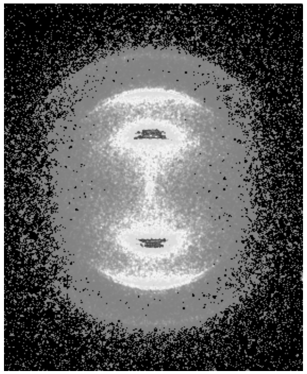
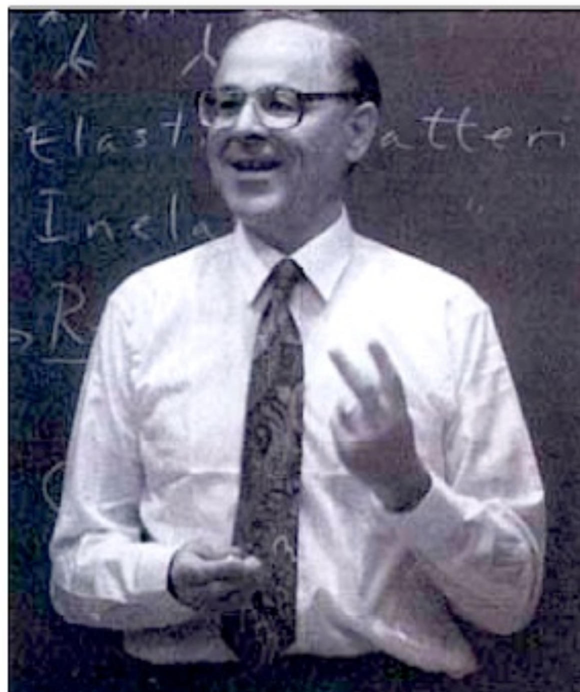
Quantum State Resolved Inelastic Collisions studied in Crossed Molecular beams: Surprising results and new directions

SAND2016-11343C

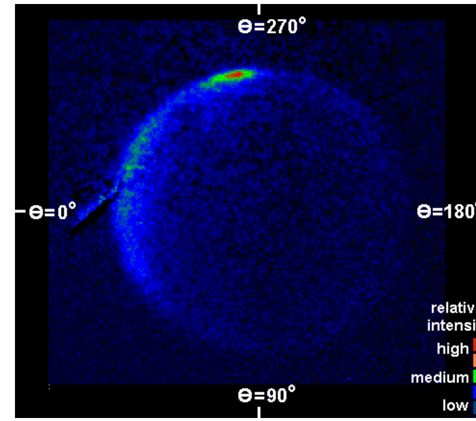


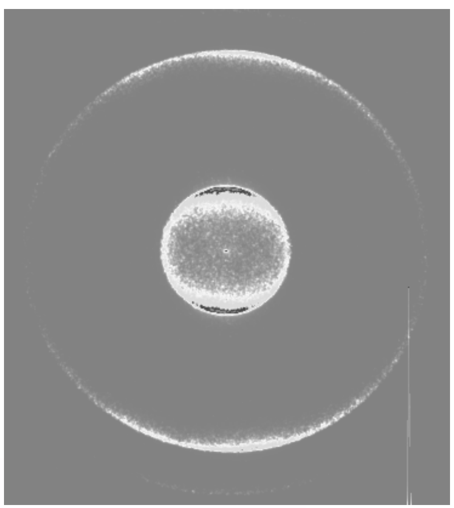
David W. Chandler

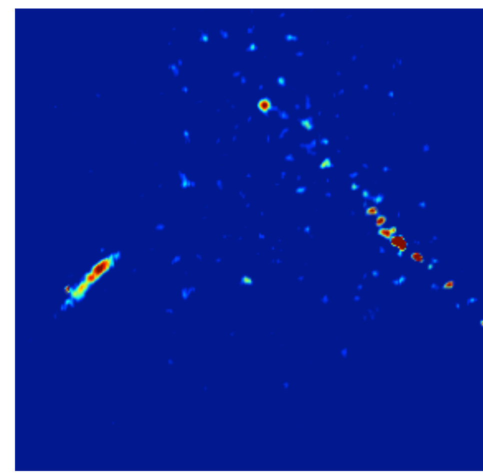
Sandia National Laboratory



Richard Bernstein







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Outline

- Tutorial on Ion Imaging with Velocity Mapping
- Photo-dissociation of H_2 example
  - Ground state versus excited state measurements.

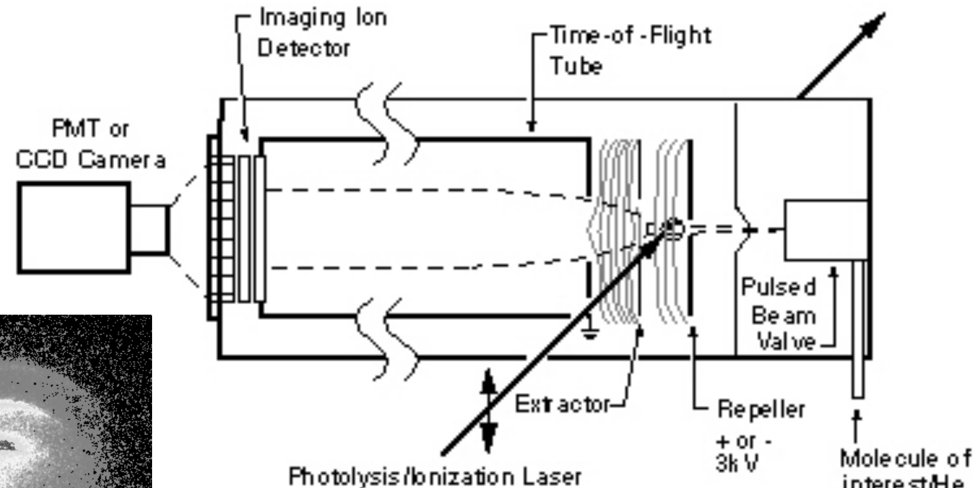
- Quantum State Selective Inelastic Scattering
  - Differential cross sections
  - Alignment of products
  - Orientation of products
  - In Electronically excited states

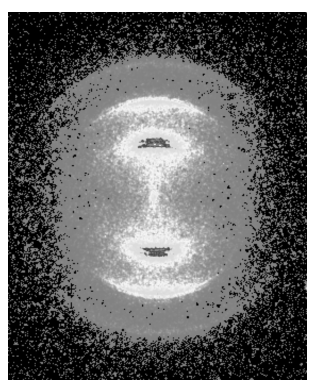
We use Ion Imaging to Study Unimolecular Dissociation Events

- One laser beam dissociates molecule
- One laser beam ionizes product of the dissociation state selectively
- All ion are projected onto phosphor screen
- Image is recorded
- Image is analyzed as a function of lasers, intensity, frequency and polarizations.

Ion Imaging apparatus with Velocity Mapping allows one to measure either the photofragment image or the photoelectron image

Chandler. D. W.: Houston. P. L. , *J. Chem. Phys.* 1987





Observed alignment with laser intensity
In H2 photodissociation at 532 nm

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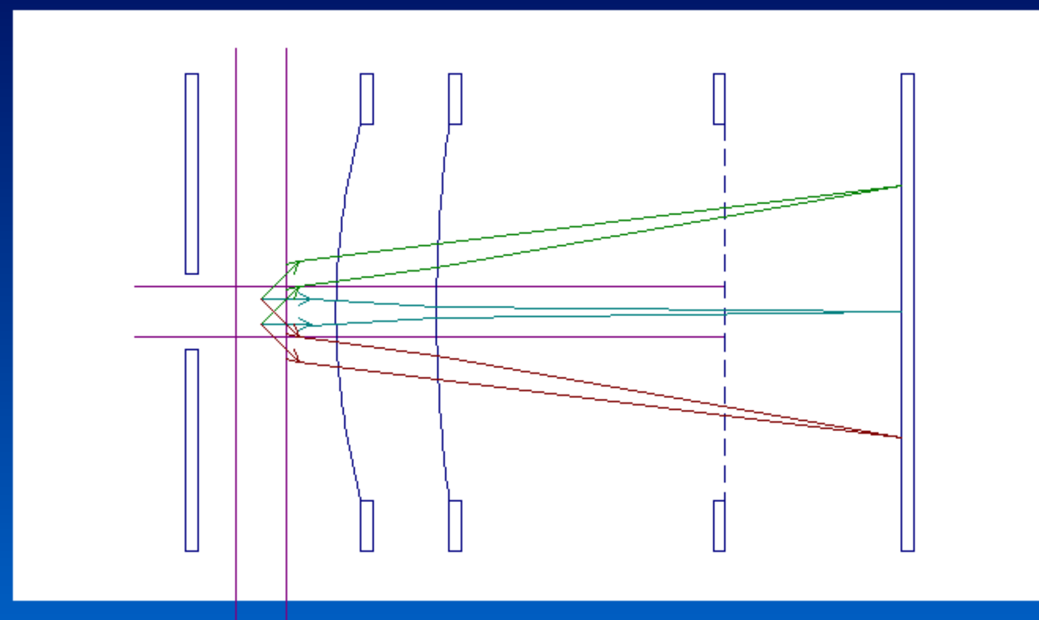
Dave Parker (Post Doc With Dick Bernstein) and Andre Eppink of Univ. of Nijmegen made resolution advance for Ion Imaging "Velocity Mapping"

- The use of lenses instead of screens in the Time-of-Flight focuses the ions and eliminates the spatial blur associated with the origin of the ions.

Velocity Mapping

An Einzel Lens Corrects for the blurring



A.. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instrum. **68**, 3477 (1997).

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Stereo-Dynamics: Study of alignment and Orientation of Reactants and Products

- Alignment and orientation only makes sense relative to a reference frame/ reference vector. Dissociation direction of a photo-fragmentation process or relative velocity vector of a collision.

- **RotatIonal Alignment of the CD3 Fragment from the 266-nm PhotodIssoclatIon of CD3I**

  Maurice H. M. Janssen, David H. Parker, Greg0.Sitz, Steven Stolte, and David *W* .Chandler *(JPC, 1990)*

Alignment was one of First Things to be Studied with Ion Imaging.

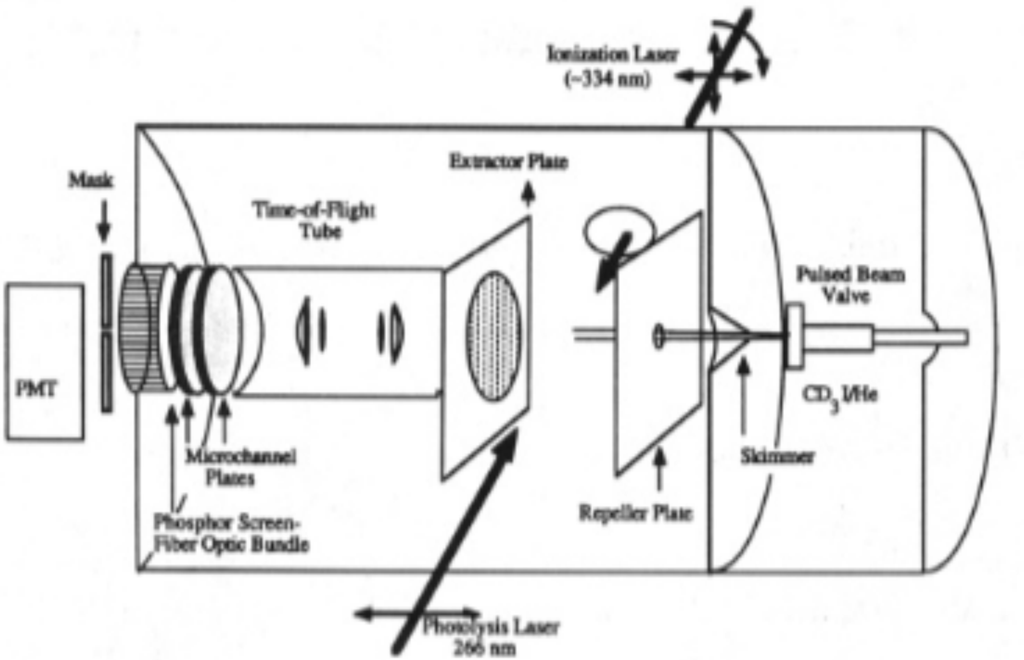
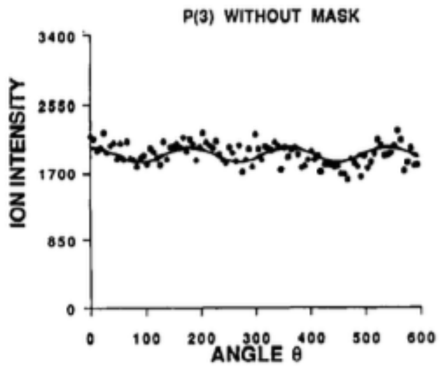
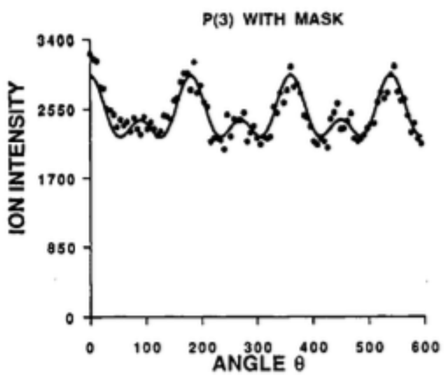
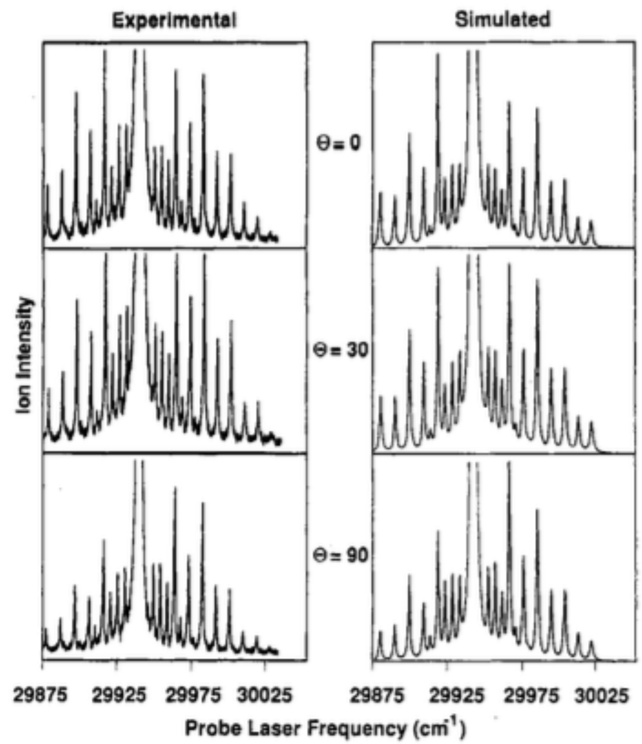


Figure 1. Schematic of apparatus used to perform the velocity selected REMPI study of the polarization dependence of the CD_3 ion intensity following CD_3I photolysis.


P(3) WITHOUT MASK
ION INTENSITY
3400
2550
1700
850
0
0 100 200 300 400 500 600
ANGLE θ


P(3) WITH MASK
ION INTENSITY
3400
2550
1700
850
0
0 100 200 300 400 500 600
ANGLE θ


Experimental
Simulated
Ion Intensity
Θ = 0
Θ = 30
Θ = 90
29875 29925 29975 30025
29875 29925 29975 30025
Probe Laser Frequency (cm⁻¹)

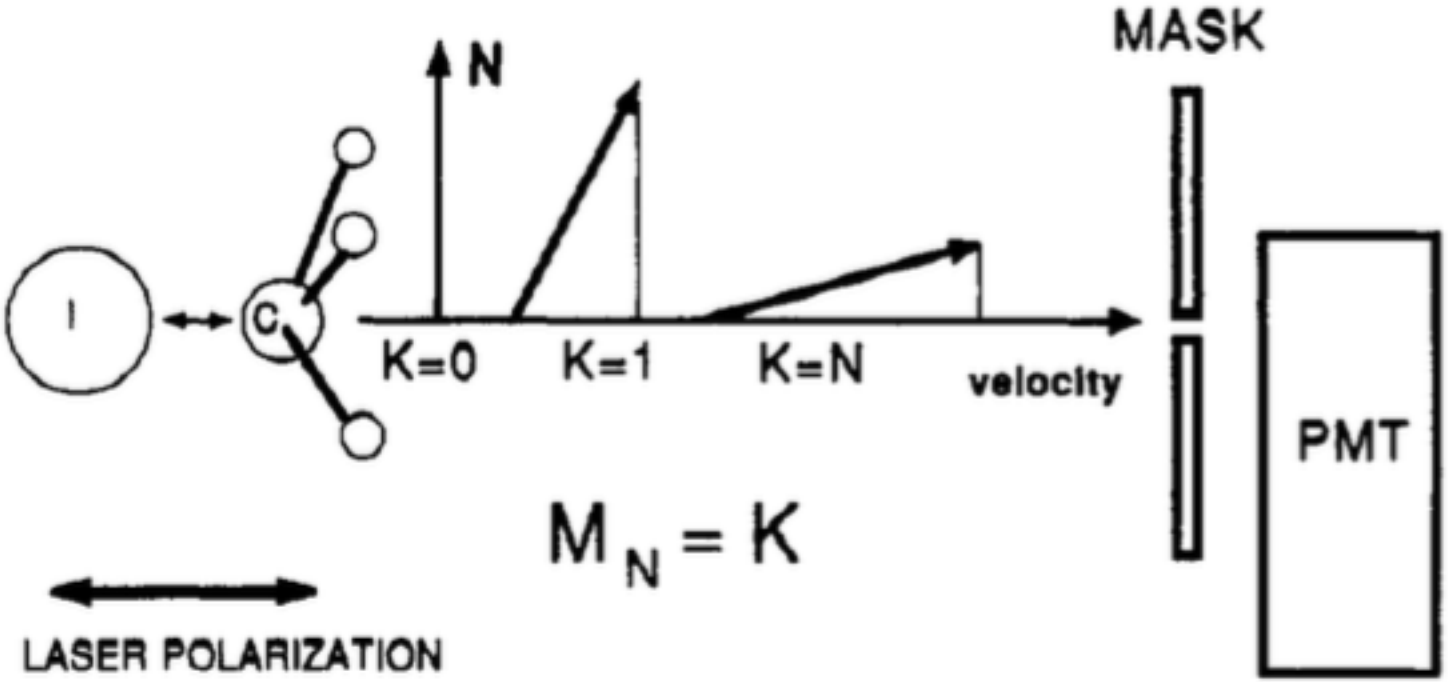
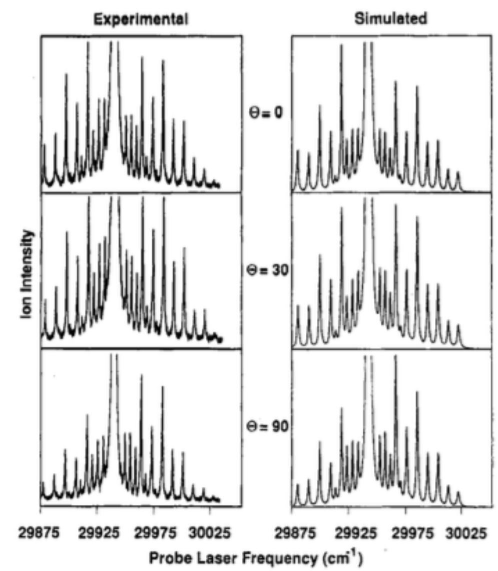

N
MASK
I
C
K=0
K=1
K=N
velocity
PMT
M N = K
LASER POLARIZATION

TABLE I: Population and Alignment Moments $A_0^{(2)}$ and $A_0^{(4)}$ of the Angular Momentum Distribution of the CD_3 Fragment from the 266-nm Photodissociation of CD_3I (Values Listed in the Columns Labeled Measured Were Used To Generate the Model Spectra of Figure 3)

		population[a]		$A_0^{(2)}$		$A_0^{(4)}$	
N	K	from ref 14	measd	measd	model[b]	measd[c]	model[b]
1	0	0.8	0.85	−1.0[d]	−1.0	0.0[e]	0.0
	1	0.62	0.62	0.50	0.5	0.0[e]	0.0
2	0	0.11	0.15	−1.0	−1.0	0.12	0.25
	1	0.8	0.85	−0.45	−0.5	−0.02	−0.167
	2	0.4	0.29	0.98[d]	1.0	0.042[e]	0.042
3	0	1.2	1.2	−0.7	−1.0	0.3[e]	0.313
	1	0.8	0.71	−0.65	−0.75	0.05	0.052
	2	0.4	0.4	0.00	0.0	−0.2	−0.365
	3	0.18	0.20	1.25	1.25	0.156[e]	0.156
4[f]	0	0.13	0.1	−0.8	−1.0	0.338[e]	0.338
	1	0.8	0.8	−0.65	−0.85	0.1	0.169
	2	0.4	0.4	−0.4	−0.40	−0.21	−0.206
	3	0.15	0.21	0.2	0.35	−0.394[e]	−0.394
	4	0.03	0.025	1.40[e]	1.40	0.263[e]	0.263

$$A_{0,\max}^{(2)} = \frac{3K^2 - N(N+1)}{N(N+1)} \quad (5)$$

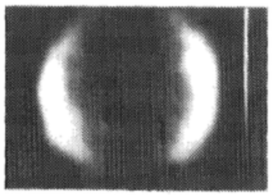
$$A_{0,\max}^{(4)} = \frac{35K^4 - 30K^2N(N+1) + 3N^2(N+1)^2 + 25K^2 - 6N(N+1)}{8N^2(N+1)^2} \quad (6)$$

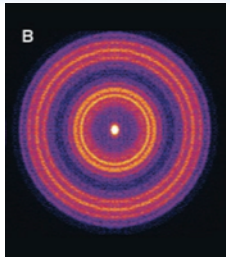


Model assumes perfect Alignment, Measurements confirm this.

