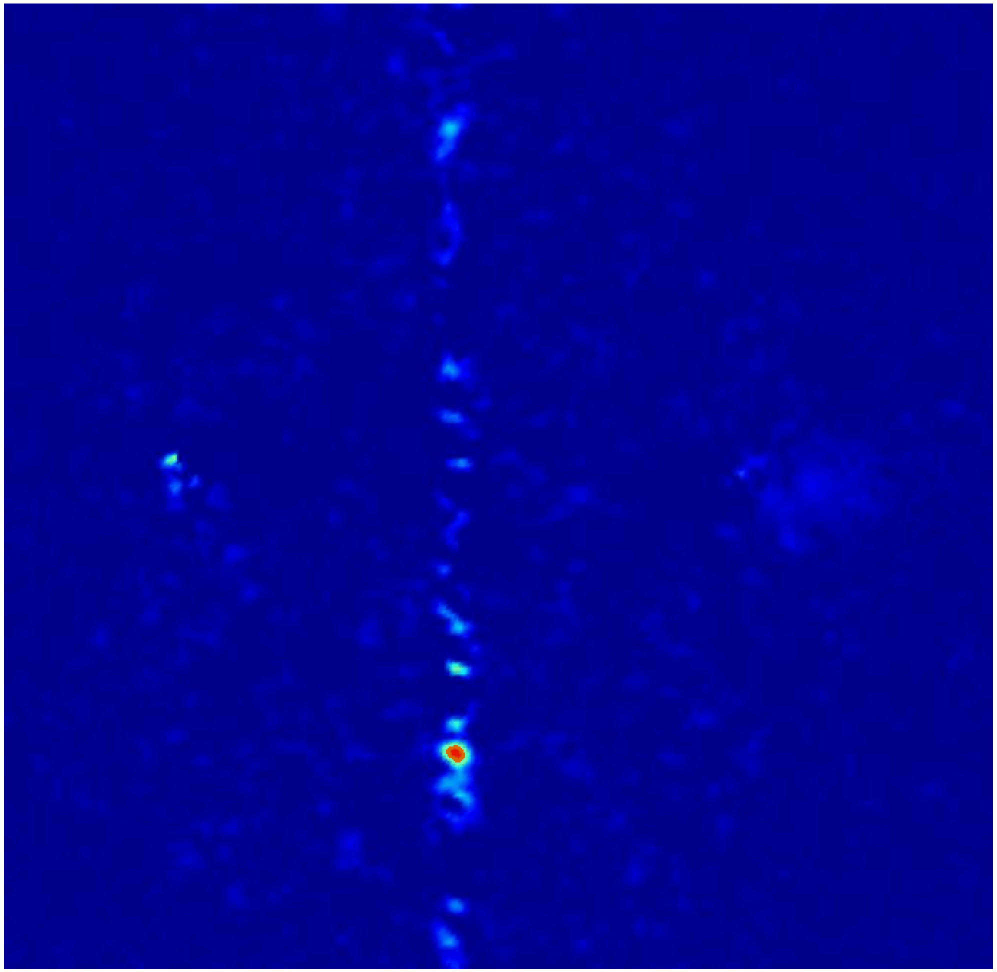
Is the scattering ground state atoms or excited state atoms?



Scattering Ring and cold atoms!

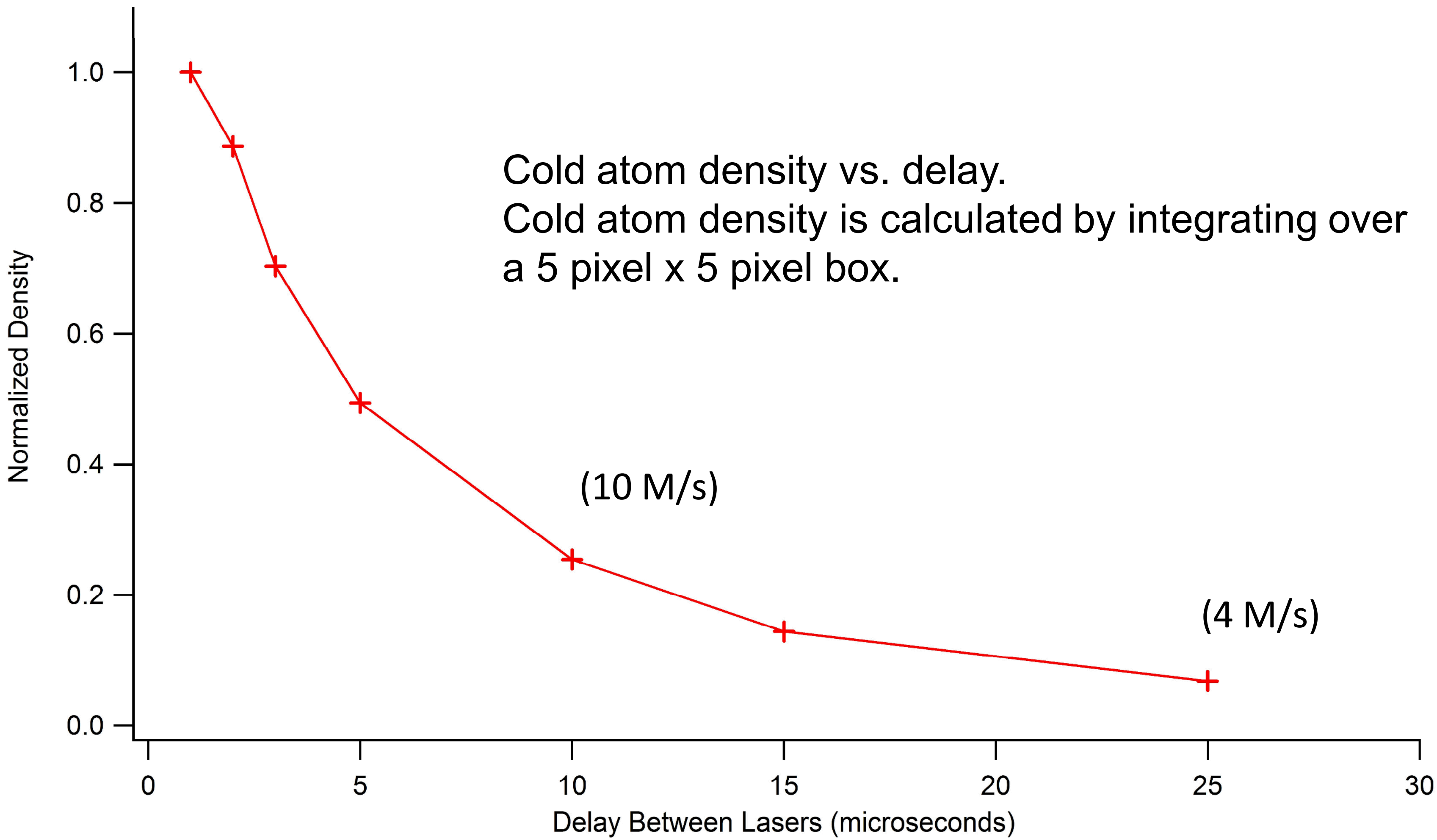
1 microsecond between
214 nm laser pulse and
266-nm laser pulses.