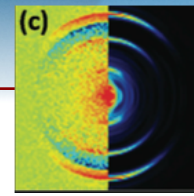
Velocity Mapped Ion Imaging: Developed in BES Program has 30 year Anniversary in 2016. Impact Grows

First Ion Image
Differential cross sections for single quantum states for Photodissociation made possible 1987
Chandler and Houston (BES)

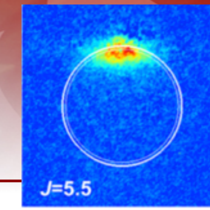




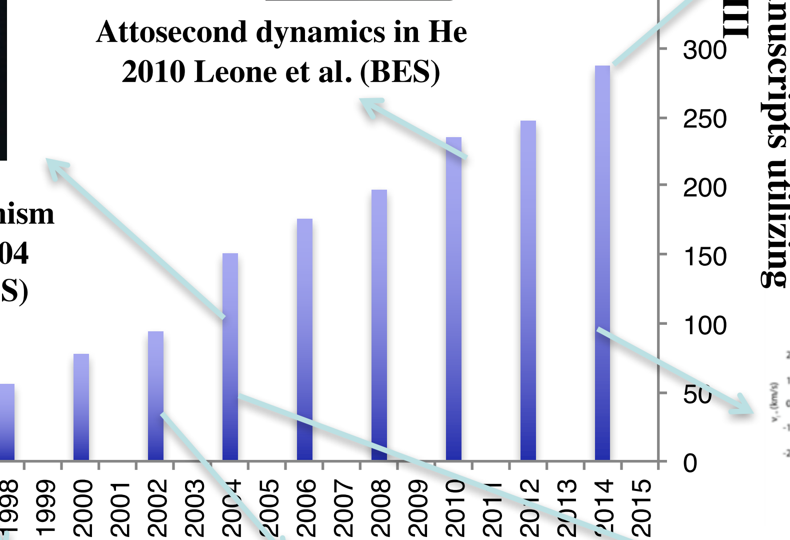
Roaming Mechanism Discovered, 2004
Suits et al. (BES)



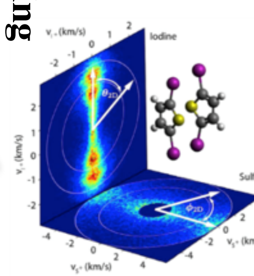
Attosecond dynamics in He 2010 Leone et al. (BES)

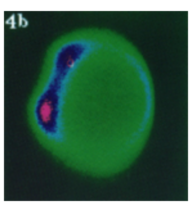


Collisional Induced Dissociation From a single collision Chandler, Jasper 2015 (BES)

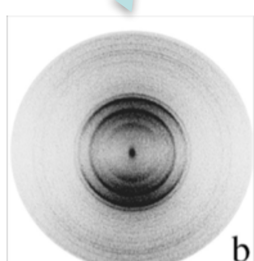


Strong Laser Field Alignment of Molecules 2015 (BES)

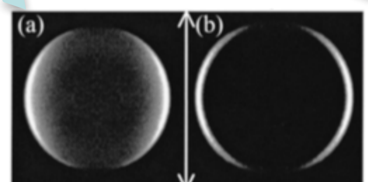




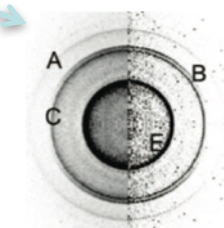
First state-selected Differential Cross Sections For Bimolecular Collisions 1992
Houston et al. (BES)



Velocity Mapping Introduced for increased resolution, 1997
Parker and Eppink (BES/CRF Visitor)



Slice Imaging for improved resolution, 2001
Kitsopoulous (ex-BES/CRF Postdoc)



Ultra high resolution electron imaging 2004
Neumark (BES)

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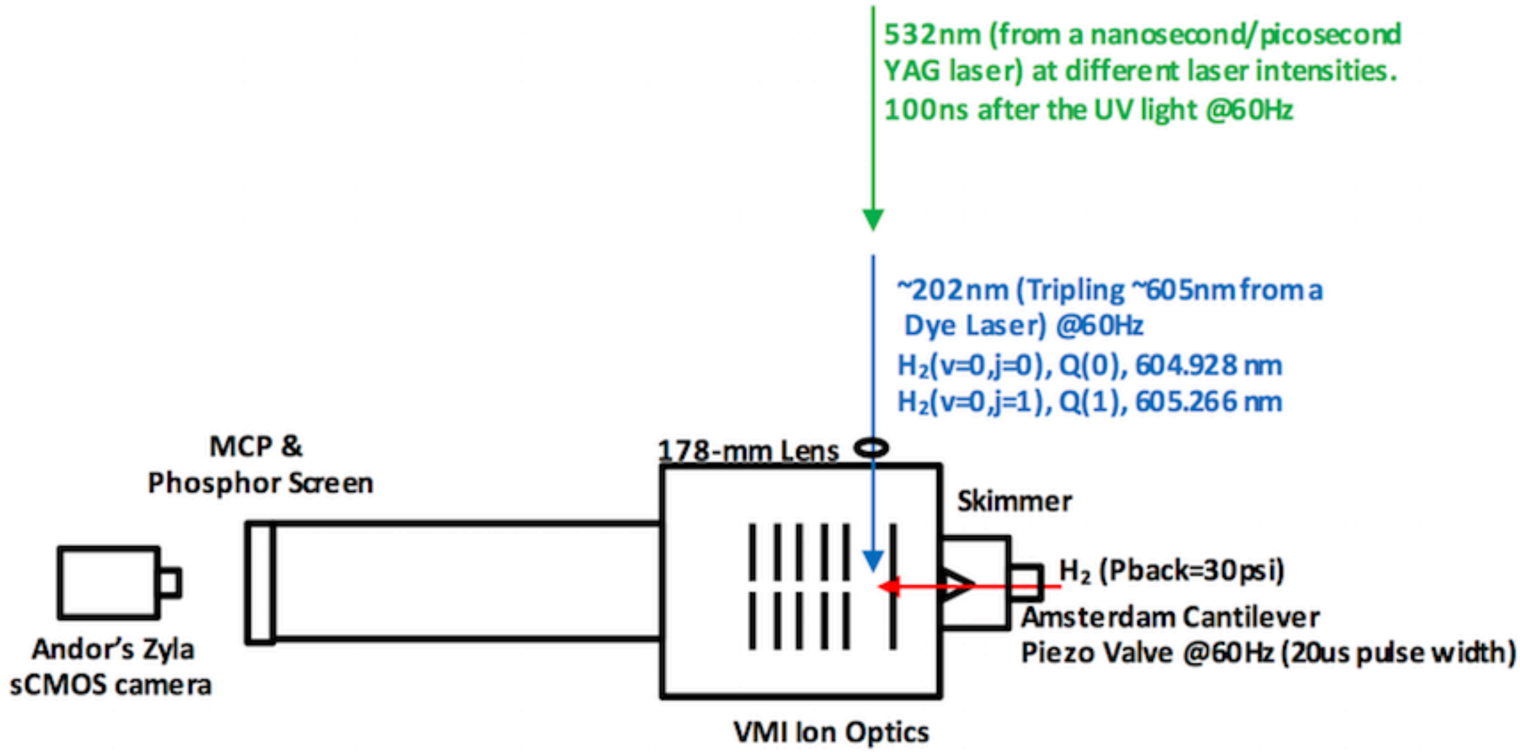
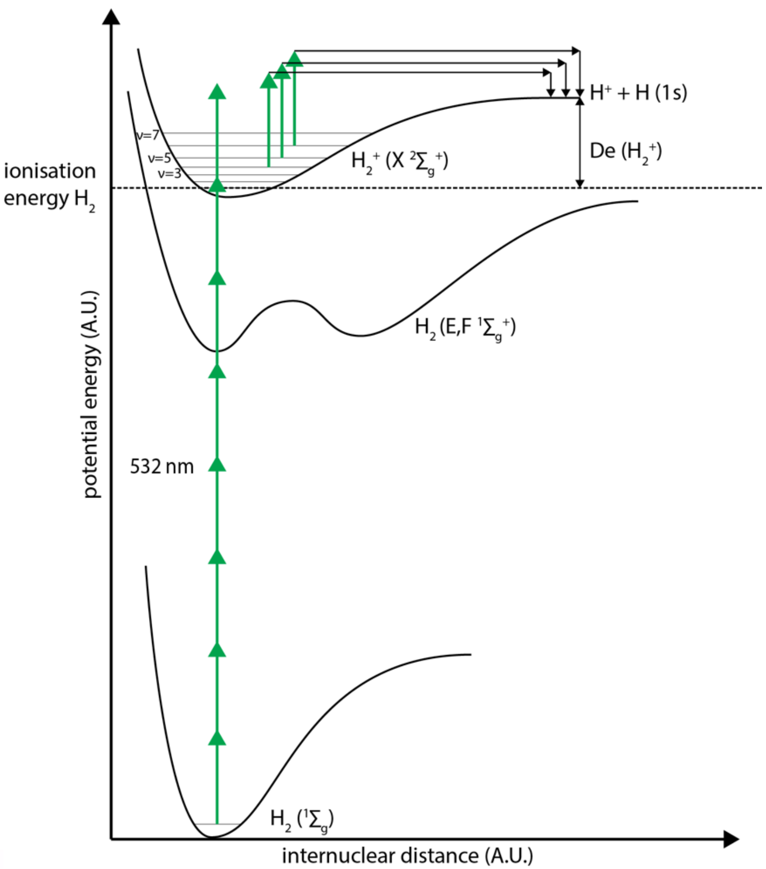
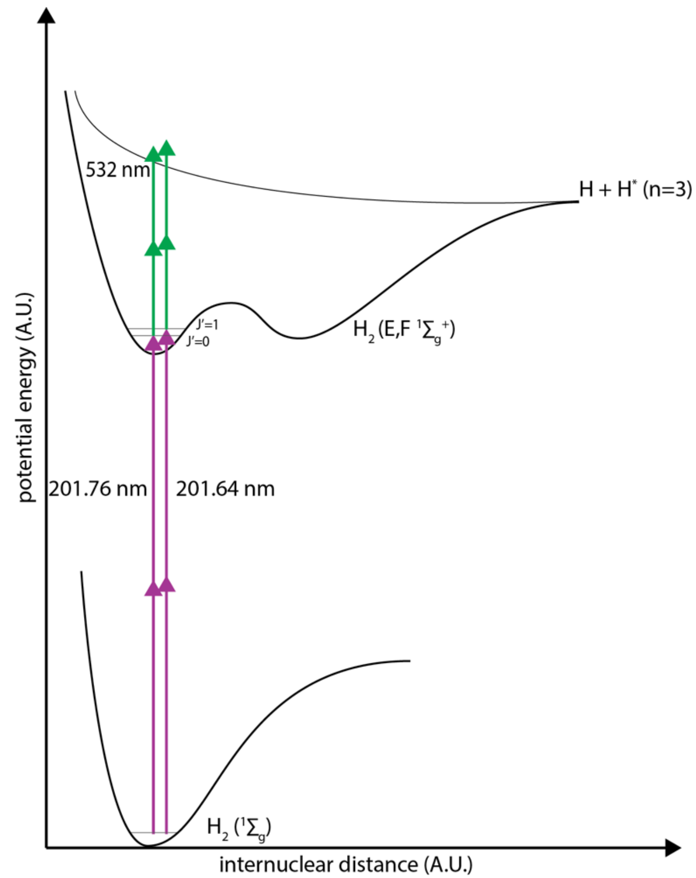


532nm (from a nanosecond/picosecond YAG laser) at different laser intensities.
100ns after the UV light @60Hz
~202nm (Tripling ~605nm from a Dye Laser) @60Hz
H2(v=0,j=0), Q(0), 604.928 nm
H2(v=0,j=1), Q(1), 605.266 nm
MCP &
Phosphor Screen
178-mm Lens
Skimmer
H2 (Pback=30psi)
Amsterdam Cantilever
Piezo Valve @60Hz (20us pulse width)
Andor's Zyla
sCMOS camera
VMI Ion Optics