We can use this to study
energy transfer in
excited electronic states!



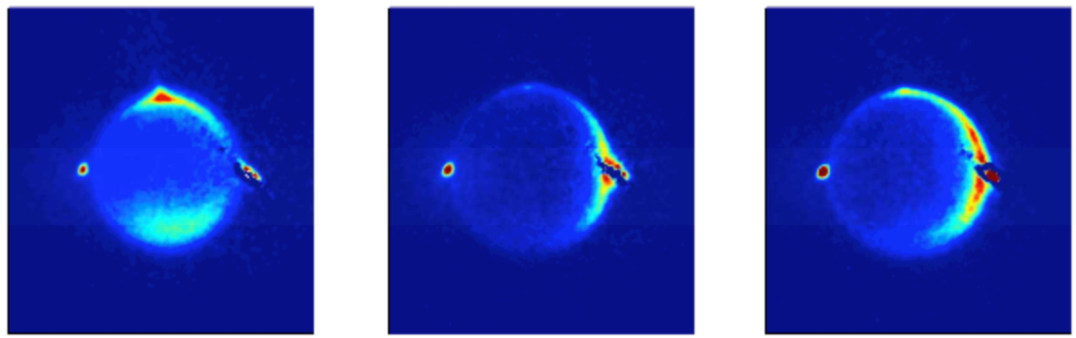
Only atoms that are moving
Enough to be inside the ~100
Micron laser beam width are
Observed. Therefore the Kr atoms
Must be moving less than 10 M/s

We observe cold atoms at
25 microseconds so about 4 m/sec (
tens of milliKelvin)

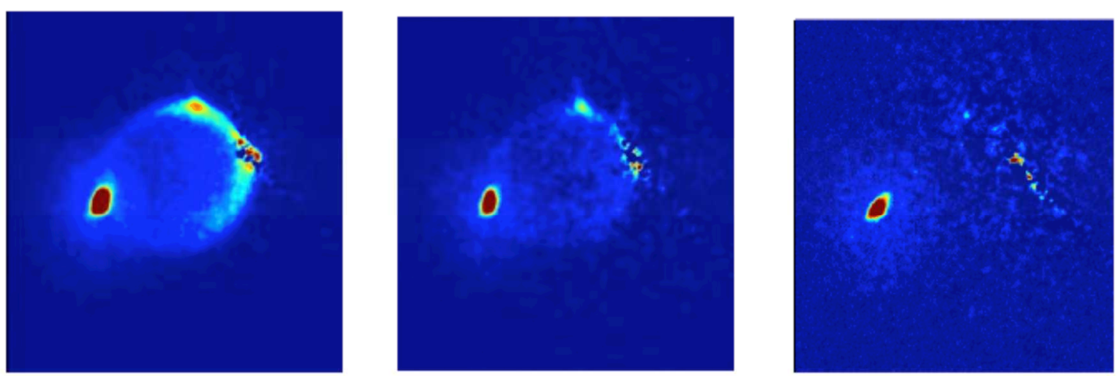

Cold atom density vs. delay.
Cold atom density is calculated by integrating over a 5 pixel x 5 pixel box.
(10 M/s)
(4 M/s)
Normalized Density
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
Delay Between Lasers (microseconds)

Ammonia Scattering from Ne should produce very cold samples

NH_3 (m = 17, B=9.444 cm-1) against Ne (m = 20)

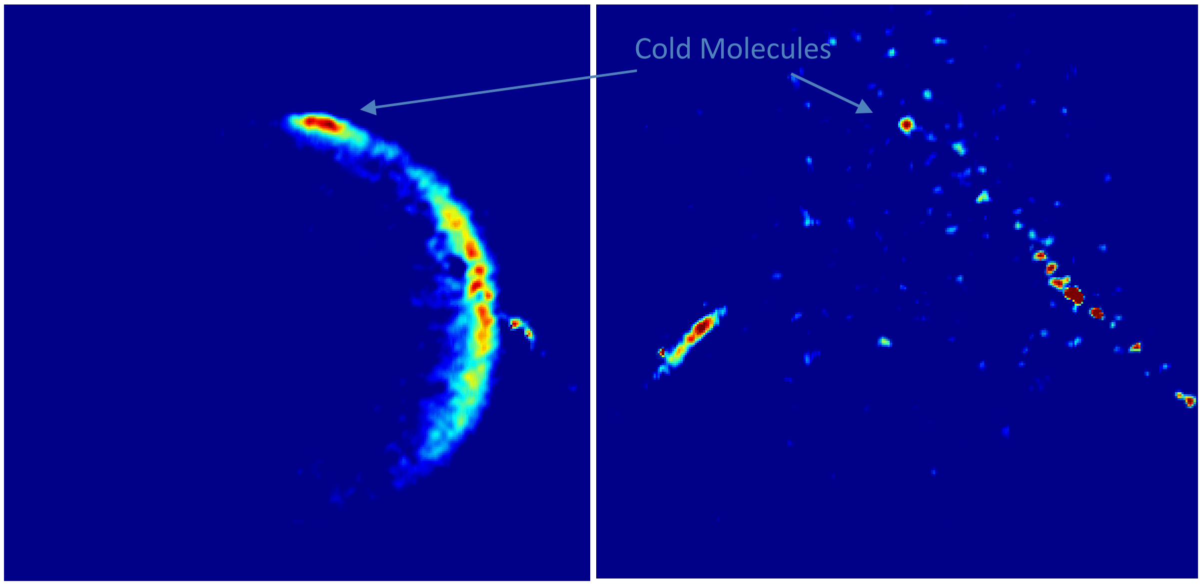


$J=7, K=7$ $J=2, K=2$ $J=4, K=4$



t = 0 μs t = 30 μs t = 40 μs

NH_3 seeded in Kr/Ar mix; J = 2 is stationary in the lab



Peak of Molecular Beam Overlap With Atomic Beam

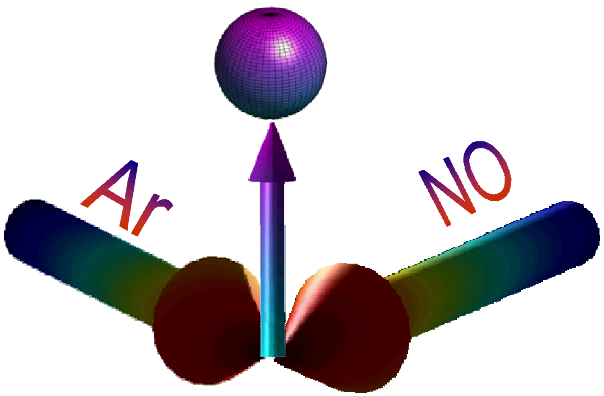
150 μSec after peak of Molecular Beam Overlap with Atomic Beam

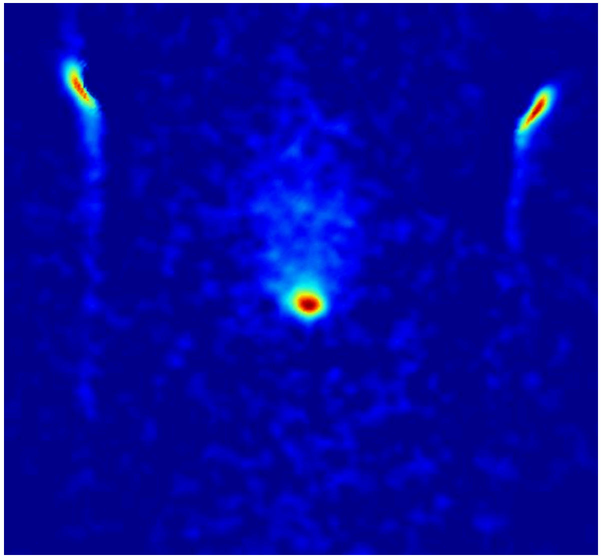
Inelastic Collisions are required for cooling if the atom and molecule do not have same mass.

Determining the velocity distribution of these molecules is difficult.

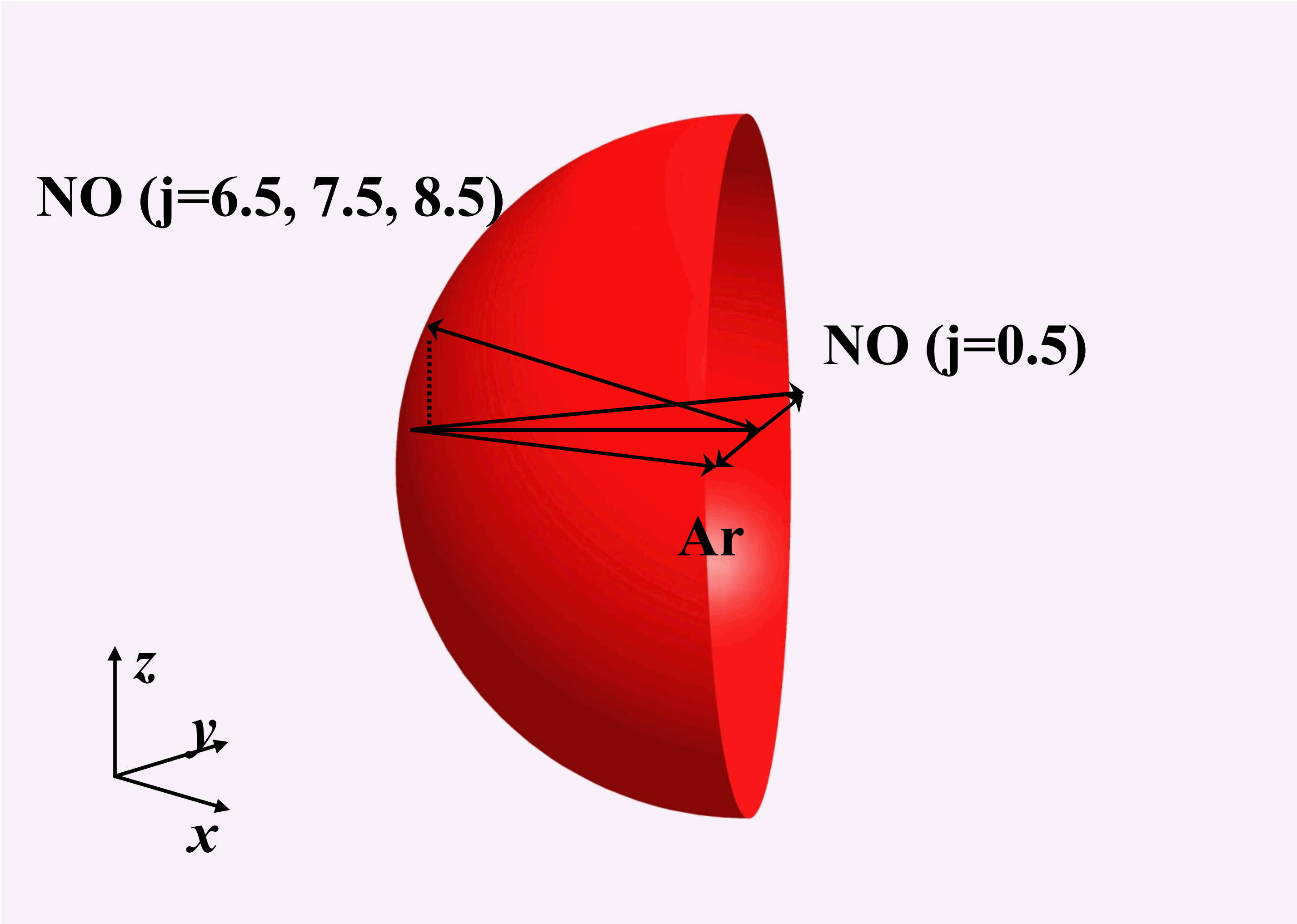
Cold Molecules Scattered Out of Scattering Plane, Up in the Laboratory Frame are Easily Observed.

Cold atoms with finite final velocities are scattered out of the interaction plane, and detected.