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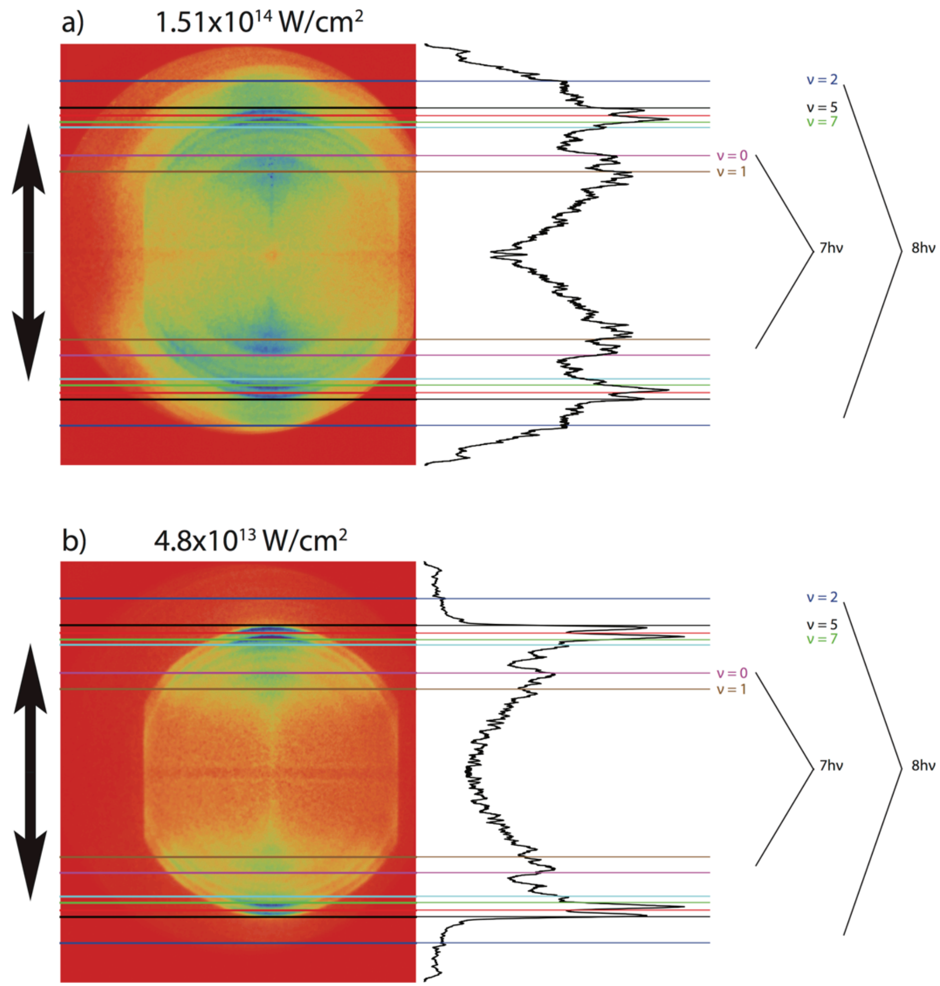
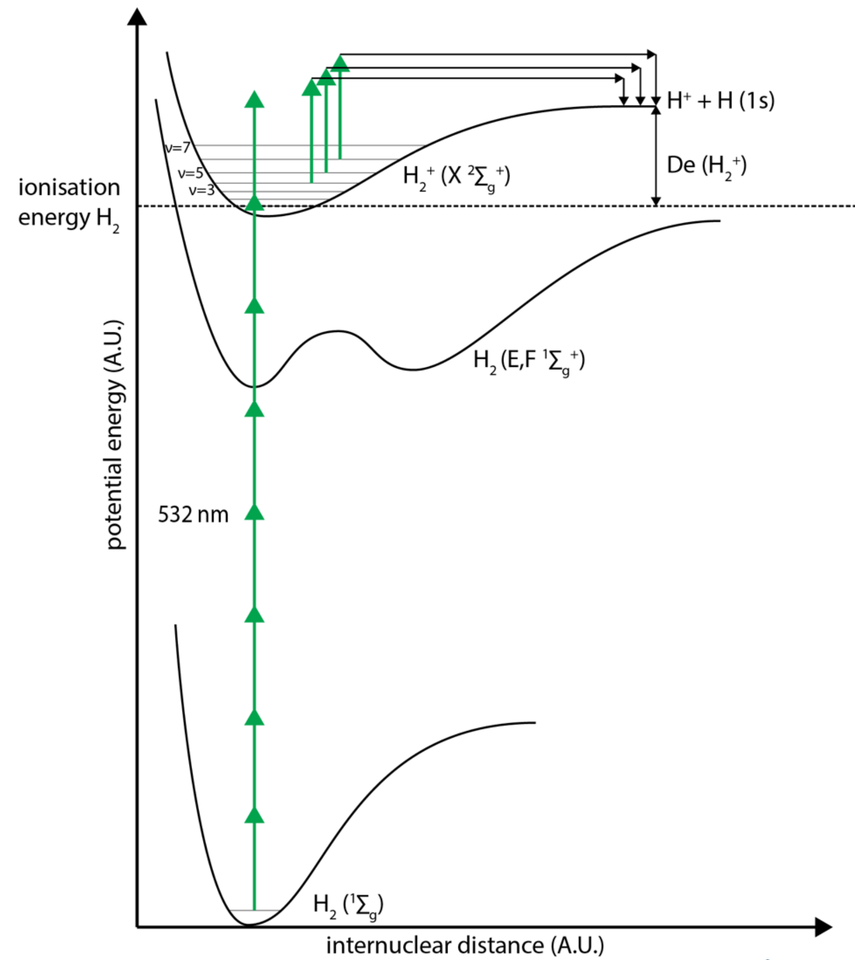
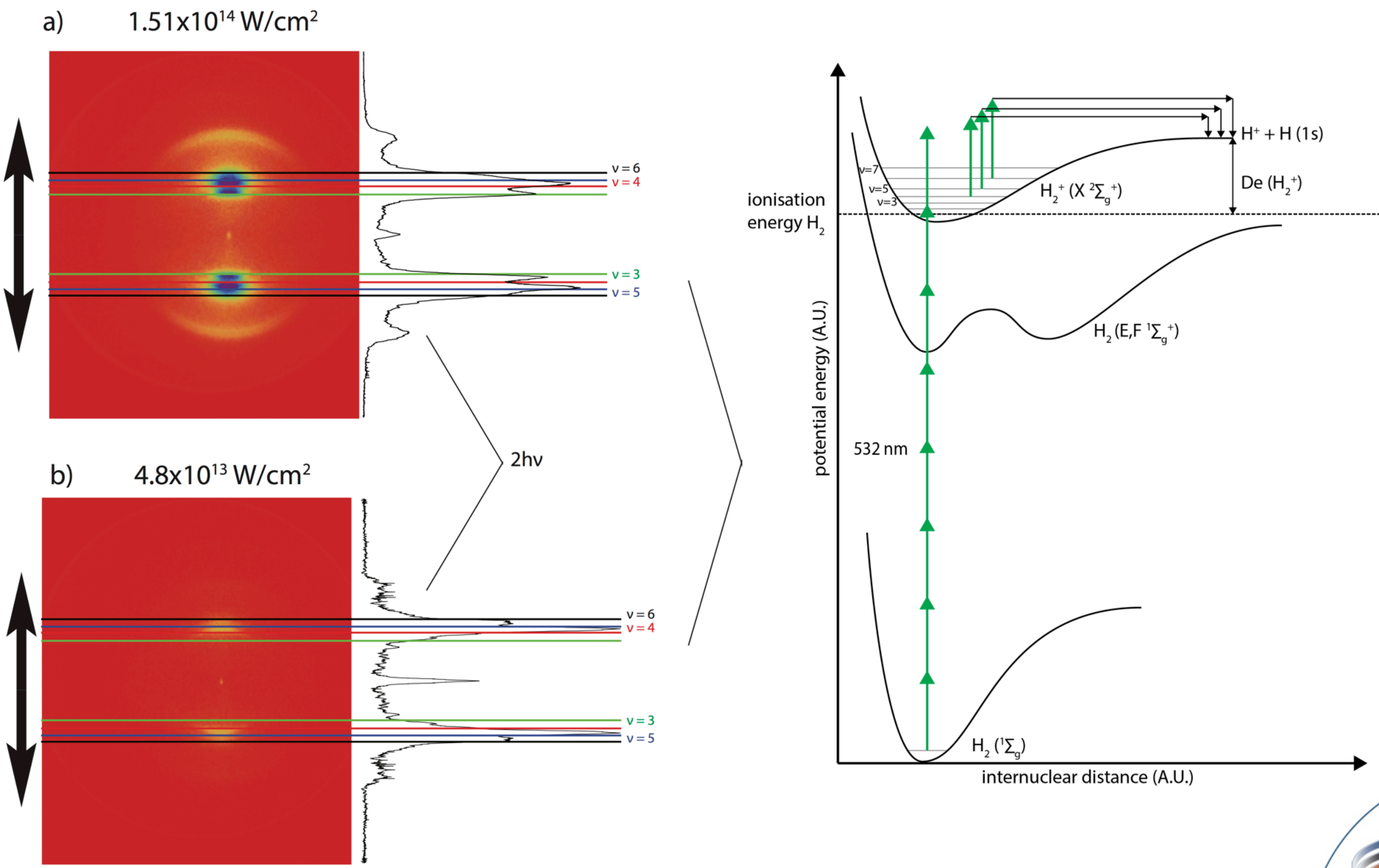


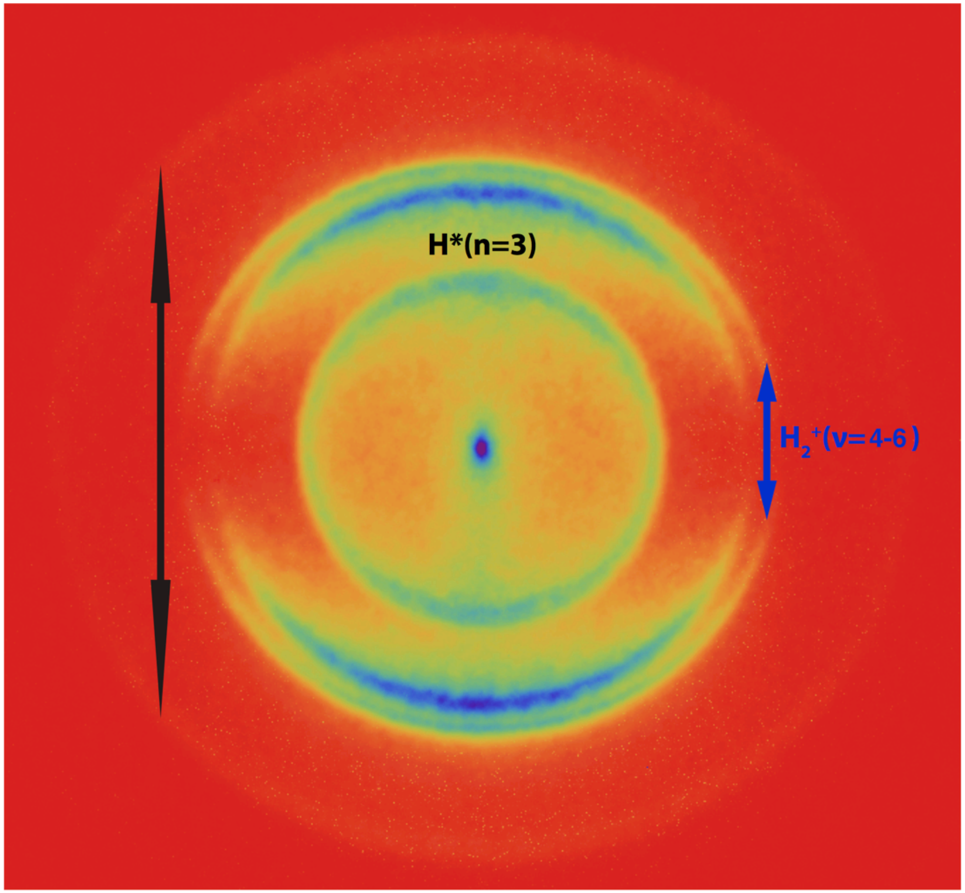
a)
1.51x10^14 W/cm^2
b)
4.8x10^13 W/cm^2
v = 2
v = 5
v = 7
v = 0
v = 1
7hv
8hv

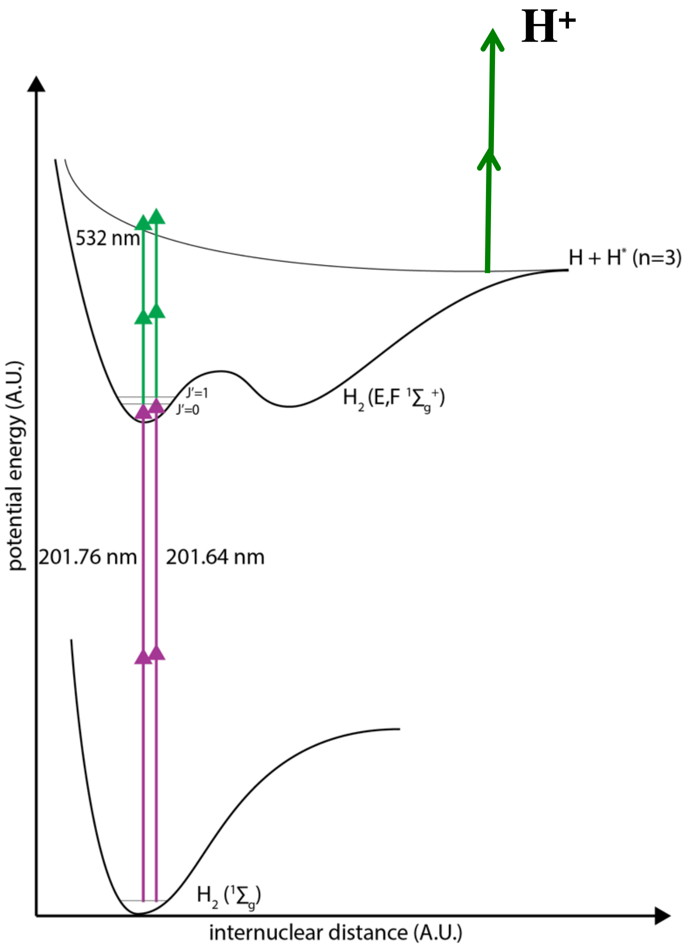


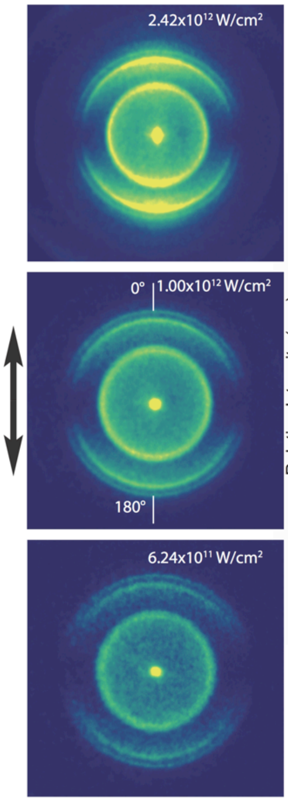
H+ + H (1s)
De (H2+)
H2+ (X 2Σg+)
v=7
v=5
v=3
ionisation energy H2
H2 (E,F 1Σg+)
potential energy (A.U.)
532 nm
H2 (1Σg)
internuclear distance (A.U.)



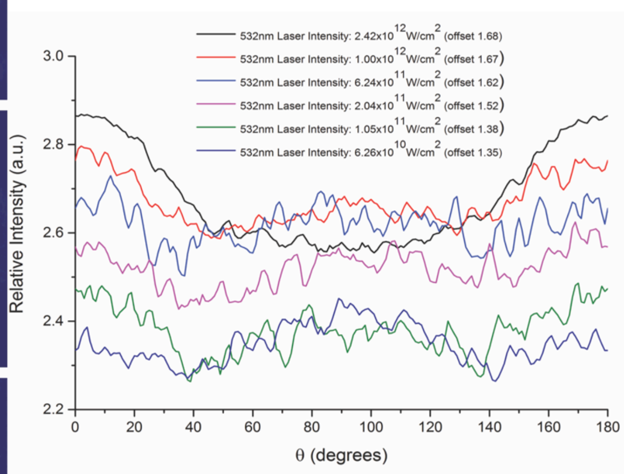
a) 1.51x10^14 W/cm^2
b) 4.8x10^13 W/cm^2
v = 6
v = 4
v = 3
v = 5
2hν
ionisation energy H2
H+ + H (1s)
De (H2+)
v=7
v=5
v=3
H2+ (X 2Σg+)
H2 (E,F 1Σg+)
532 nm
potential energy (A.U.)
H2 (1Σg)
internuclear distance (A.U.)


H*(n=3)
H_2^+(v=4-6)

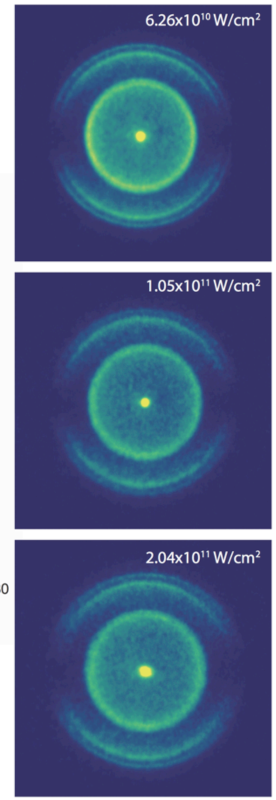

H^+
532 nm
H + H* (n=3)
J'=1
J'=0
H_2 (E,F $^1\Sigma_g^+$)
potential energy (A.U.)
201.76 nm
201.64 nm
H_2 ($^1\Sigma_g$)
internuclear distance (A.U.)



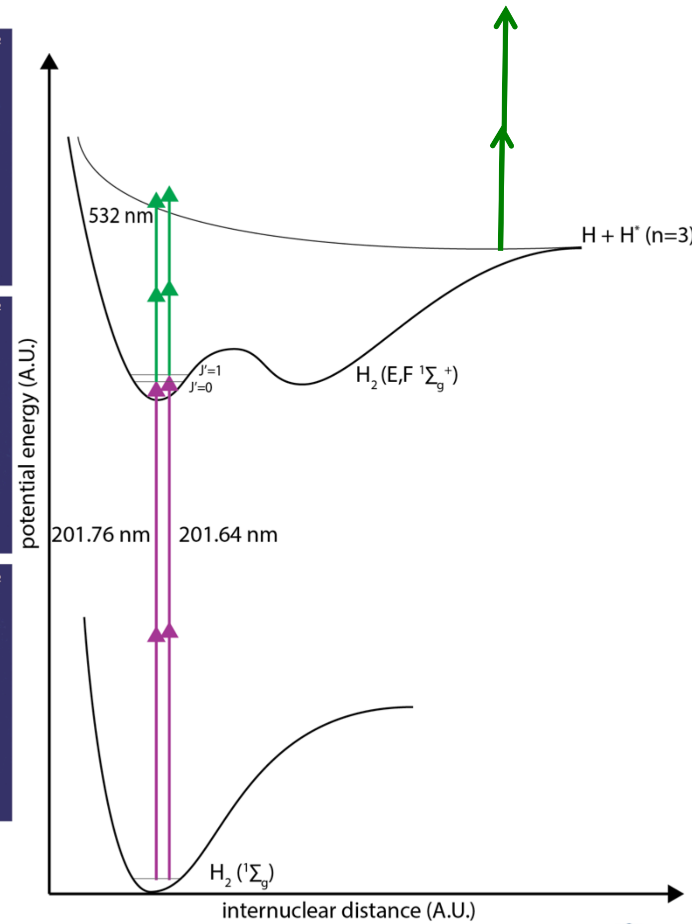
2.42x10^12 W/cm^2
0°
1.00x10^12 W/cm^2
180°
6.24x10^11 W/cm^2



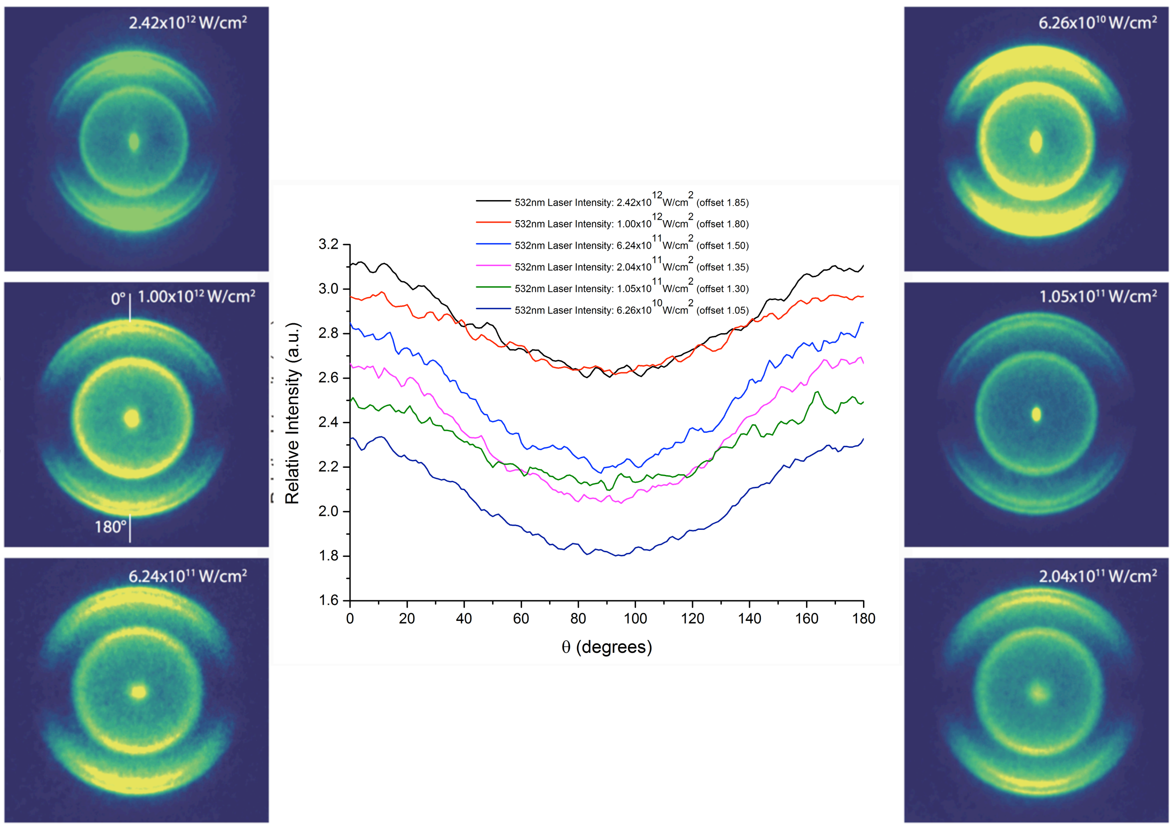
532nm Laser Intensity: 2.42x10^12 W/cm^2 (offset 1.68)
532nm Laser Intensity: 1.00x10^12 W/cm^2 (offset 1.67)
532nm Laser Intensity: 6.24x10^11 W/cm^2 (offset 1.62)
532nm Laser Intensity: 2.04x10^11 W/cm^2 (offset 1.52)
532nm Laser Intensity: 1.05x10^11 W/cm^2 (offset 1.38)
532nm Laser Intensity: 6.26x10^10 W/cm^2 (offset 1.35)
Relative Intensity (a.u.)
θ (degrees)

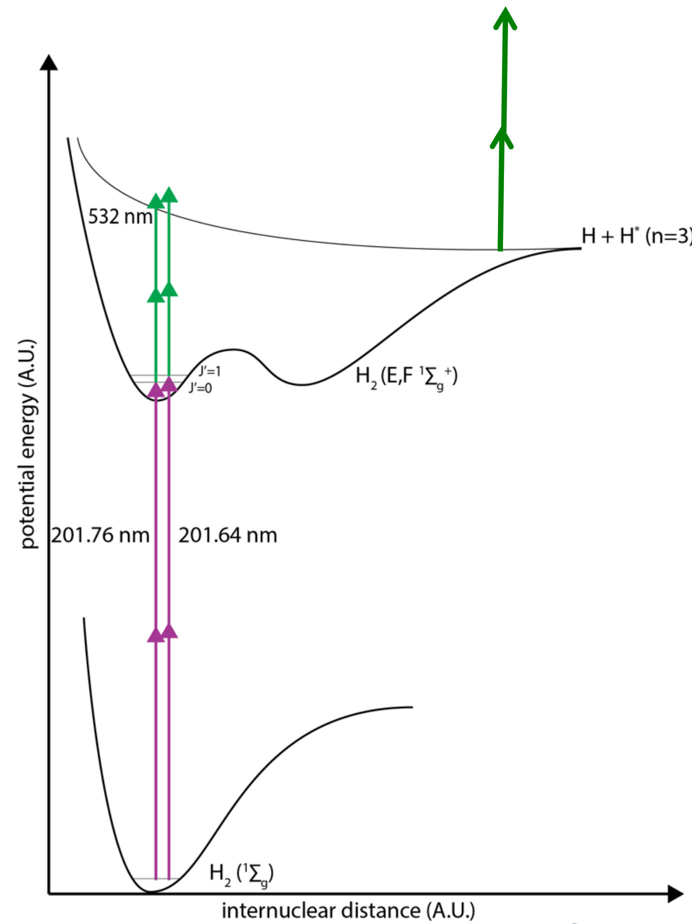


6.26x10^10 W/cm^2
1.05x10^11 W/cm^2
2.04x10^11 W/cm^2



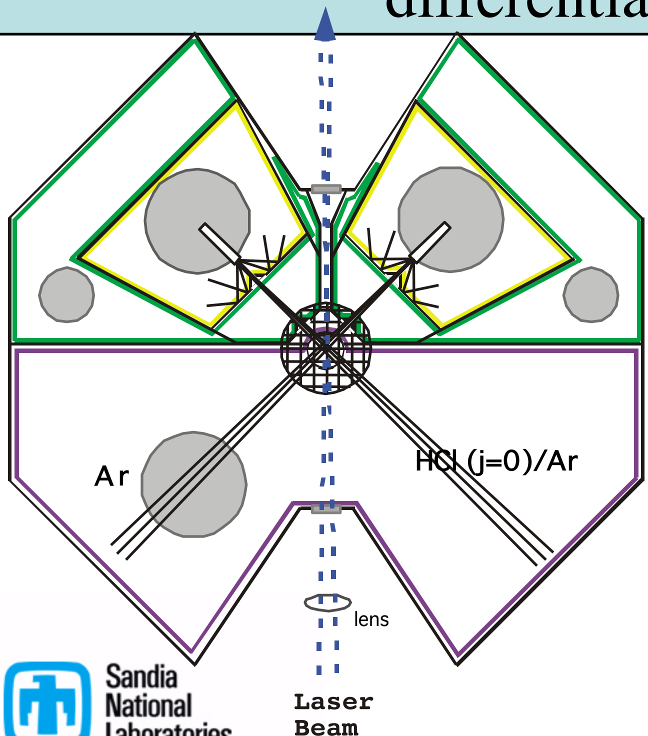
potential energy (A.U.)
532 nm
H + H* (n=3)
J'=1
J'=0
H2 (E,F 1Σg+)
201.76 nm
201.64 nm
H2 (1Σg)
internuclear distance (A.U.)

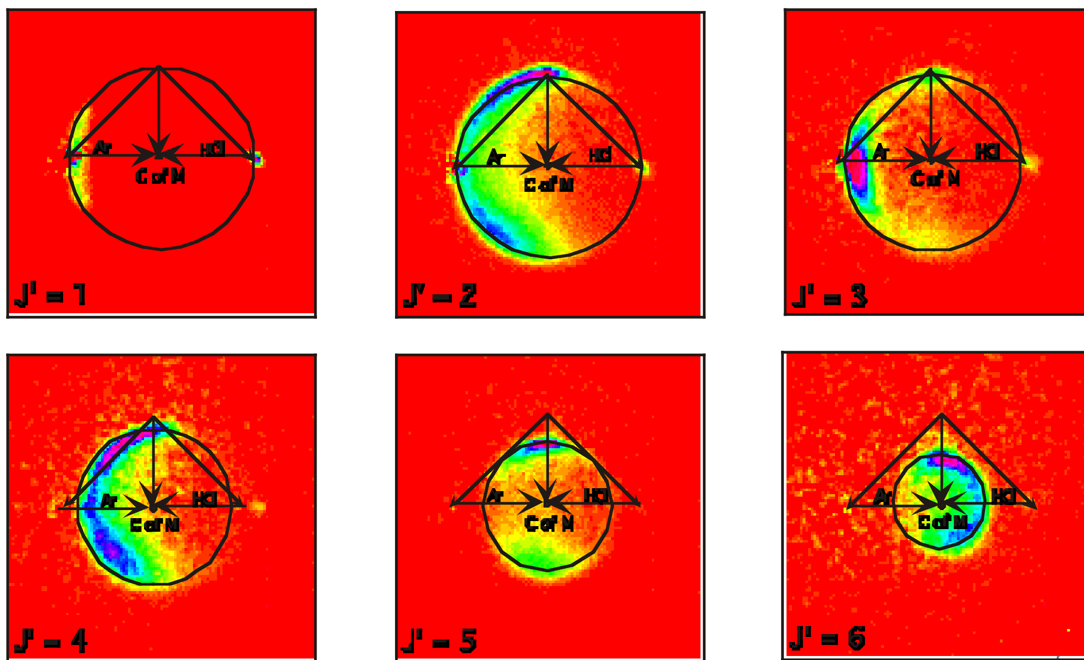

2.42x10¹² W/cm²
0°
1.00x10¹² W/cm²
180°
6.24x10¹¹ W/cm²
532nm Laser Intensity: 2.42x10^12 W/cm^2 (offset 1.85)
532nm Laser Intensity: 1.00x10^12 W/cm^2 (offset 1.80)
532nm Laser Intensity: 6.24x10^11 W/cm^2 (offset 1.50)
532nm Laser Intensity: 2.04x10^11 W/cm^2 (offset 1.35)
532nm Laser Intensity: 1.05x10^11 W/cm^2 (offset 1.30)
532nm Laser Intensity: 6.26x10^10 W/cm^2 (offset 1.05)
Relative Intensity (a.u.)
θ (degrees)
6.26x10¹⁰ W/cm²
1.05x10¹¹ W/cm²
2.04x10¹¹ W/cm²


532 nm
H + H* (n=3)
J'=1
J'=0
H2 (E,F 1Σg+)
potential energy (A.U.)
201.76 nm
201.64 nm
H2 (1Σg)
internuclear distance (A.U.)

Kinematic Cooling of Molecules is a Technique for the Slowing of a Molecule by a Single Collision with an Appropriate Atom.

We first discovered this technique for the creation of a samples of Molecules with milliKelvin temperatures by observing the angular distributions we obtained when doing atom-molecule scattering using Velocity Mapped Ion Imaging to detect the differential cross sections of the products.





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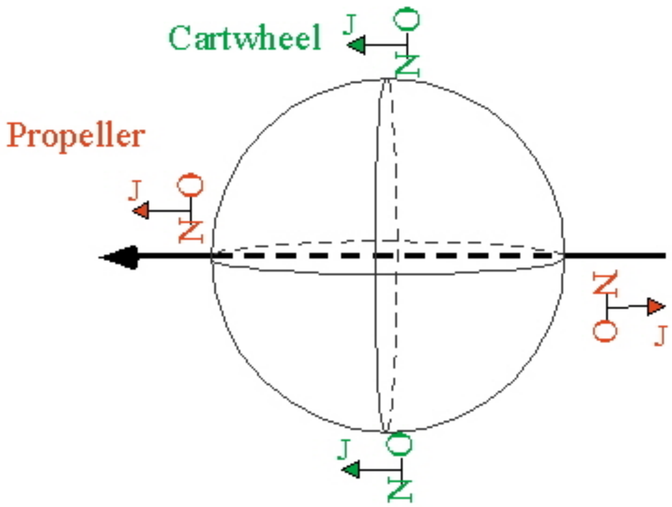
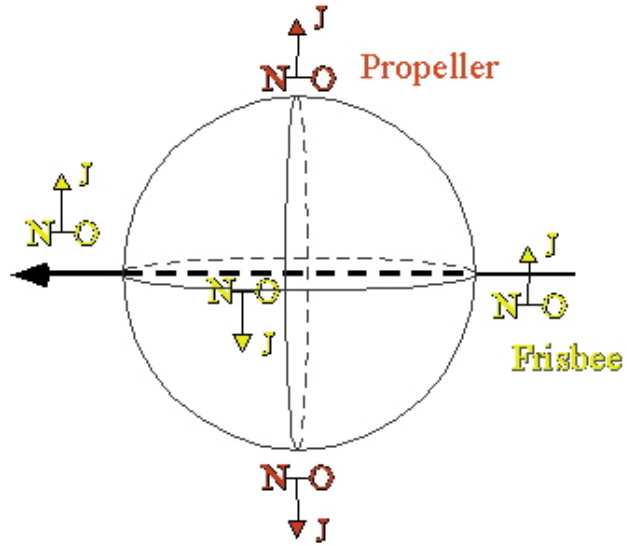
II. Rotational Alignment of $NO(^2X)$ + Ar Collisional Products

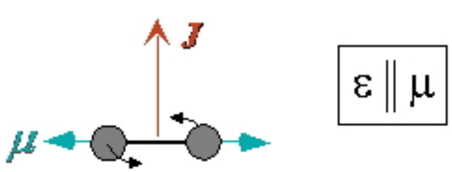




Vertical Polarization Probe Geometry

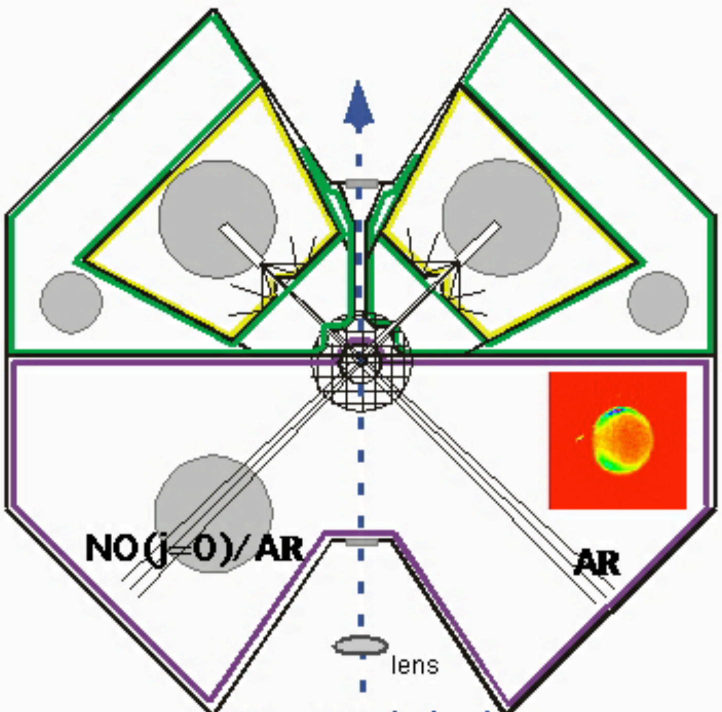
Horizontal Polarization Probe Geometry

R-Branch Spectroscopy ($^2\Sigma \leftarrow {}^2\Pi$)

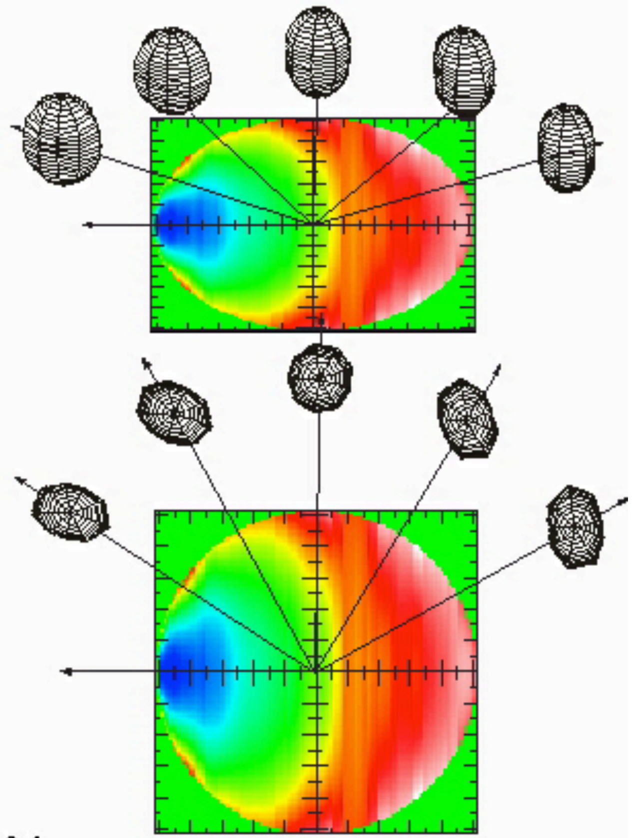


- Probe light is linearly polarized and set to either vertical or horizontal in the laboratory frame.
- Two alternate probe polarizations can discriminate between NO molecules with their *J* vectors aligned in the scattering plane or orthogonal to the plane.

The alignment of the J vector of the NO can be measured as well as its scattering angle (DCS).



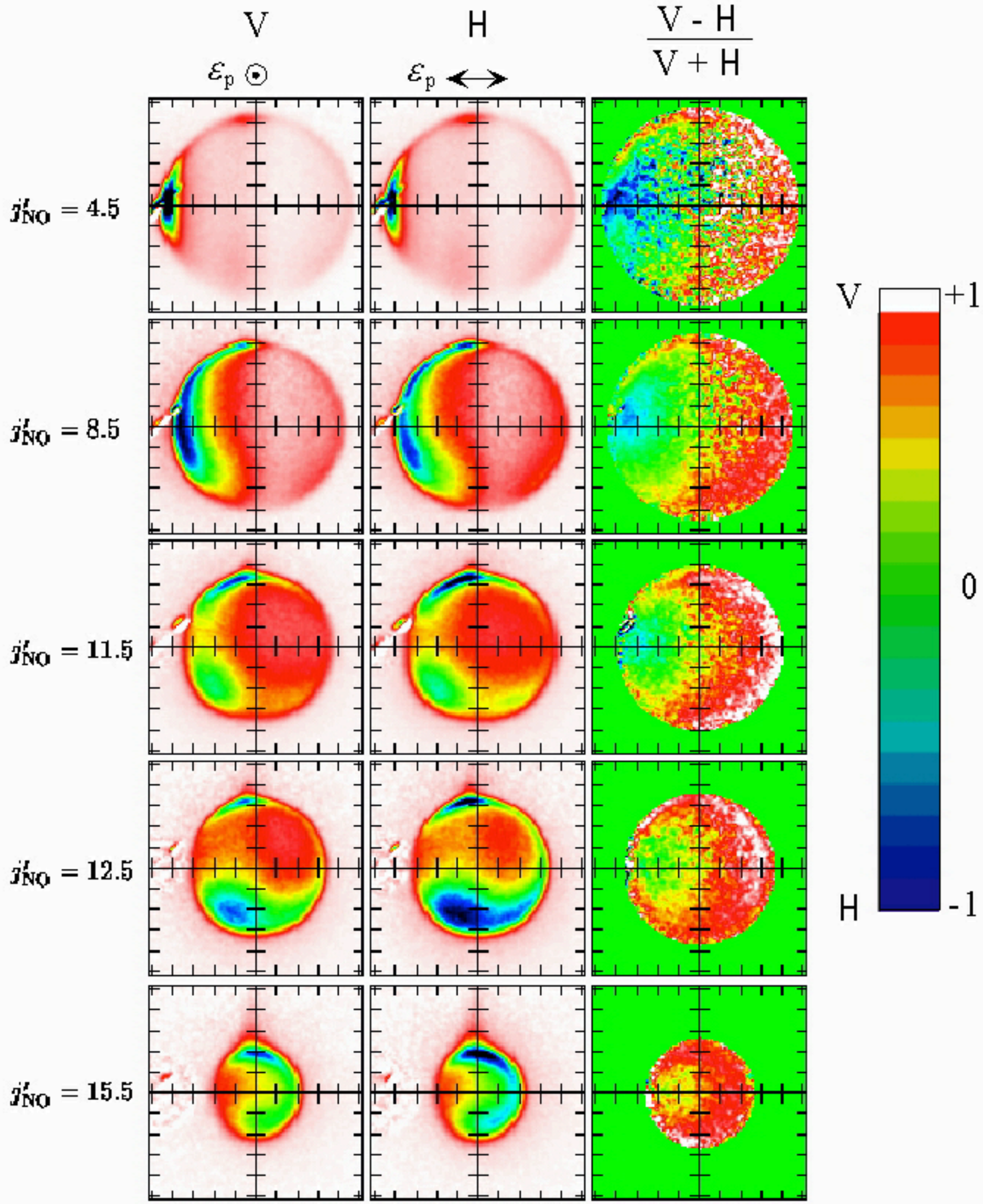
- Obloids represent the J-distribution as a function of the final scattering velocity.
- Scattering products are dominantly aligned orthogonal to the scattering plane - classical, hard ellipse model.