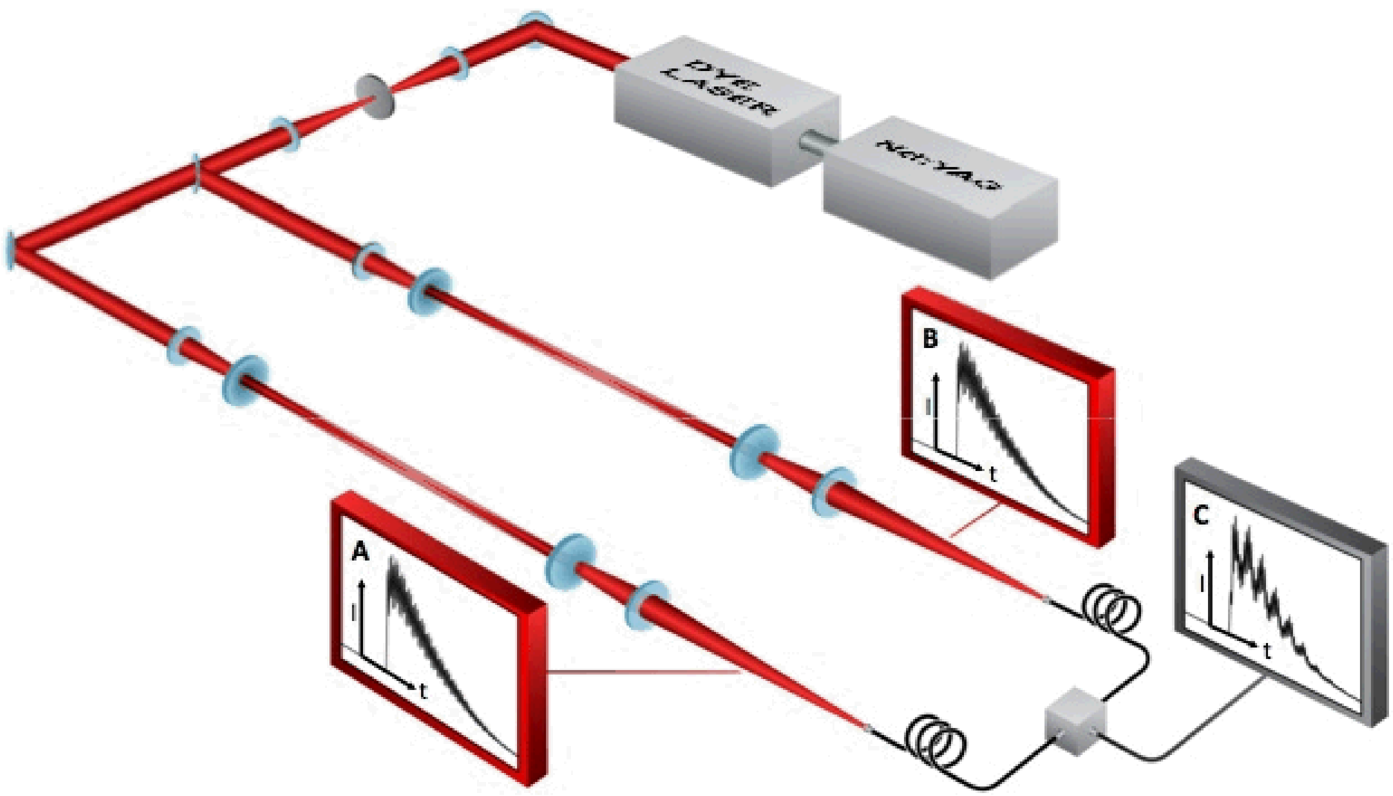


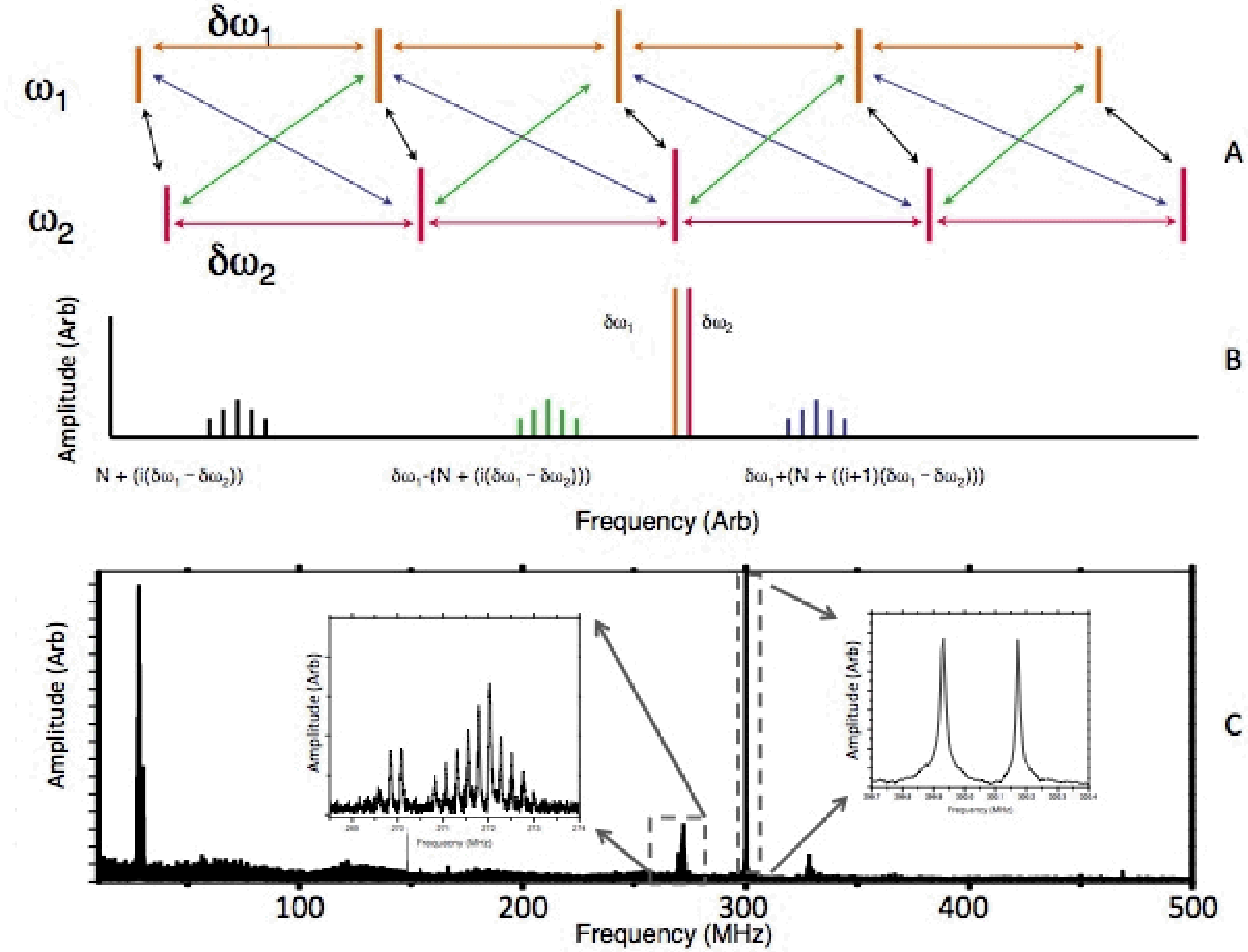
Separates cold atoms or molecules from remaining beam; molecular fountain for high resolution spectroscopy