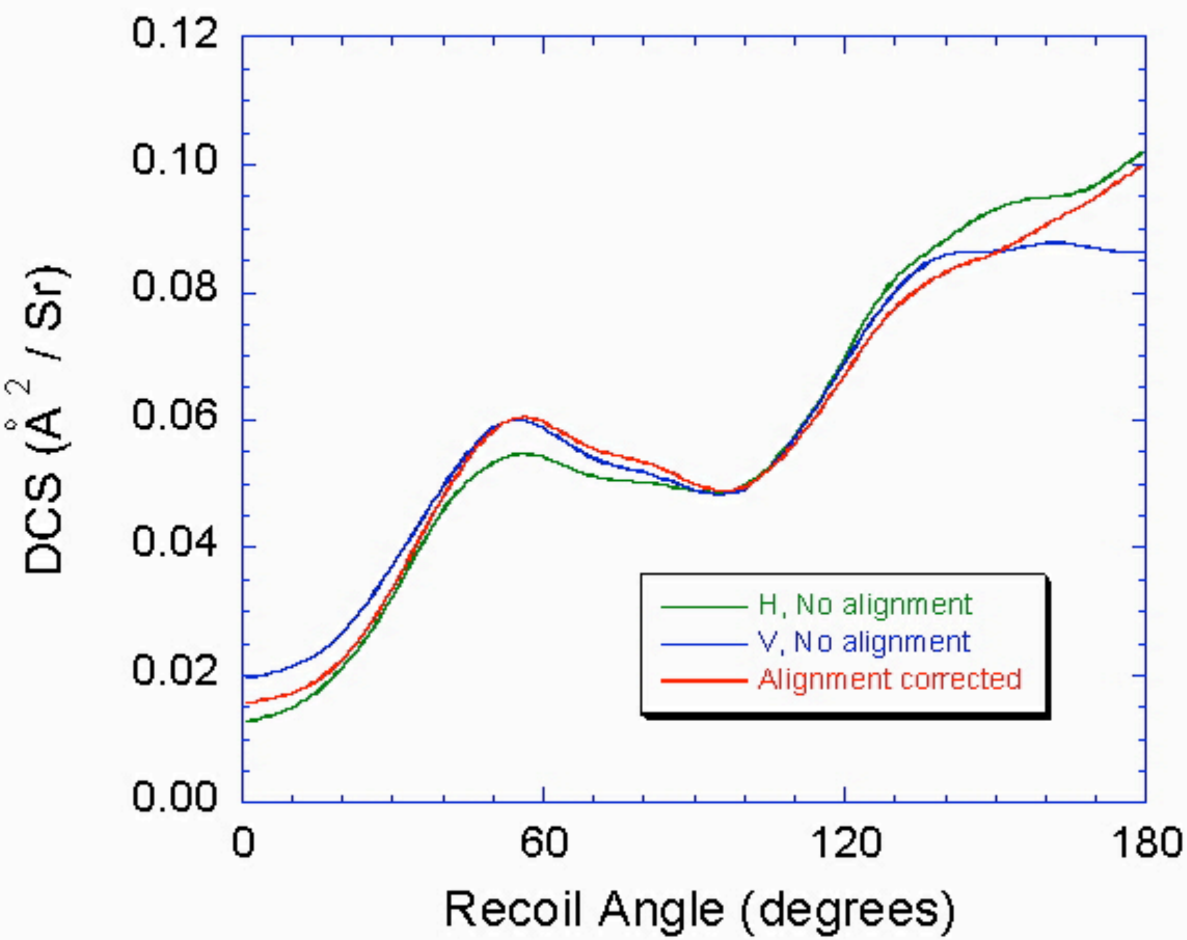
R_{21} (J=12.5)
(H-V)/(H+V)

NO/AR Images
V and H images

- 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

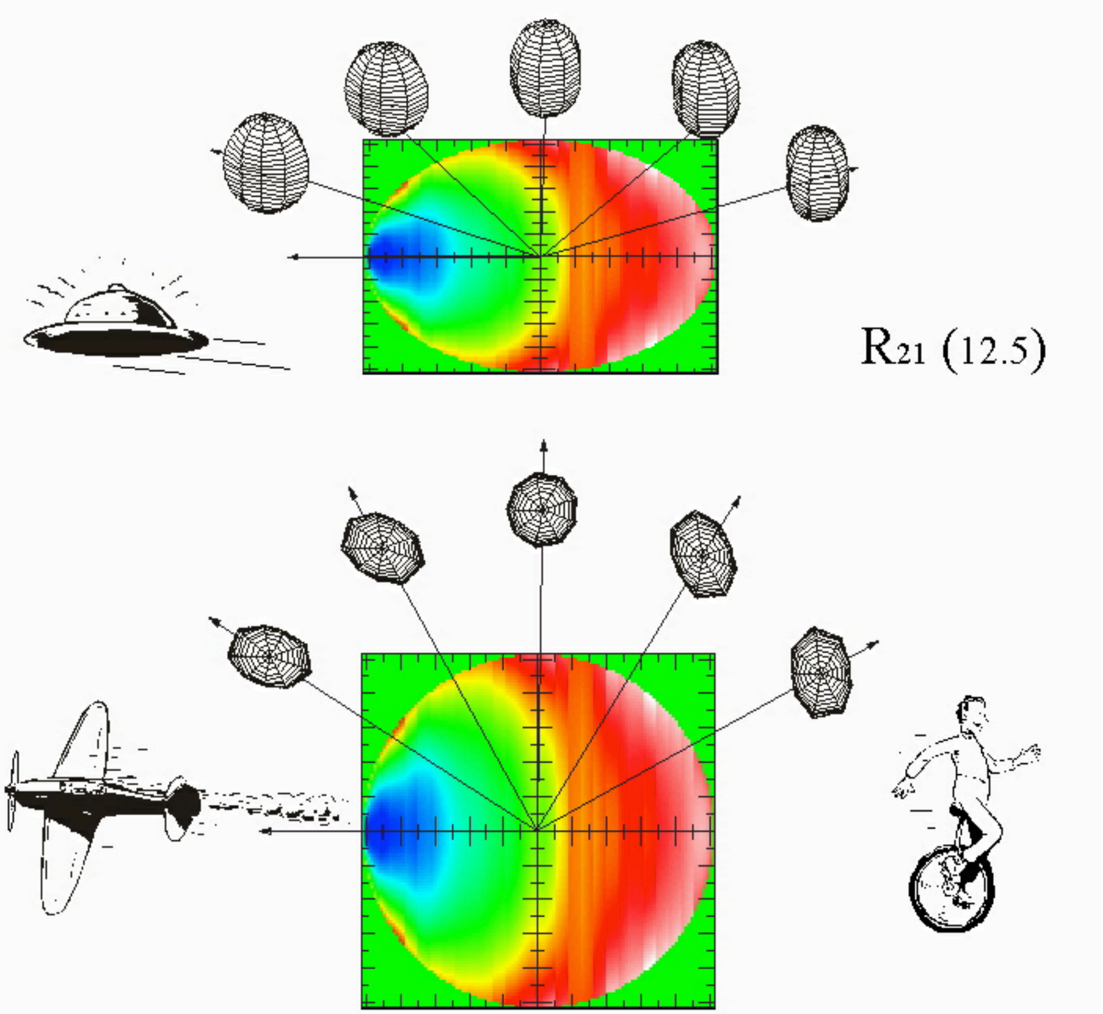


Surprisingly (to me) the alignment does not effect the determination of the DCS except at 0 and 180 degrees



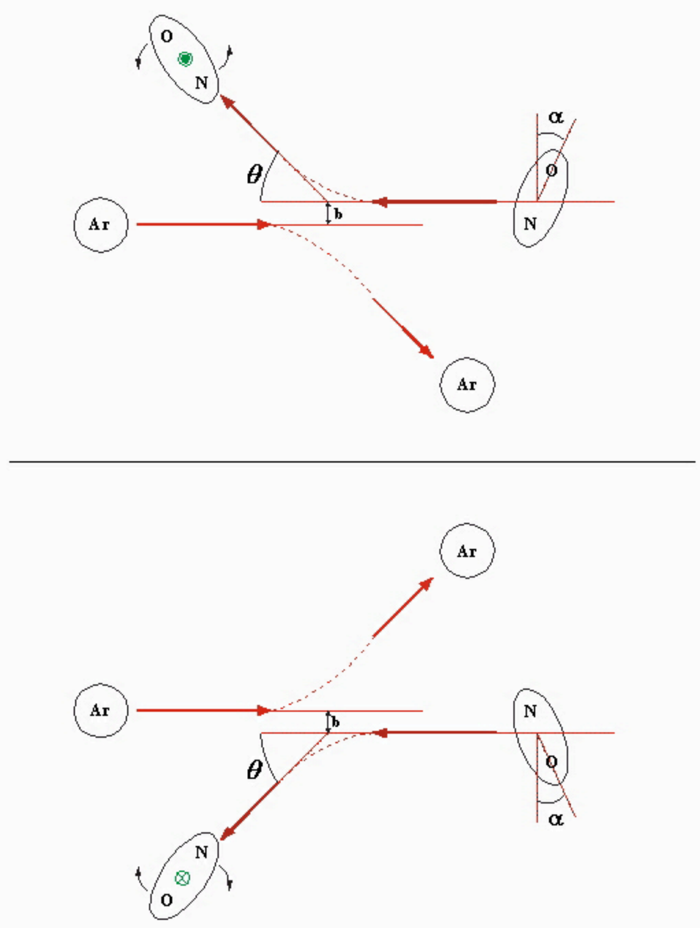
The alignment moments (when turned into pictures!) provide physical insight into the scattering process.

- 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

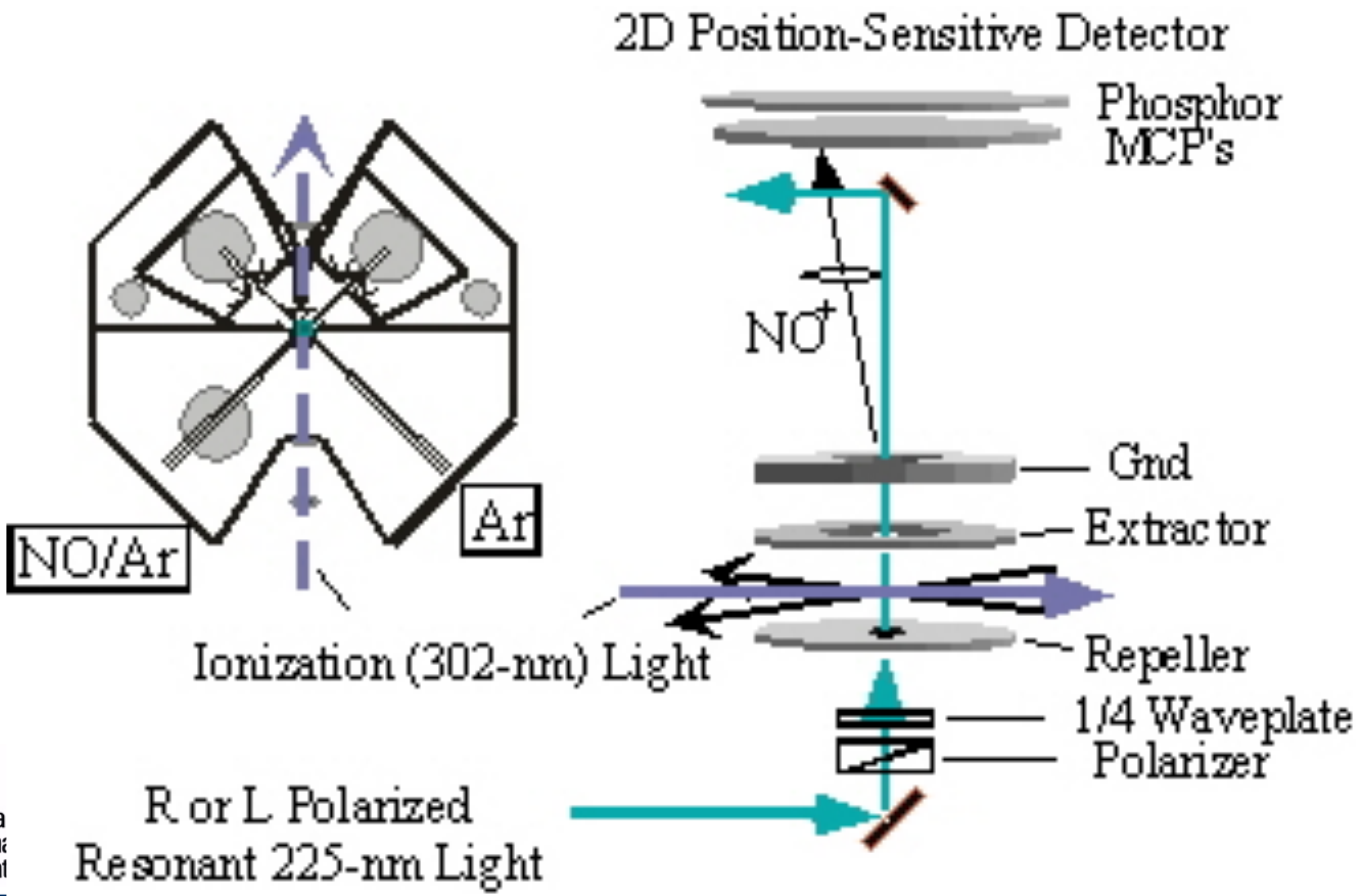


Orientation of the J vector refers to the absolute sense of rotation, clockwise or counter clockwise.

- What do you predict?
- Should there be a preferred sense of rotation for NO scattering at a certain angle when it collides with an atom?

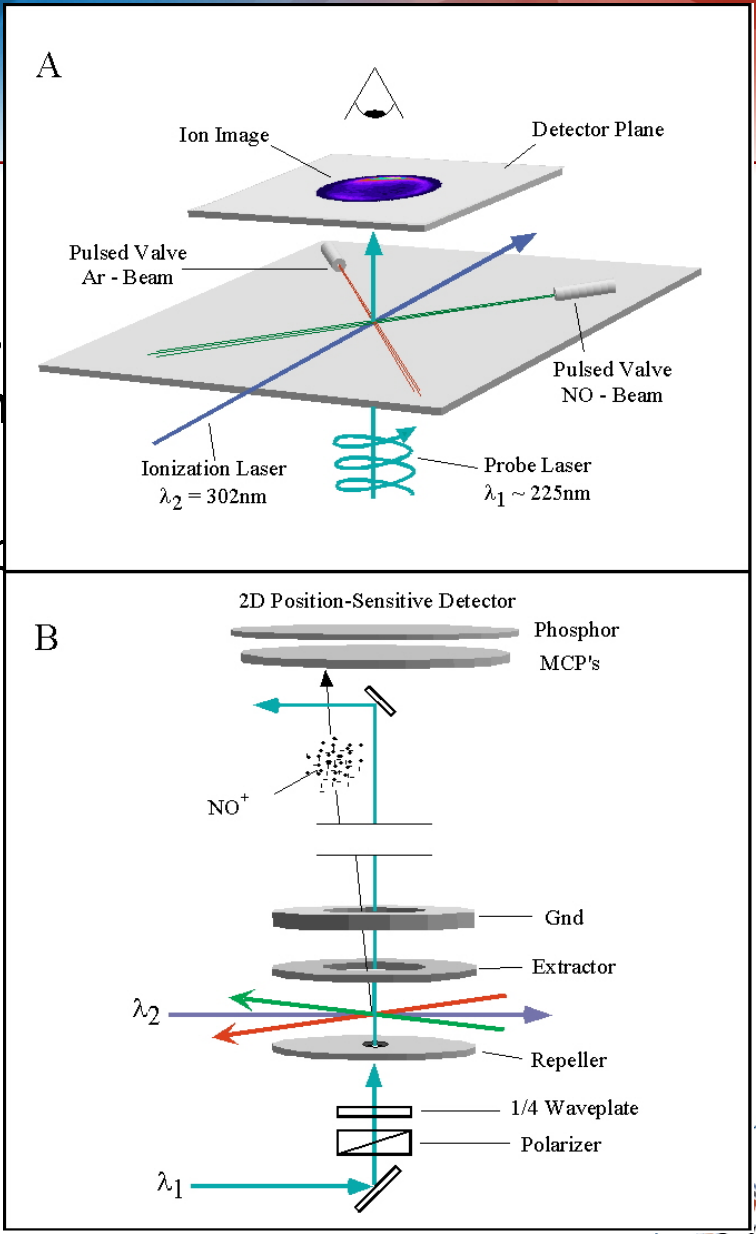


In order to determine the orientation of the NO we will use circularly polarized light and shine it from below the scattering plane.

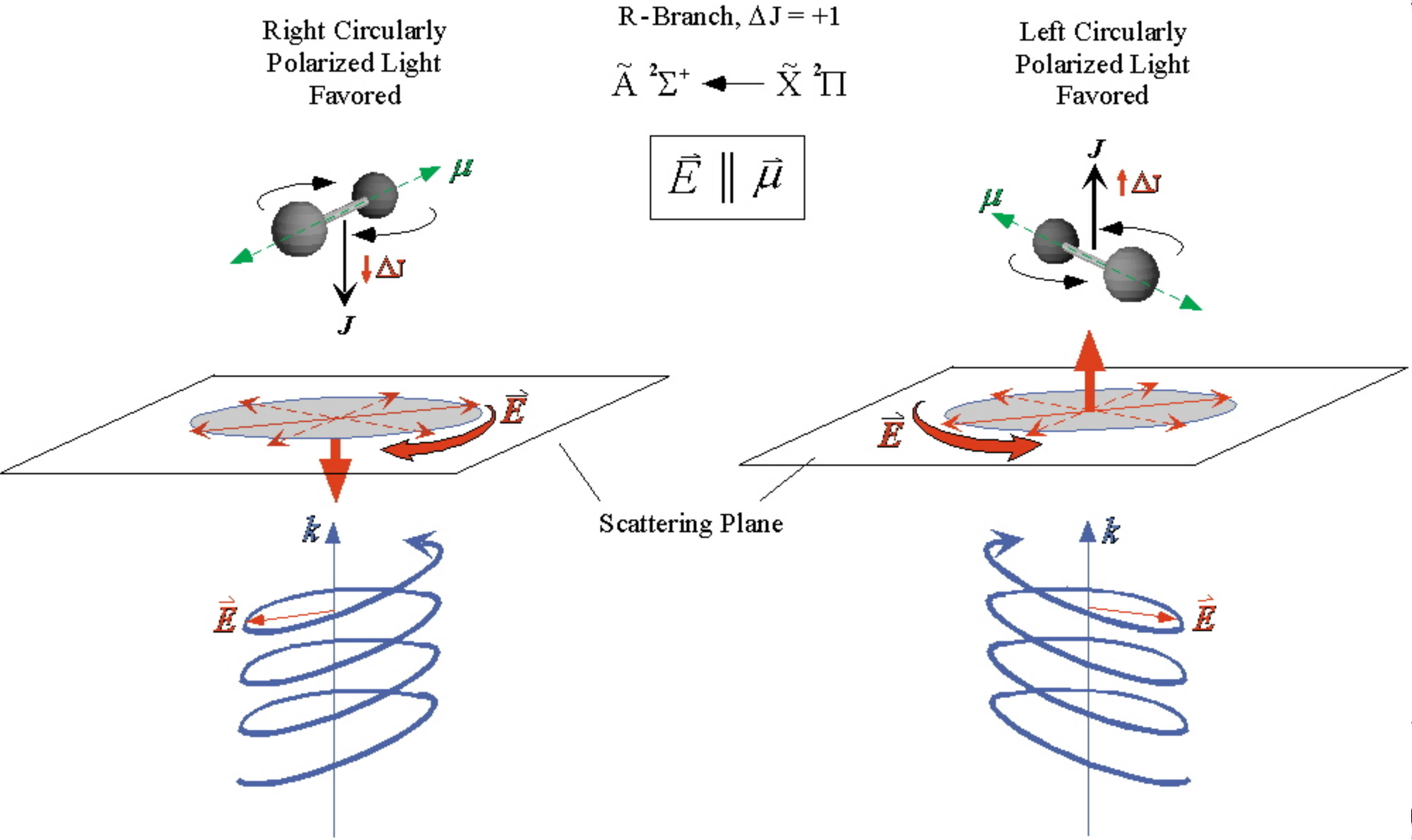


The apparatus for measuring orientation of molecules.

- This apparatus geometry allows orientation as a function of quan angle.
- The results can be directly comp of the scattering distribution.