NO (j=6.5, 7.5, 8.5)
NO (j=0.5)
Ar
z
y
x

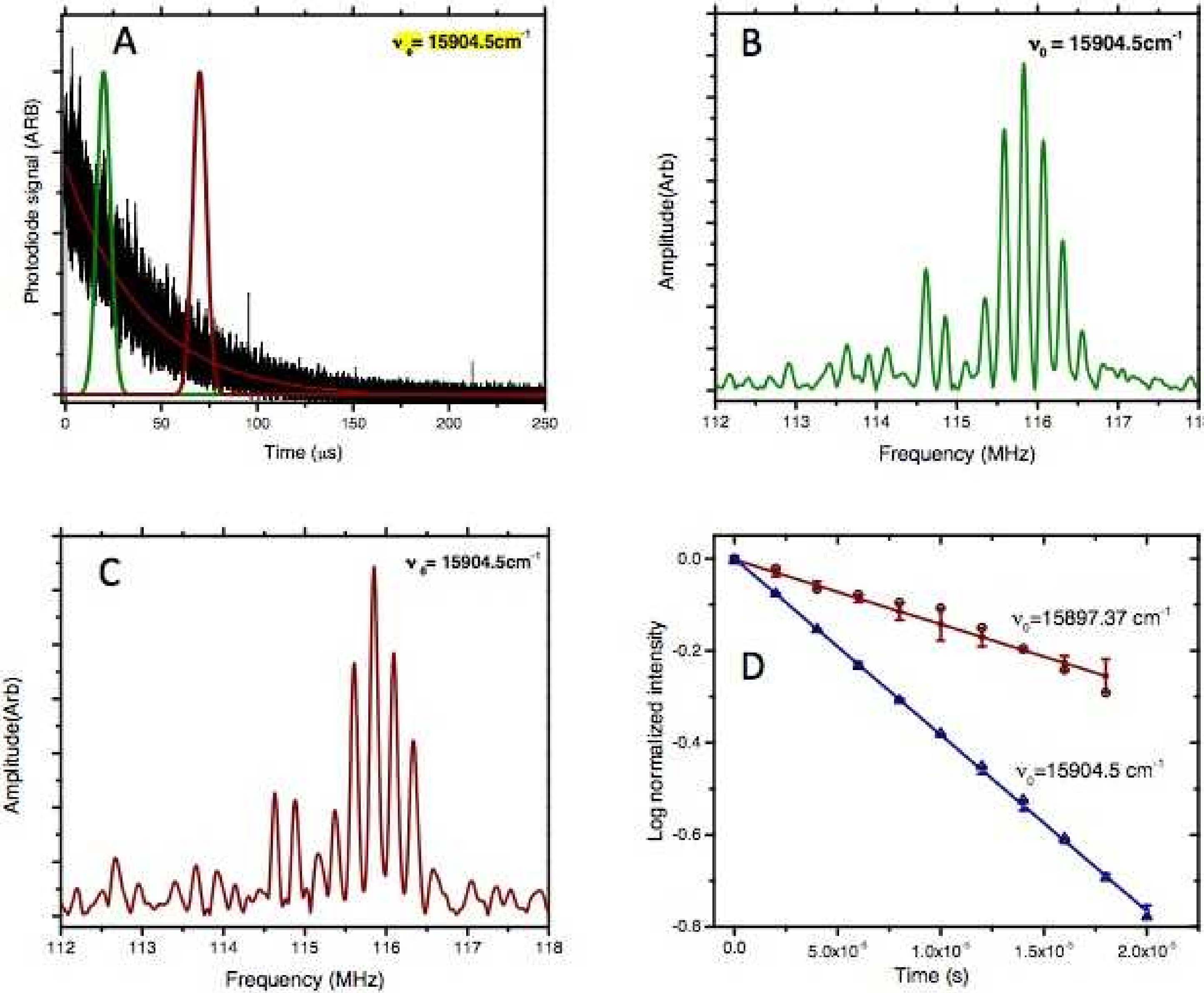
A atom or Molecule that can be observed for 100 microseconds
Can be subjected to about 2 kHz spectroscopy.

How to makes high resolution light?
Dual Etalon Frequency Comb Spectroscopy.


DYE LASER
Nd:YAG
A
I
t
B
I
t
C
I
t

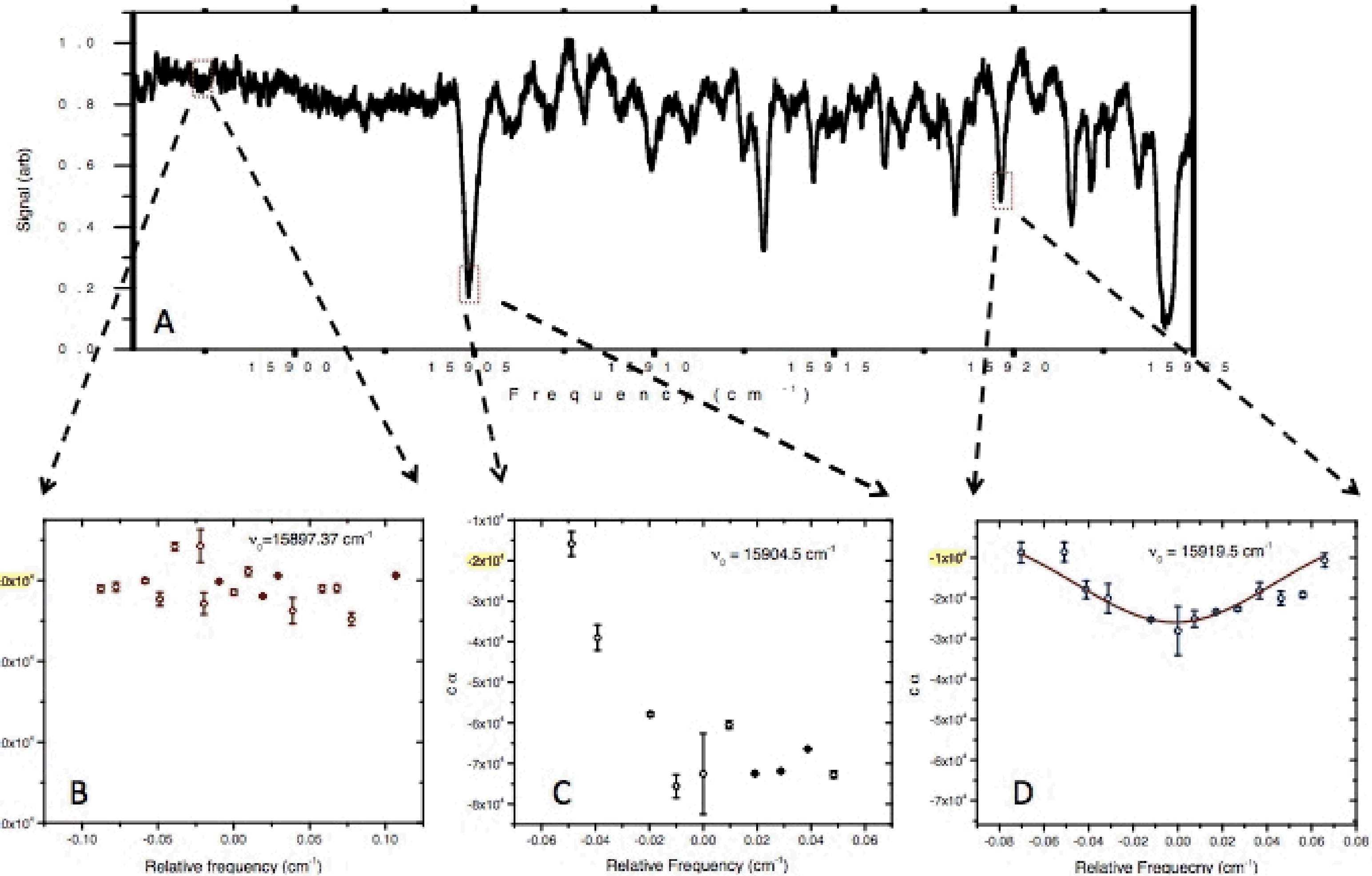


δω1
ω1
ω2
δω2
A
Amplitude (Arb)
δω1
δω2
B
N + (i(δω1 − δω2))
δω1-(N + (i(δω1 − δω2)))
δω1+(N + ((i+1)(δω1 − δω2)))
Frequency (Arb)
Amplitude (Arb)
Amplitude (Arb)
Amplitude (Arb)
C
100
200
300
400
500
Frequency (MHz)