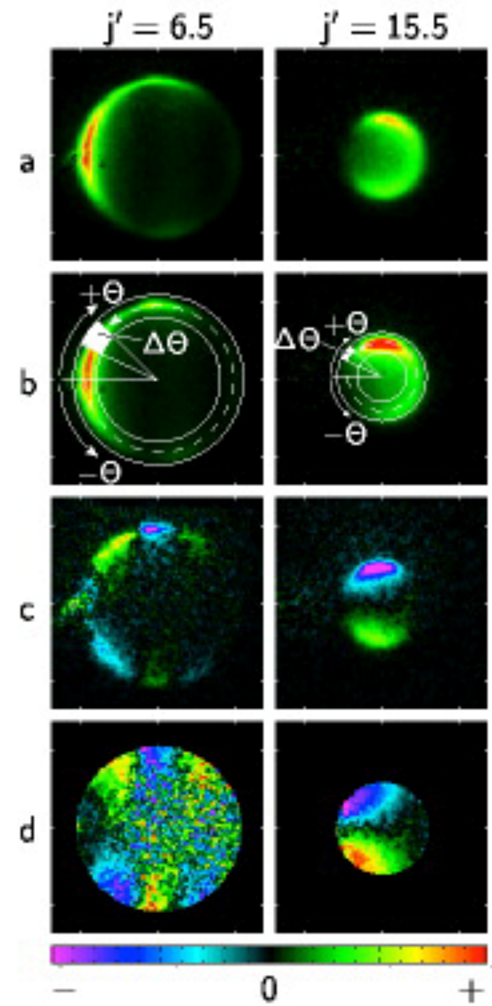


The Absolute Sense of Rotation of the NO Collision Products Can Be Probed Using Circularly Polarized Light

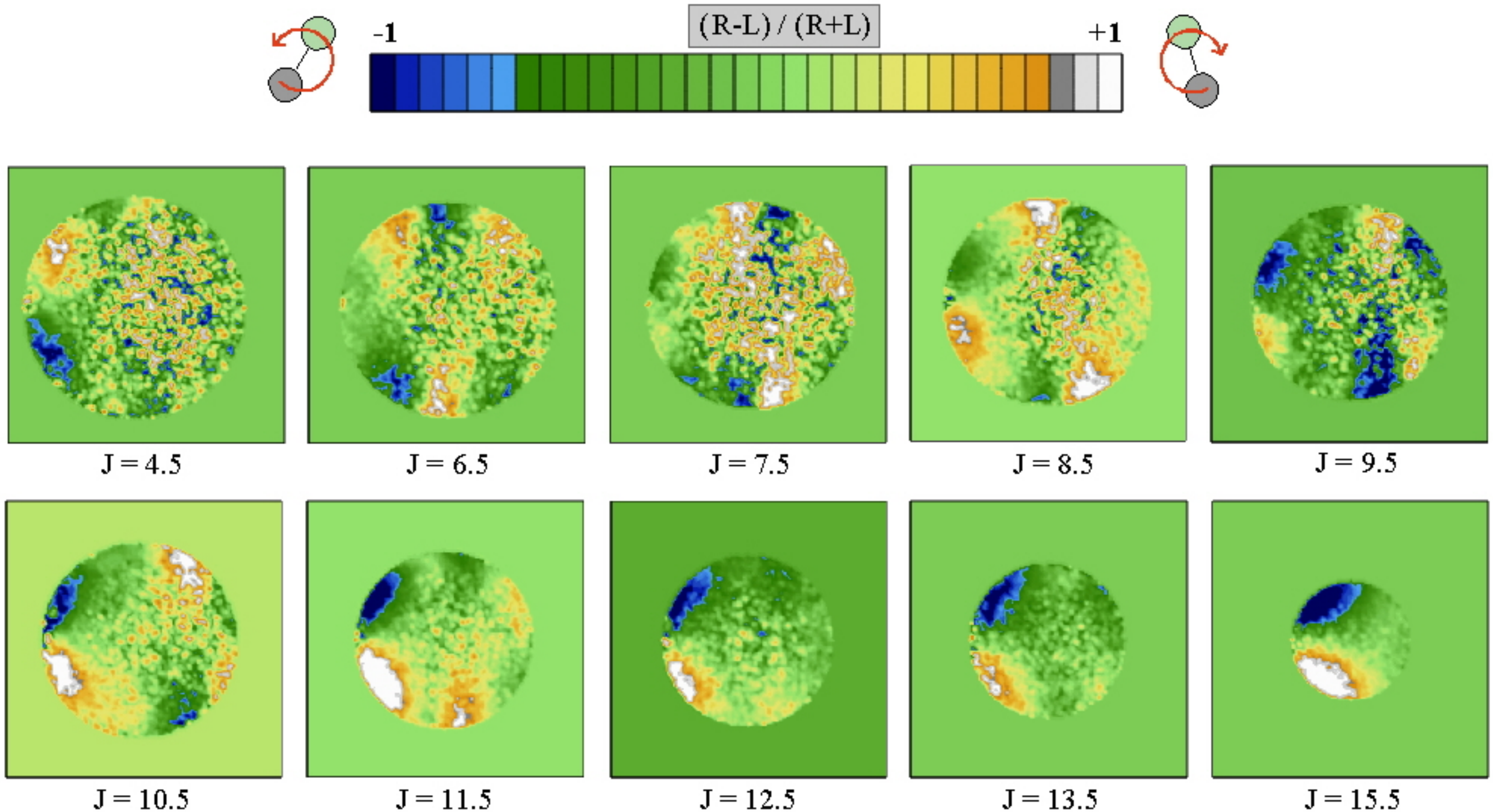


The normalized difference image is a direct measure of the orientation.

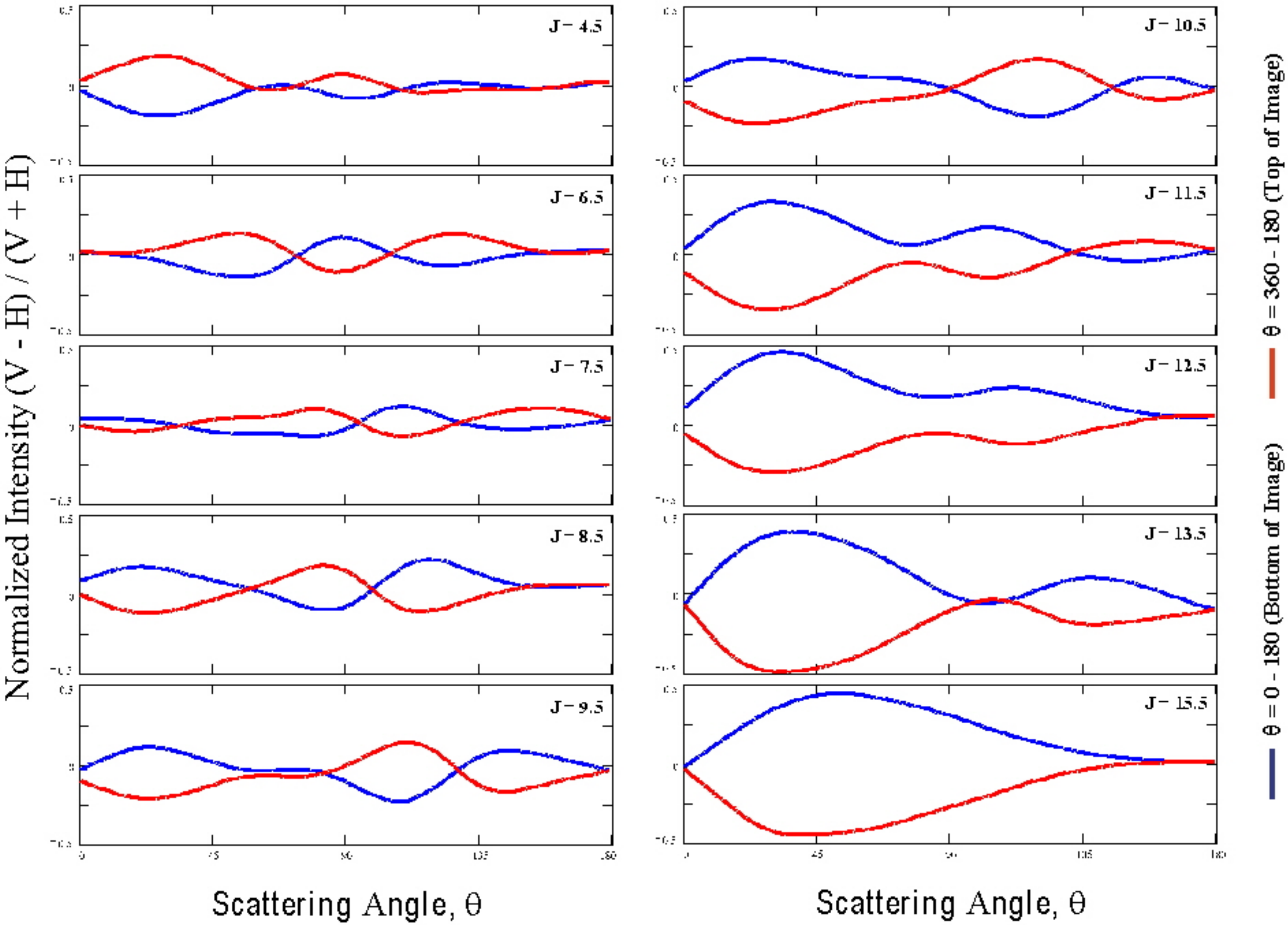
- A) Right circularly polarized Image
- B) Left Circularly polarized Image
- C) difference image A-B
- D) Normalized difference image (A-B).



Normalized Difference Images for Selected Rotational States of NO + Ar Collision Products R$_{21}$ Branch

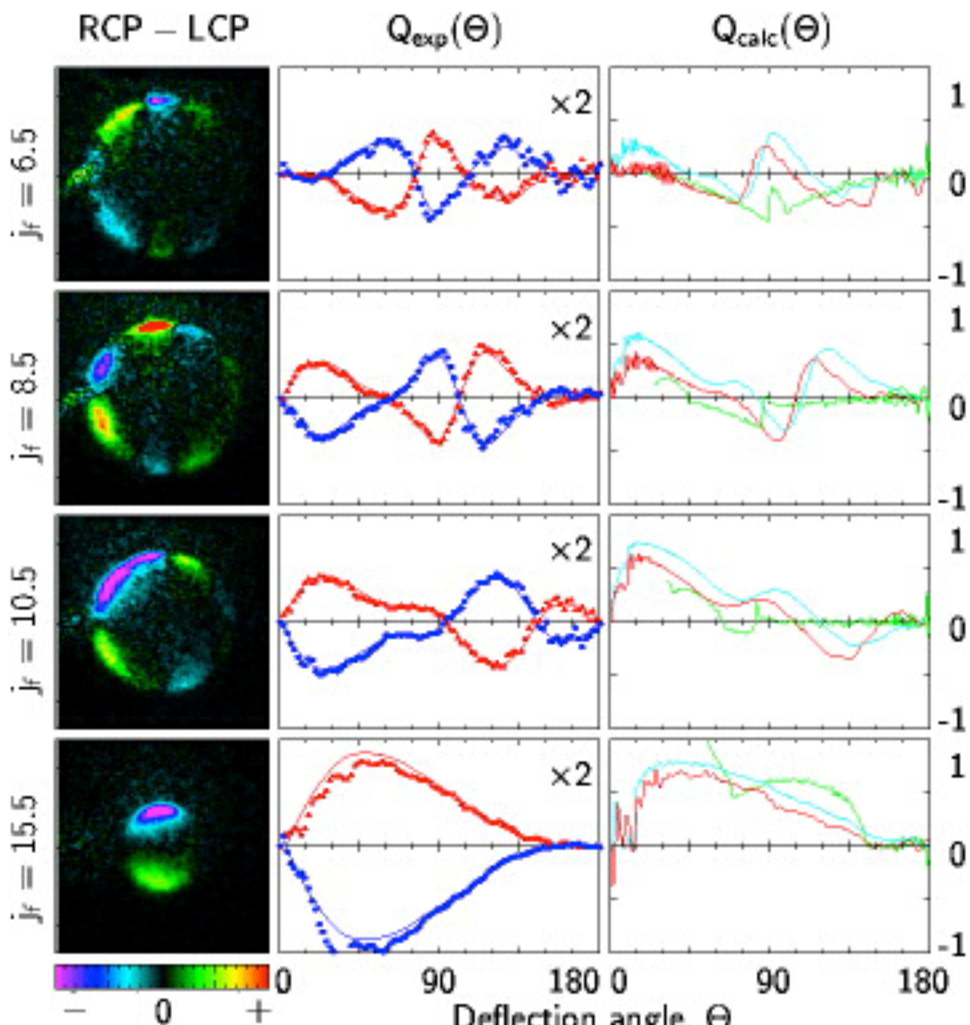


The Normalized Orientation-Dependent J-Changing DCS's



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.



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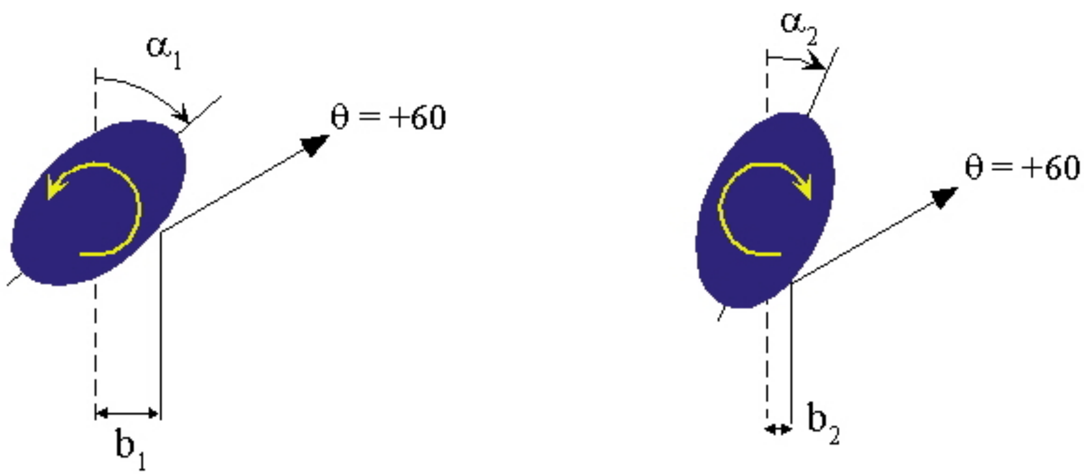
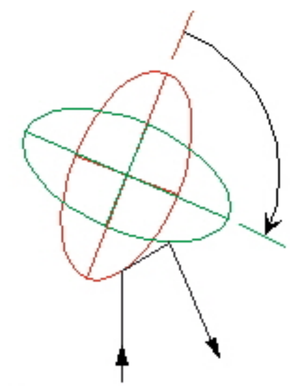
2D Hard Ellipse Calculations Show That There Should Be No Orientation Effect Without Invoking Multiple Collisions

- There are equal numbers of orientation / impact parameter combinations giving CW as CCW rotation for any given deflection angle, θ. The net result is cancellation of any measurable rotational orientation.





- However, for high Δj collisions, some impact parameters are more likely to suffer secondary impacts - the chattering effect.

- Chattering eliminates the net balance between the number of trajectories producing CW and CCW motion for any given deflection angle

Semi-Classical Interferences May Account for the Modulation in the Orientation-Dependent DCS's

Two sources of interference

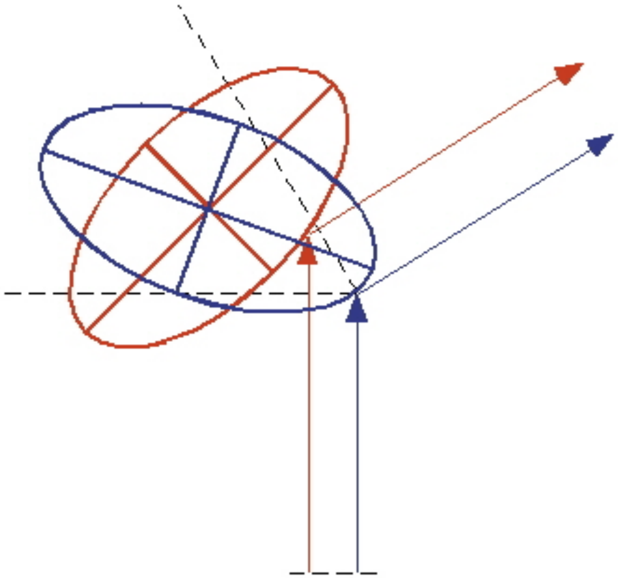
- Interference due to phase-additive differences in the path lengths of the DeBroglie plane waves for red and blue trajectories.

$$1_{\text{deBroglie}} = \frac{h}{|\vec{p}|}$$

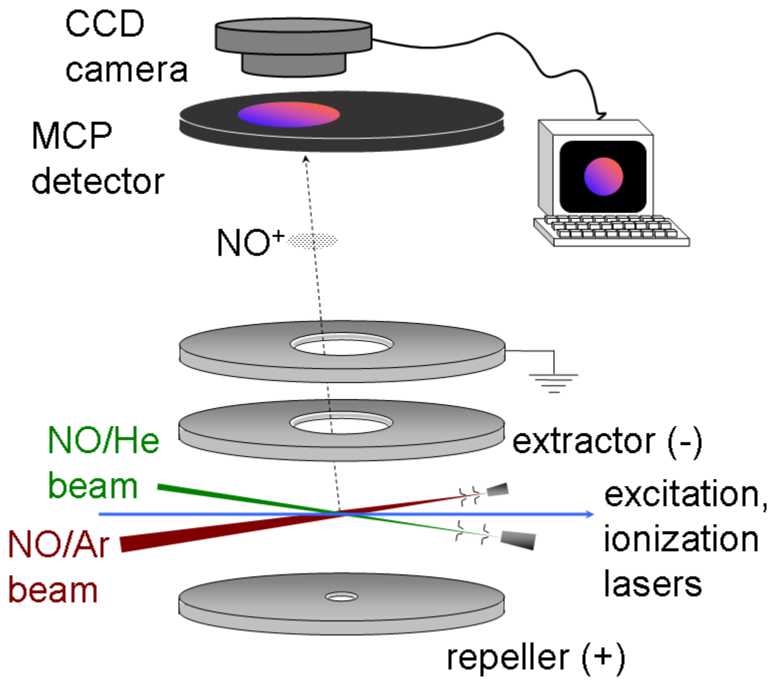
- Interference due to phase-additive differences in the rotational path of the rotor for the two trajectories.

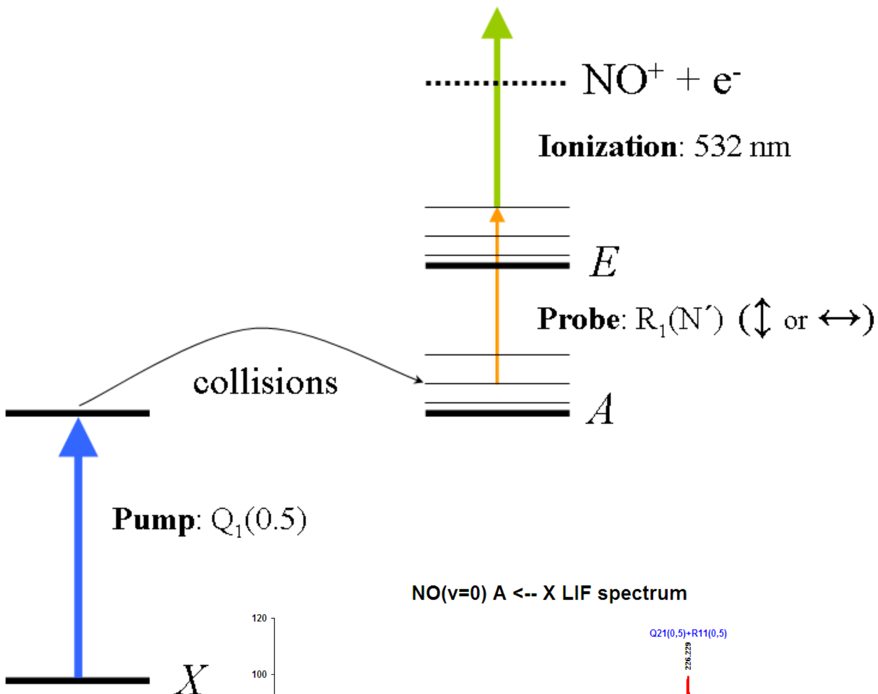
$$\Psi(\alpha) = \frac{1}{\sqrt{2\pi}} e^{(-i\, j\, a)}$$

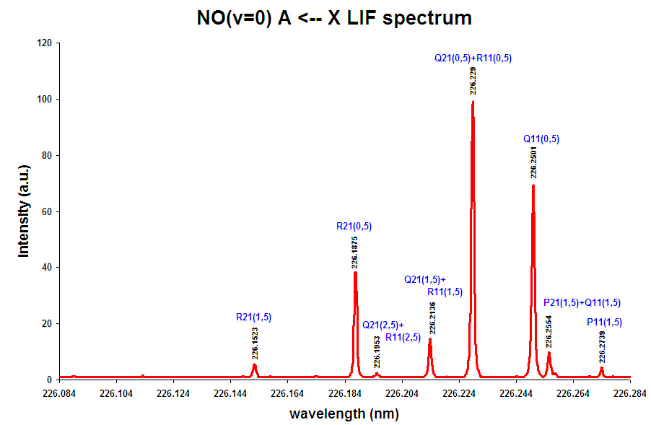
$$\text{Intensity Modulation} \sim \cos\left[j(a_B - a_R)\right]$$



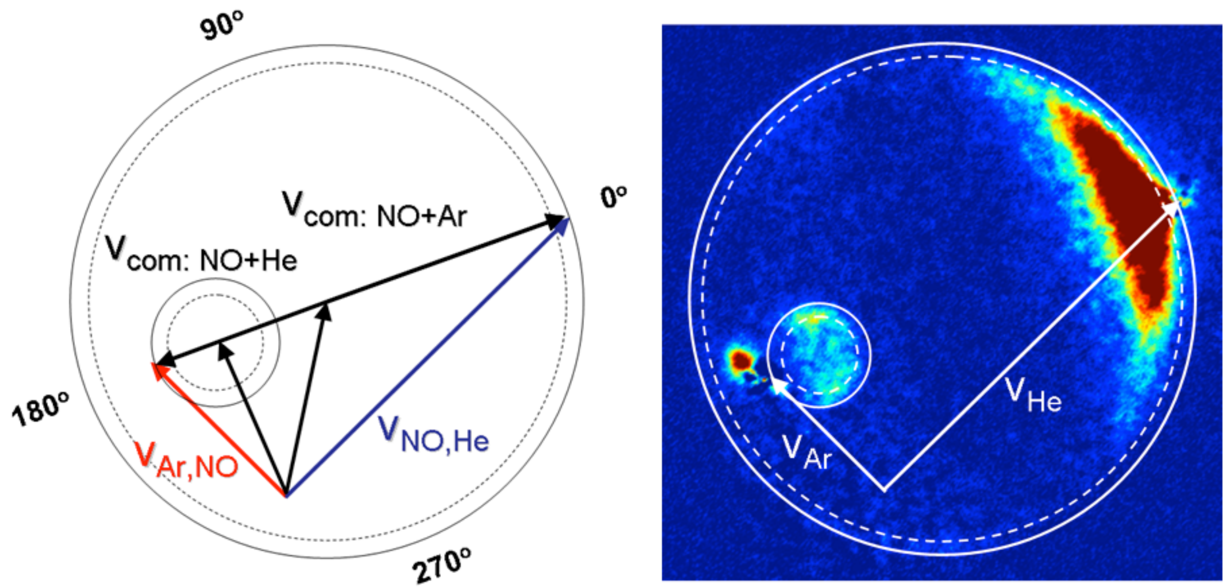
Apparatus and Detection Mode for measuring DCS and Alignment of Electronically Excited State Molecules.







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



(a) (b)

Three dimensional scattering of unequal mass particles capable of
Also constrained by conservation of energy and momentum, The N

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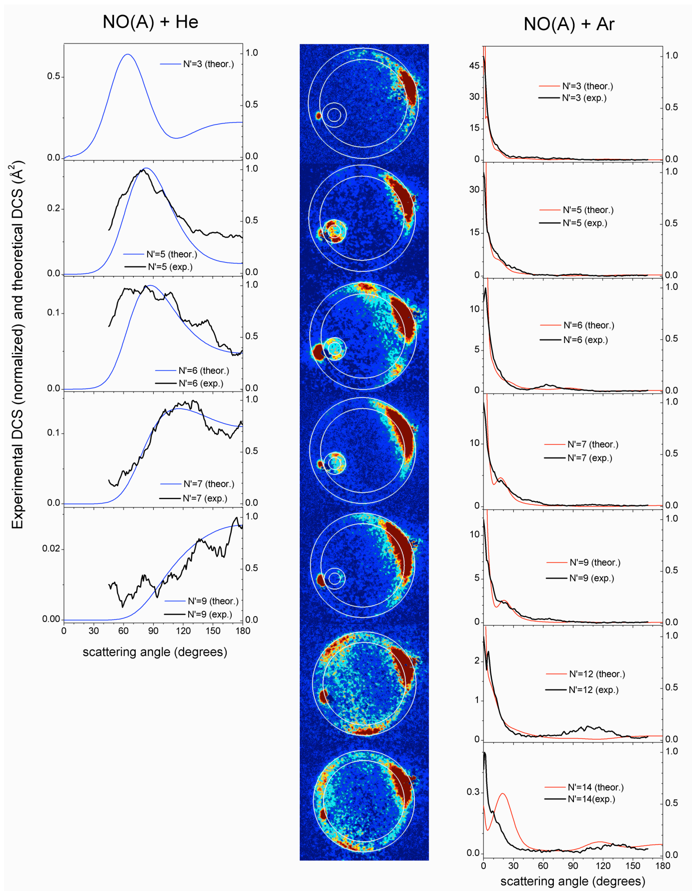
Background Subtracted Scattering Data and the Differential Cross Sections Obtained from Data.

NO scattering from He | **NO scattering from Ar**



NO scattering from He	NO scattering from Ar
N=3	N=3
N=5	N=5
N=6	N=6
N=7	N=7
N=9	N=9
	N=12
	N=14

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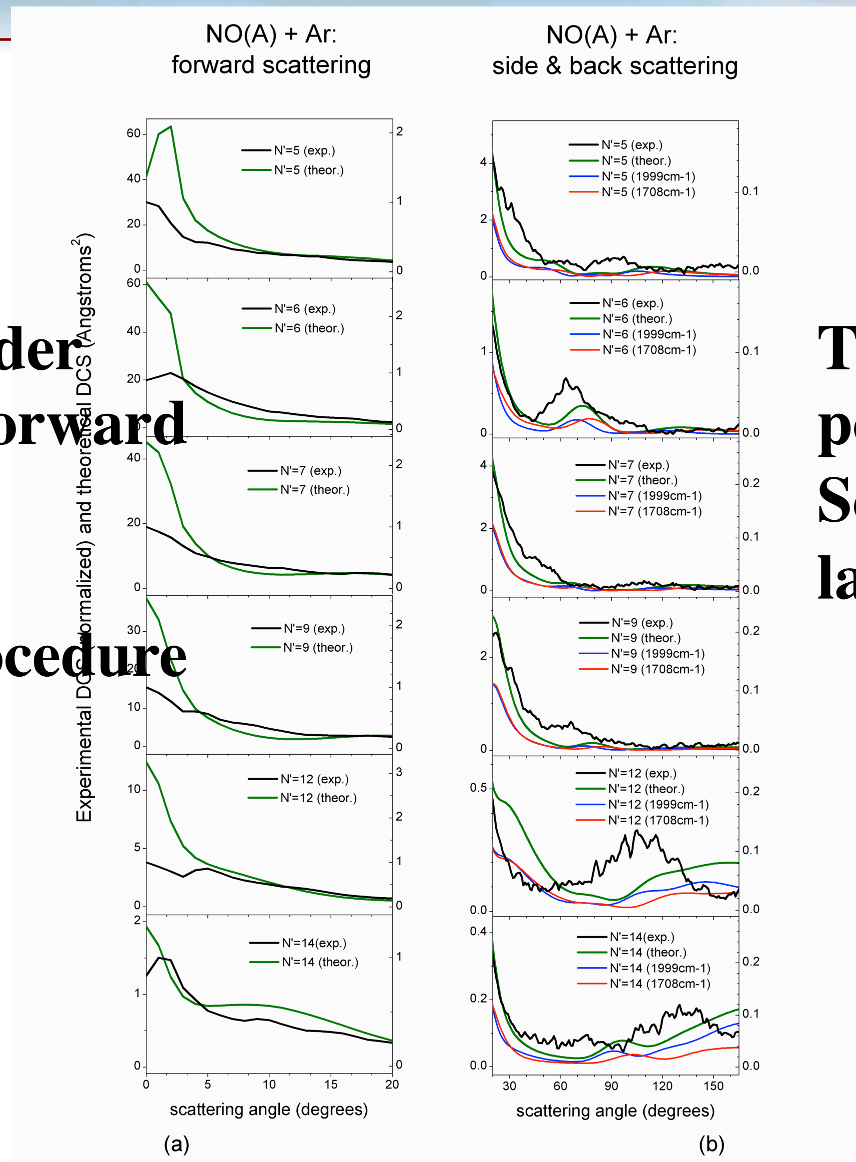
Expanded view of Differential Cross Sections

Experiment under Estimates the forward scattering due background subtraction procedure



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

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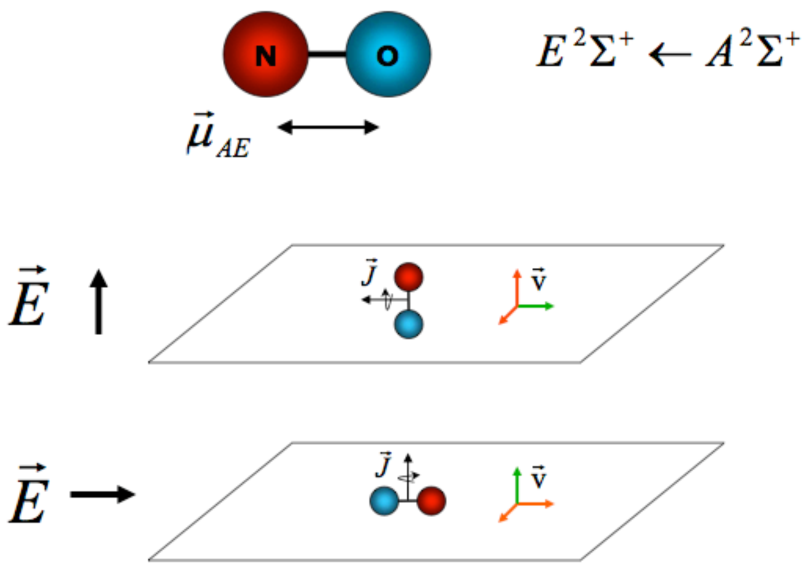
Is the Scattering is Polarization Dependent? Can we Measure Alignment of Electronically Excited State Scattering?



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.

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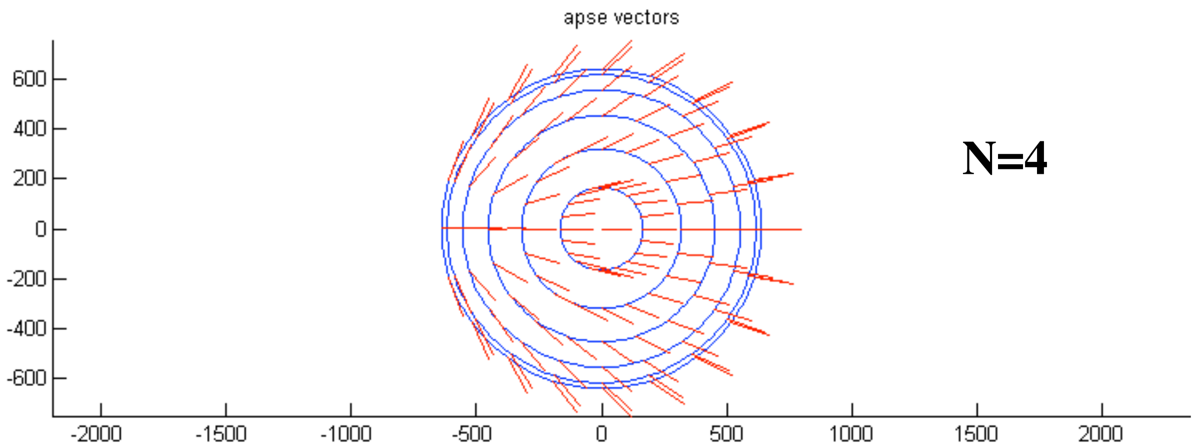
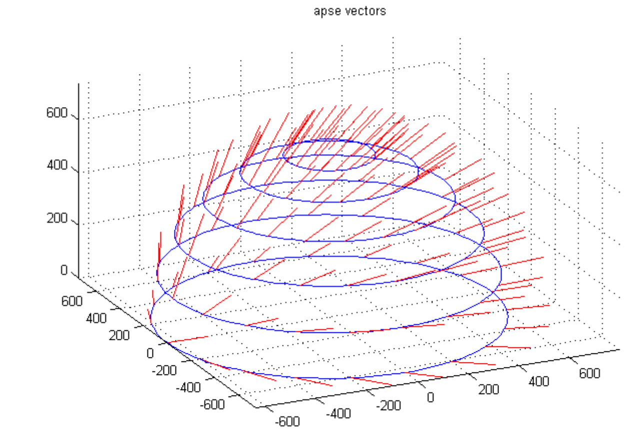
Classical 'Apse' Model: Calculate Apse Vector for Every Scattering Angle and Calculate Projection of J on Scattering Axis.



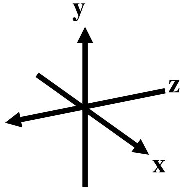
N=4

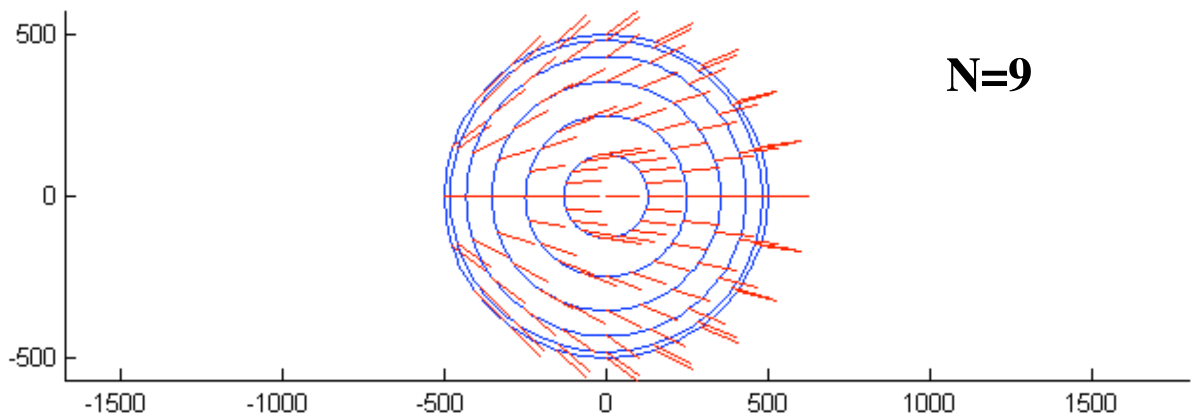


z-axis defined as COM $v_{initial}$

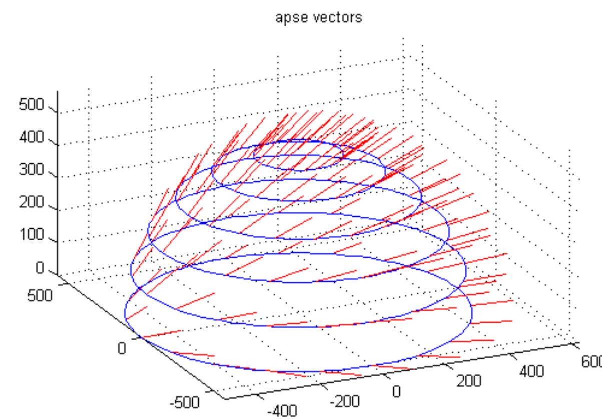
x-axis is laser vector

y-axis is m/z detection





N=9



Alignment Moments: Calculations

- Quantum scattering (QS) calculations are performed with HIBRIDON on a calculated NO(A)-Ne potential energy surface, these yield a collision energy- and rotational state-specific DCS and collisional alignment propensity.
- The classical 'Apse' model is also used to model the collisional alignment.
- The alignment models yield a vector distribution in the molecular collision frame which is captured by the $A_{0+}^{(2)COL}$ and the $A_{2+}^{(2)COL}$ moments. The J_z^{COL}, J_y^{COL}, and J_x^{COL} rotational vectors define the alignment moments as follows:

$$A_{0+}^{(2)COL} = 3^*J_z - 1 \quad \textit{and} \quad A_{2+}^{(2)COL} = J_x - J_y$$

where the z-axis is defined by the COM collision vector.