A
ν0= 15904.5cm-1
Photodiode signal (ARB)
0
50
100
150
200
250
Time (μs)
B
ν0 = 15904.5cm-1
Amplitude(Arb)
112
113
114
115
116
117
118
Frequency (MHz)
C
ν0= 15904.5cm-1
Amplitude(Arb)
112
113
114
115
116
117
118
Frequency (MHz)
D
ν0=15897.37 cm-1
ν0=15904.5 cm-1
Log normalized intensity
0.0
-0.2
-0.4
-0.6
-0.8
Time (s)

O_2 forbidden b $^1\Sigma_g^+$--$X^3\Sigma_g^-$ and H_2O $4\nu+\delta$ (000) -> (113) overtone



Memory Lane: Simple Cavity Ring Down Apparatus

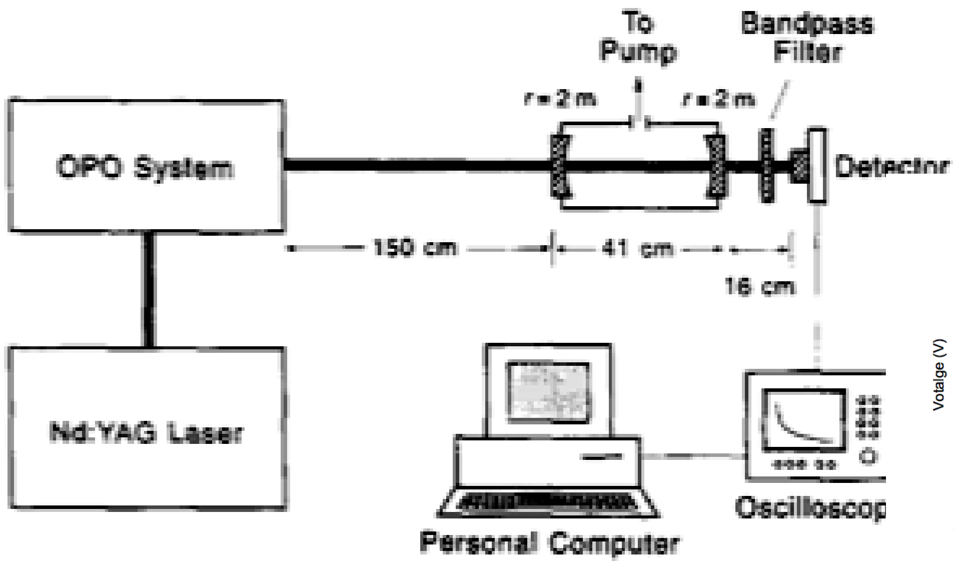
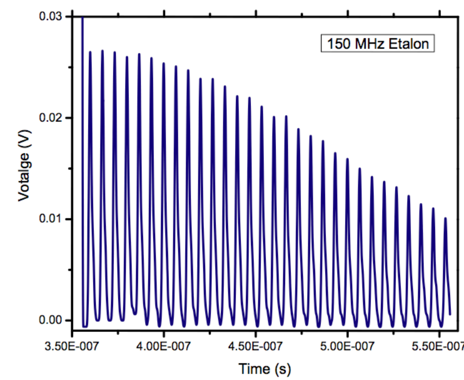


Fig. 2. Schematic view of the experimental setup.



If Ring Down Cell was in Confocal Etalon Arrangement Interference Between Equally Spaced Modes are Seen in Decay

What to do About Those Interferences? Get Rid of Them!

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Coherent cavity ring down spectroscopy

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Received 29 October 1993

In a cavity ring down experiment the multi-mode structure of a short resonant cavity has been explicitly manipulated to allow a high spectral resolution, which is advantageous for the overall detection sensitivity as well. Coherent cavity ring down spectroscopy is performed around 298 nm on OH in a flame.

- Mess up the cavity
- Average for a while
- Low Pass Filter

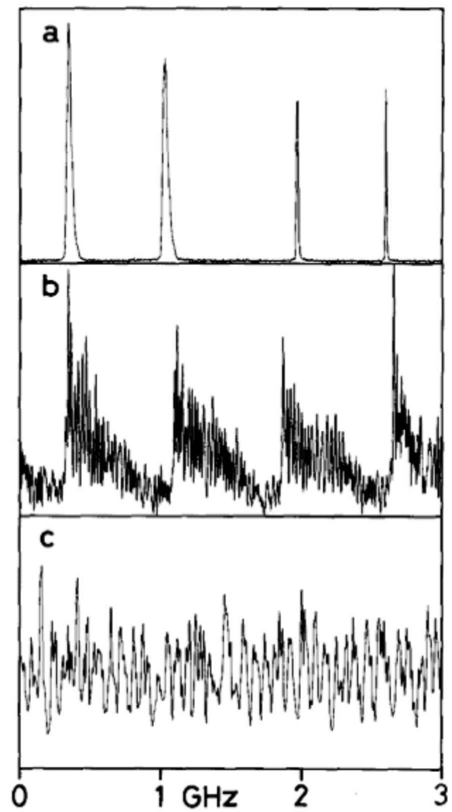
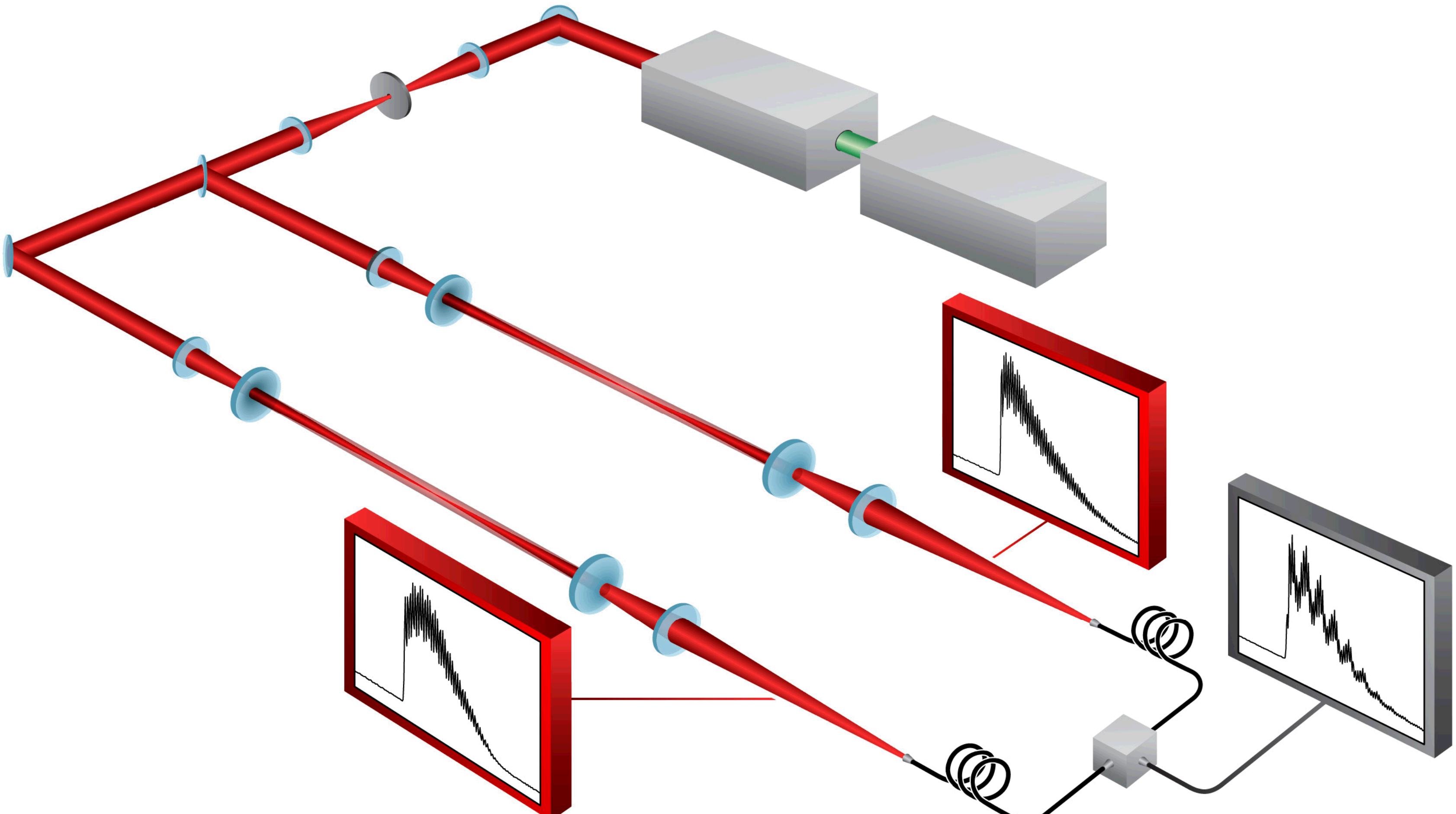


Fig. 1. Mode-spectrum of the ring down cavity for three different mirror separations *d*: (a) $d=10.0$ cm; (b) $d=10.2$ cm; (c) $d=11.5$ cm. A rapid congestion of the spectrum is seen when the cavity is detuned from confocal. The spectra are measured by monitoring the transmission of the cavity while a narrowband (≤5 MHz) cw UV laser is scanned over 3 GHz (6 GHz/min scan-rate) around 318 nm.

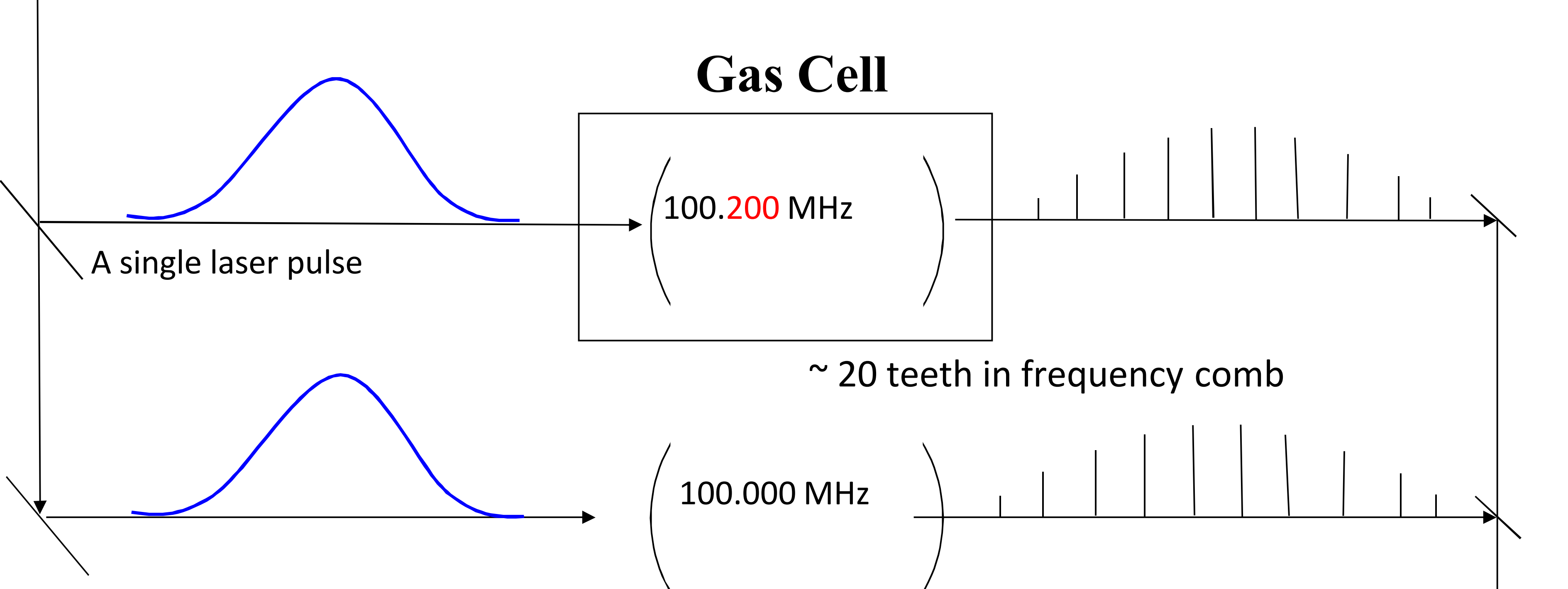
- Uses traditional laser sources (3 GHz Dye Lasers (1/10 cm-1) for example)
- On single laser shot gives ~300 MHz resolution (1/100 cm-1) over bandwidth of laser source
- With averaging one can get ~30 KHz resolution (1/1,000,000 cm-1).
- Works in absorption and in fluorescence.
- Cavity Ring Down Spectroscopy is natural with the technique.
- It is inexpensive and easy to build, single photodiode detector.

DEFCOM Spectrometer



DEFCOM apparatus.

Use two ~100 MHz etalons and a 2 GHz Dye laser (or OPO, or ASE, or Femtosecond pulse)



Etalons create frequency combs that when combined the cross beats
Between 0 and 50 MHz contain the spectrum with 100 MHz (.03 cm-1)
Spectral resolution. (this requires about a 10 microsecond ring down time).

Reference: S. Schiller Opt. Lett. 27, 766 (2002),
Hansch (2006), Keilmann (2005), Jun Ye (2007), Nathalie Picque 2010

Spectrometry with frequency combs

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Received December 19, 2001

A method is proposed for performing accurate spectral characterization of samples with frequency combs, e.g., from mode-locked lasers, over the spectral range covered by the combs. The essence of the method is the use of two combs of slightly different mode spacing to achieve spectral resolution. The advantages of the method are speed, frequency resolution, sensitivity, absence of dispersive components, and high spatial resolution.

OCIS codes: 300.6190, 140.4050.

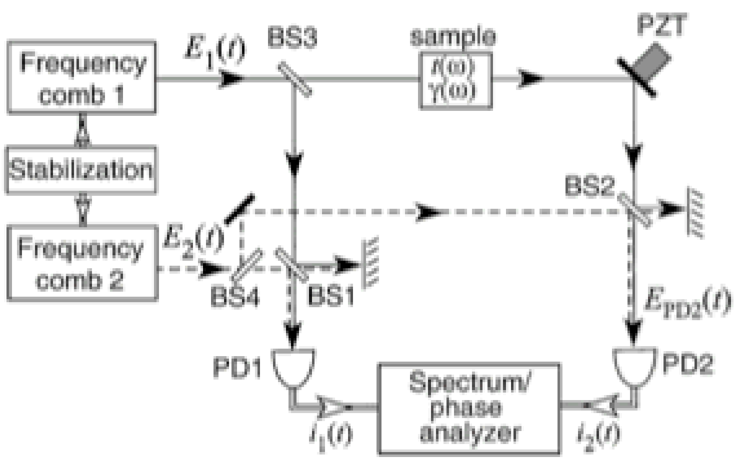


Fig. 1. Setup for measurement of transmission spectrum $t(\omega)$ and (or) phase spectrum $\gamma(\omega)$ of the sample. BS1–BS4, beam splitters; PD1–PD2, rf photodetectors; PZT, translator.

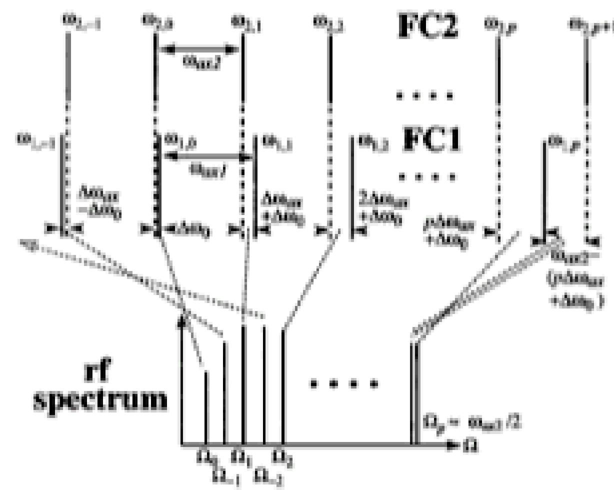
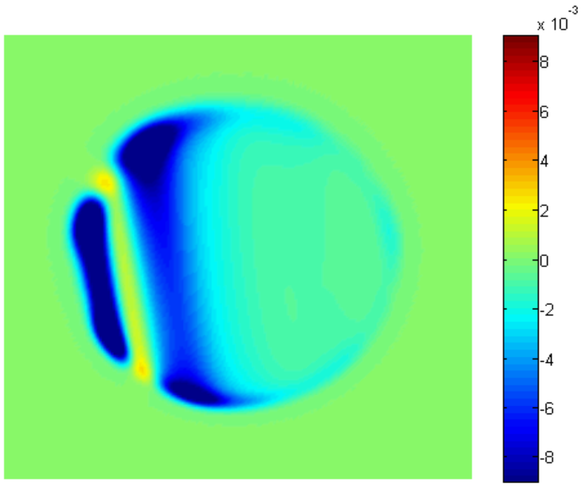
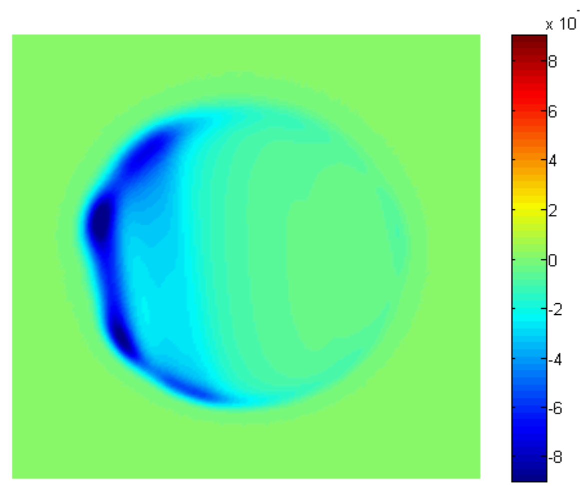


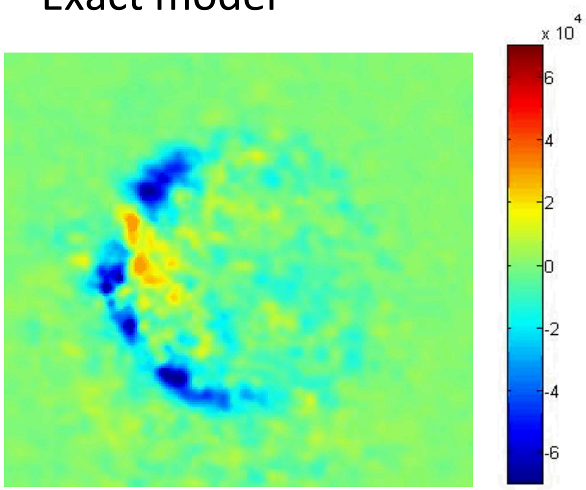
Fig. 2. Schematic of the modes of the two combs and relevant beats. The beats between modes ω_{1n} and ω_{2n} of equal index give rise to a rf spectrum with interleaving. Its discrete frequencies $\Omega_0, \Omega_{-1}, \Omega_1, \Omega_{-2}, \ldots$ arise alternatingly from modes below and above ω_{10}. Beats between modes of different index, e.g., $\omega_{2n+1} - \omega_{1n} = \omega_{rr2} - (\Delta\omega_0 + n\Delta\omega_{rr})$ decrease in frequency with increasing n and will overlap the rf spectrum of beats of equal index starting at the beat frequency $\Omega_p = \omega_{rr2}/2$, once n is sufficiently large (see the double dashed lines).



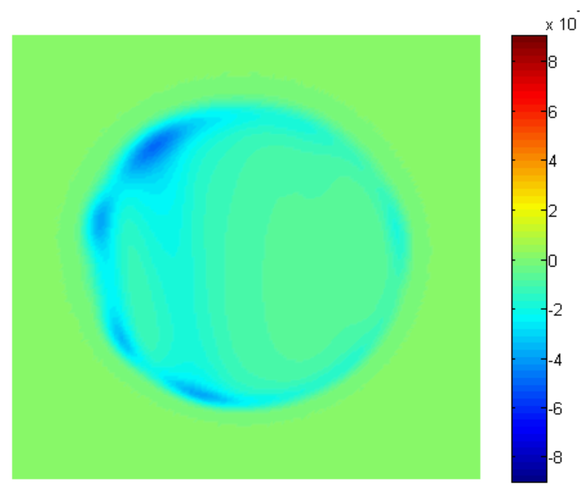
Exact model



Fraunhofer model



Experimental image



Apse model