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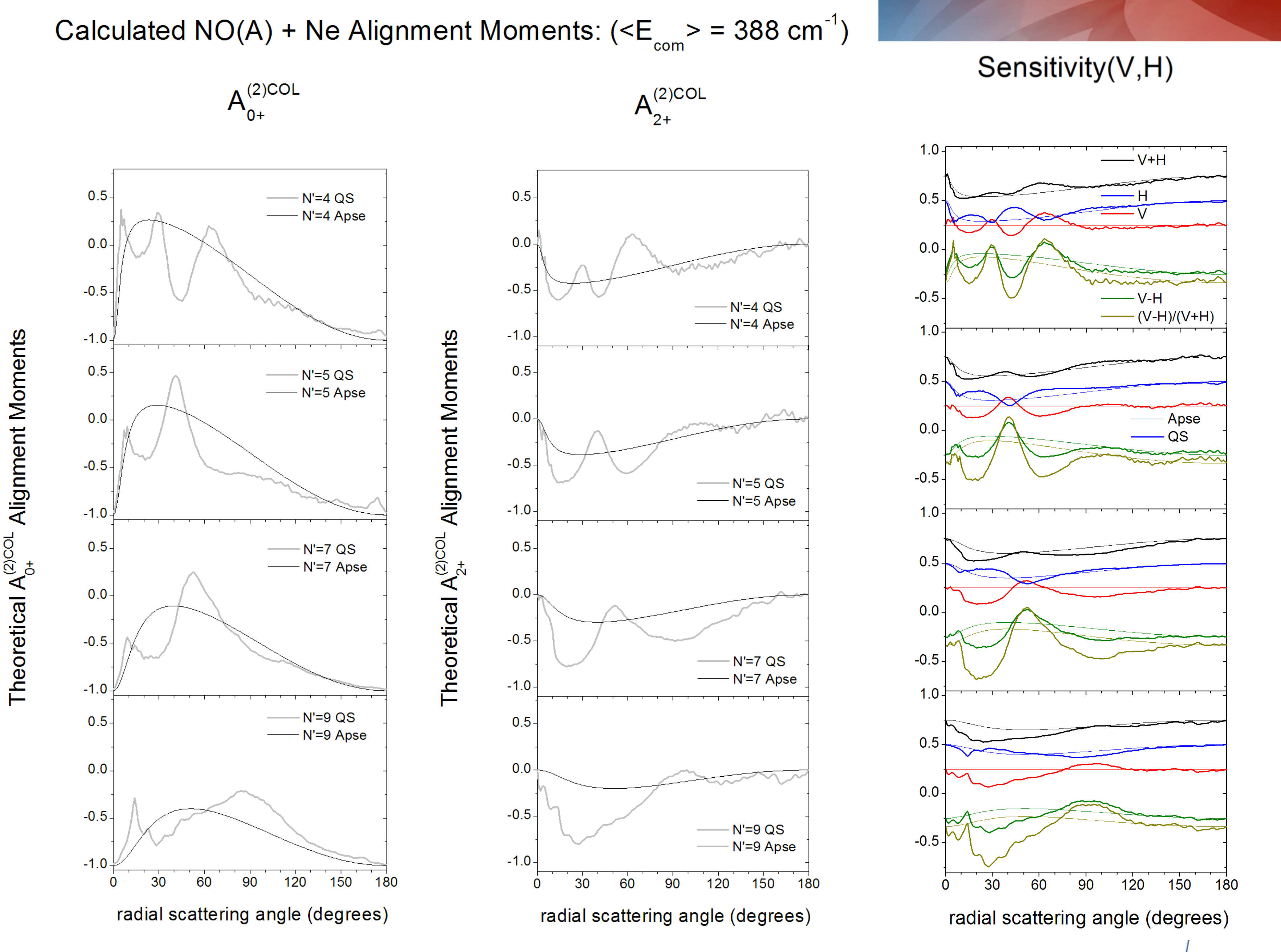
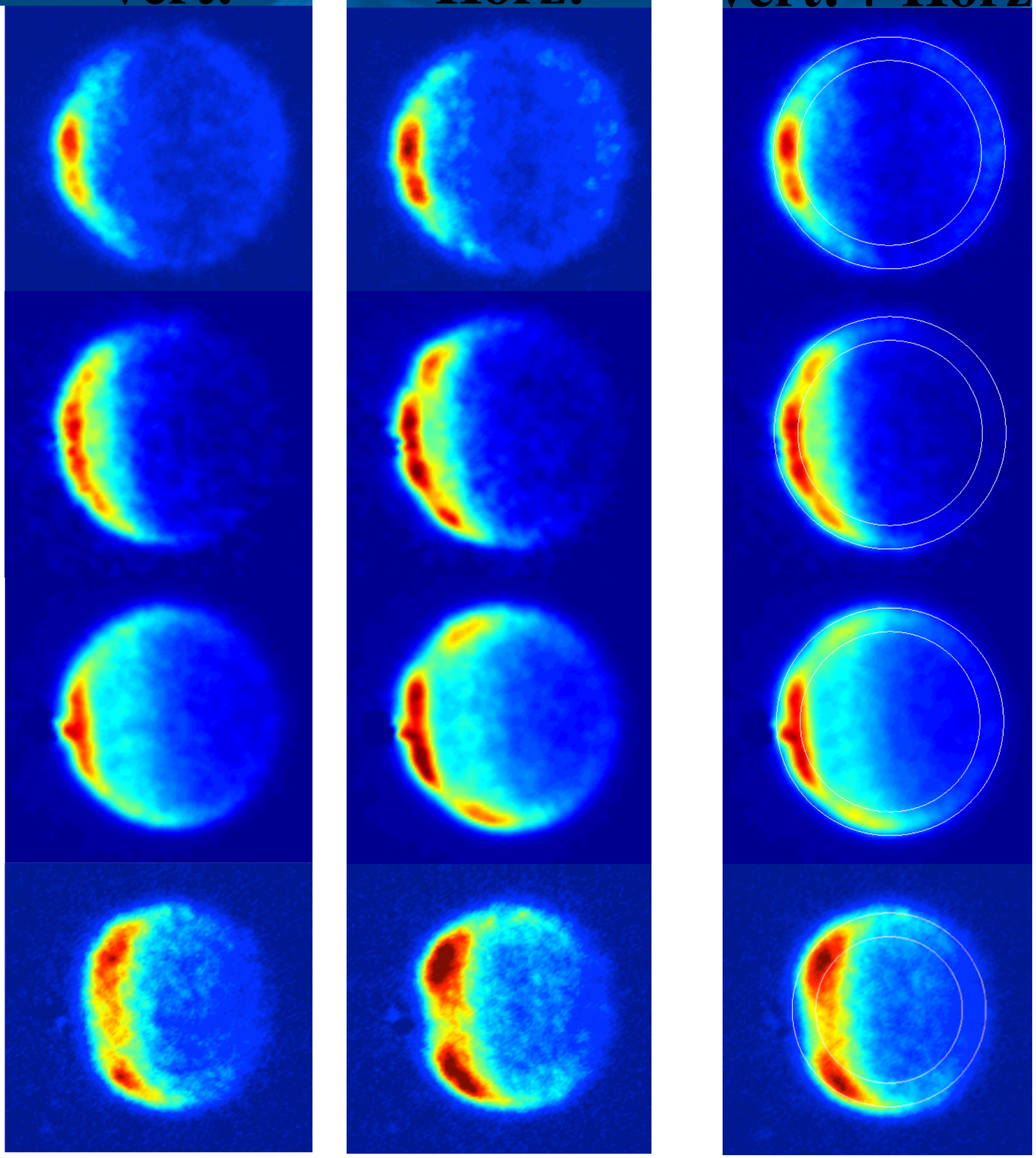
Apse and Calculated Alignment Moments are Similar in

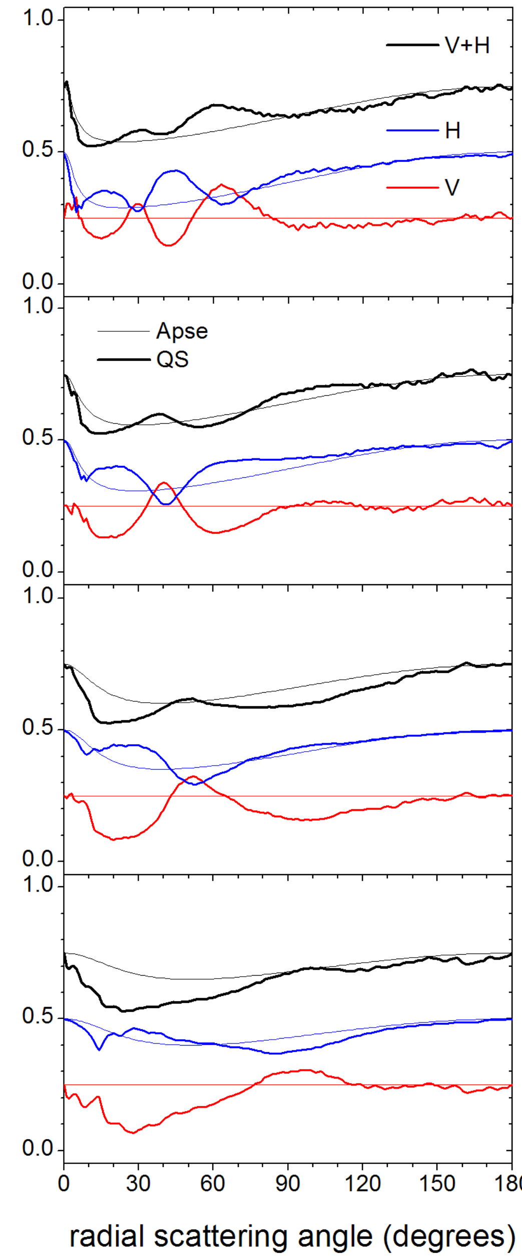


Vert.	Horz.	Vert. + Horz

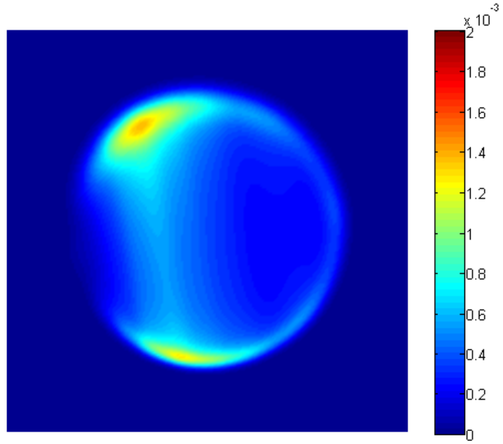


DCS_{EXP}*(V)	DCS_{EXP}*(H)	DCS_{EXP}*(V+H)

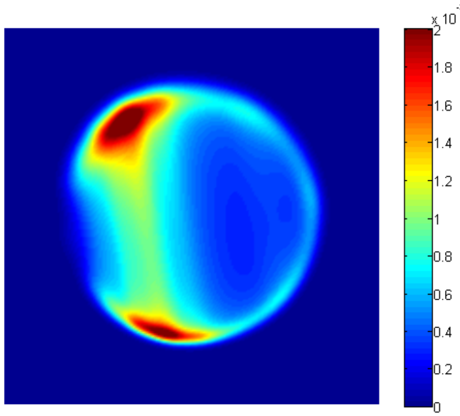
Sensitivity(V,H)



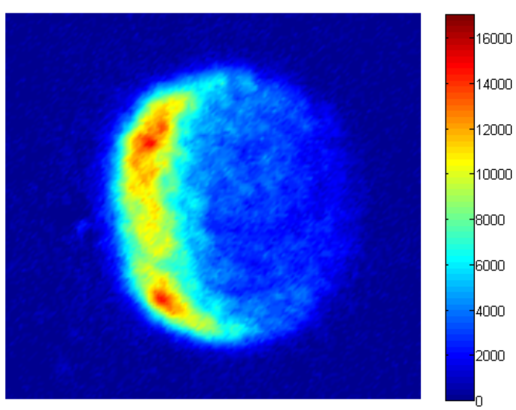
Images of NO (N’ = 9) for Vertical and Horizontal polarization of Ionization beams



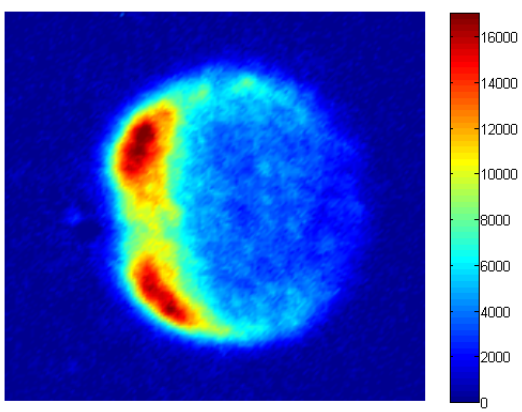
Exact model: V



Exact Model: H



Experiment: V



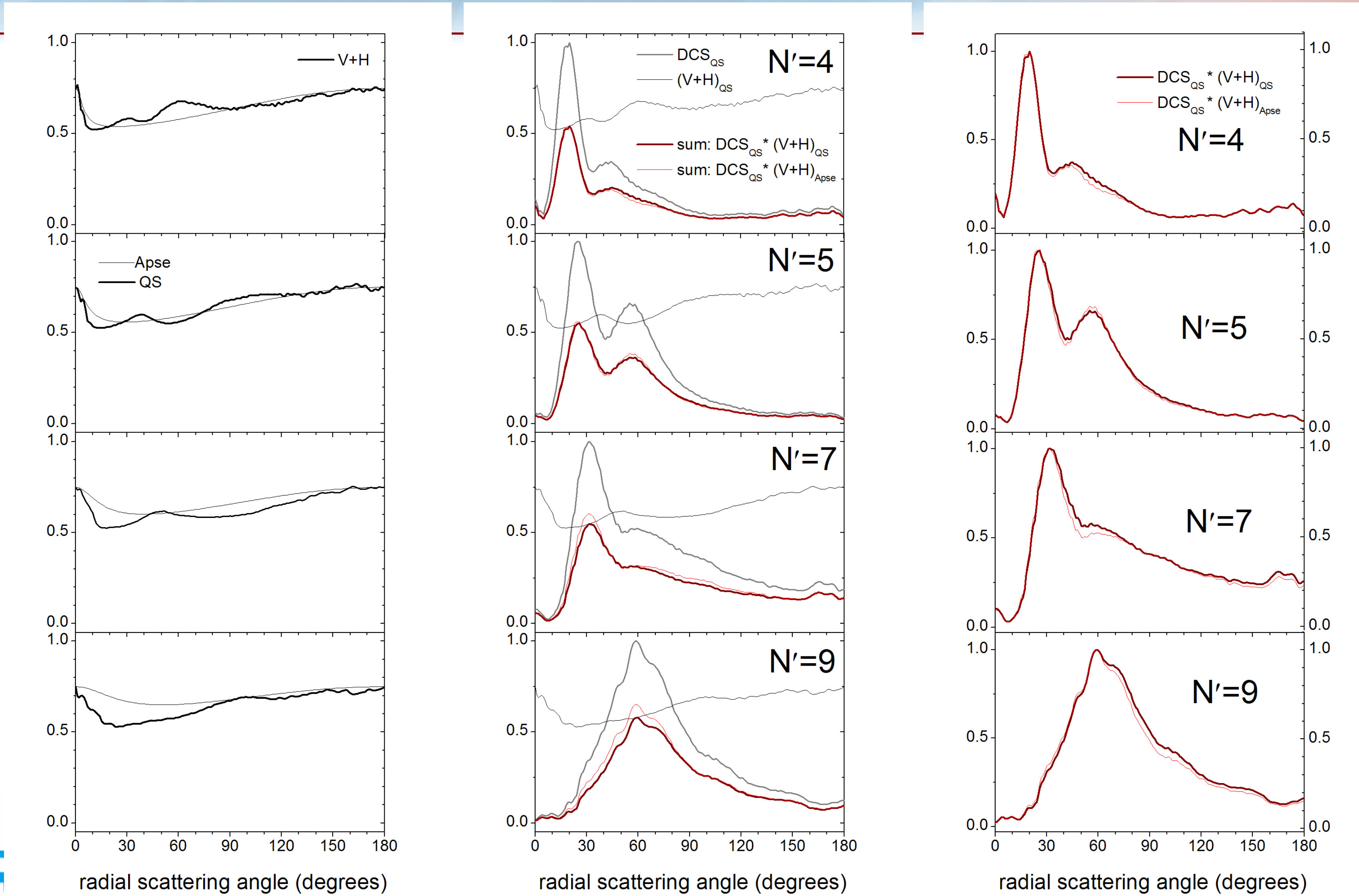
Experiment: H

*Comparison of the **angular intensity of a summed theoretical** (vertical + horizontal) image with the angular intensity from a summed experimental image*

Sensitivity(V,H)

DCS,A_0,A_2 → sum

Modeled sum



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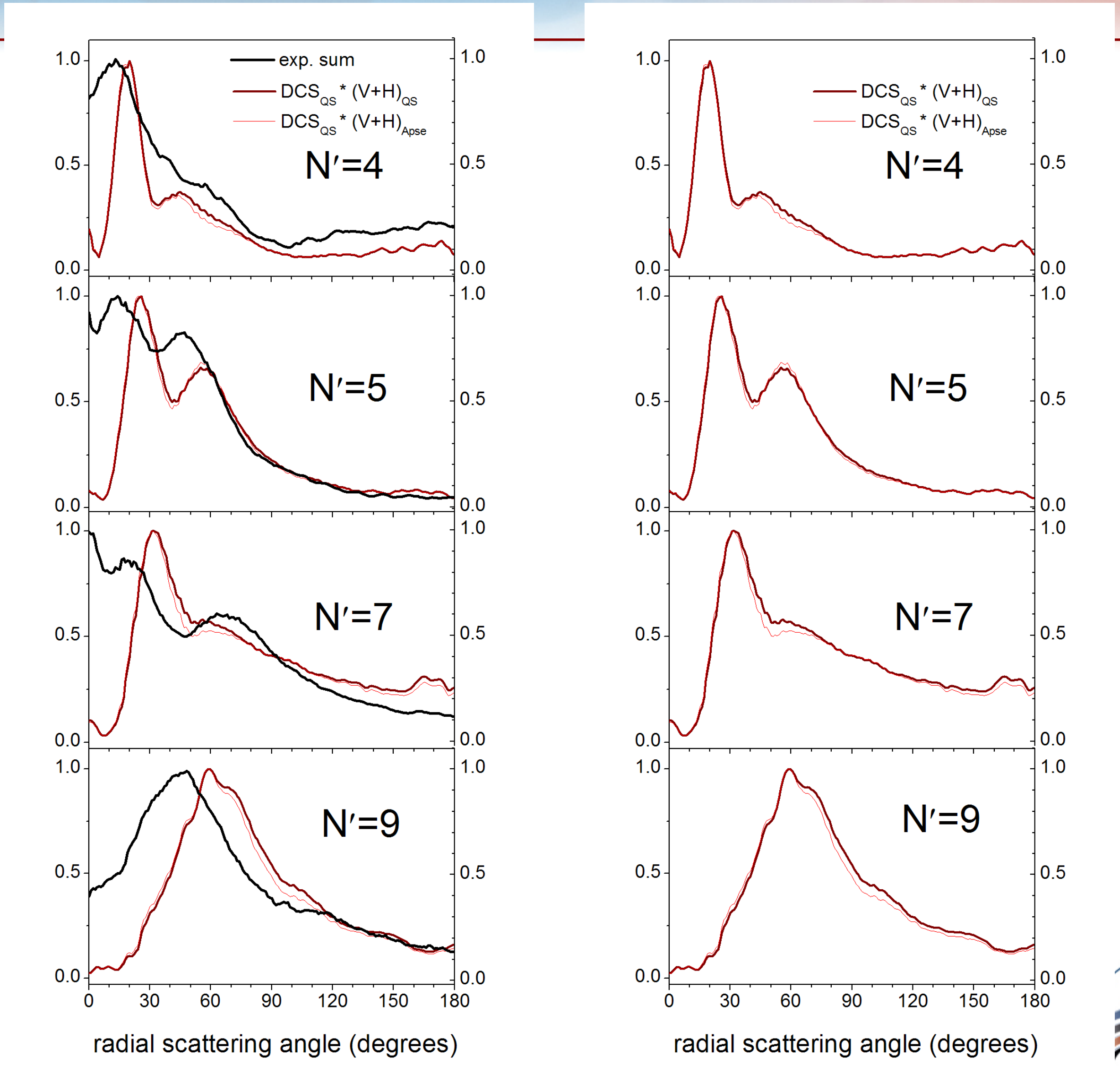
How does Calculated DCS compare to Experimental DCS?

Note there is a relative insensitivity to the alignment model but unsatisfactory agreement due to error in calculated DCS. Experiment sees more forward scattering



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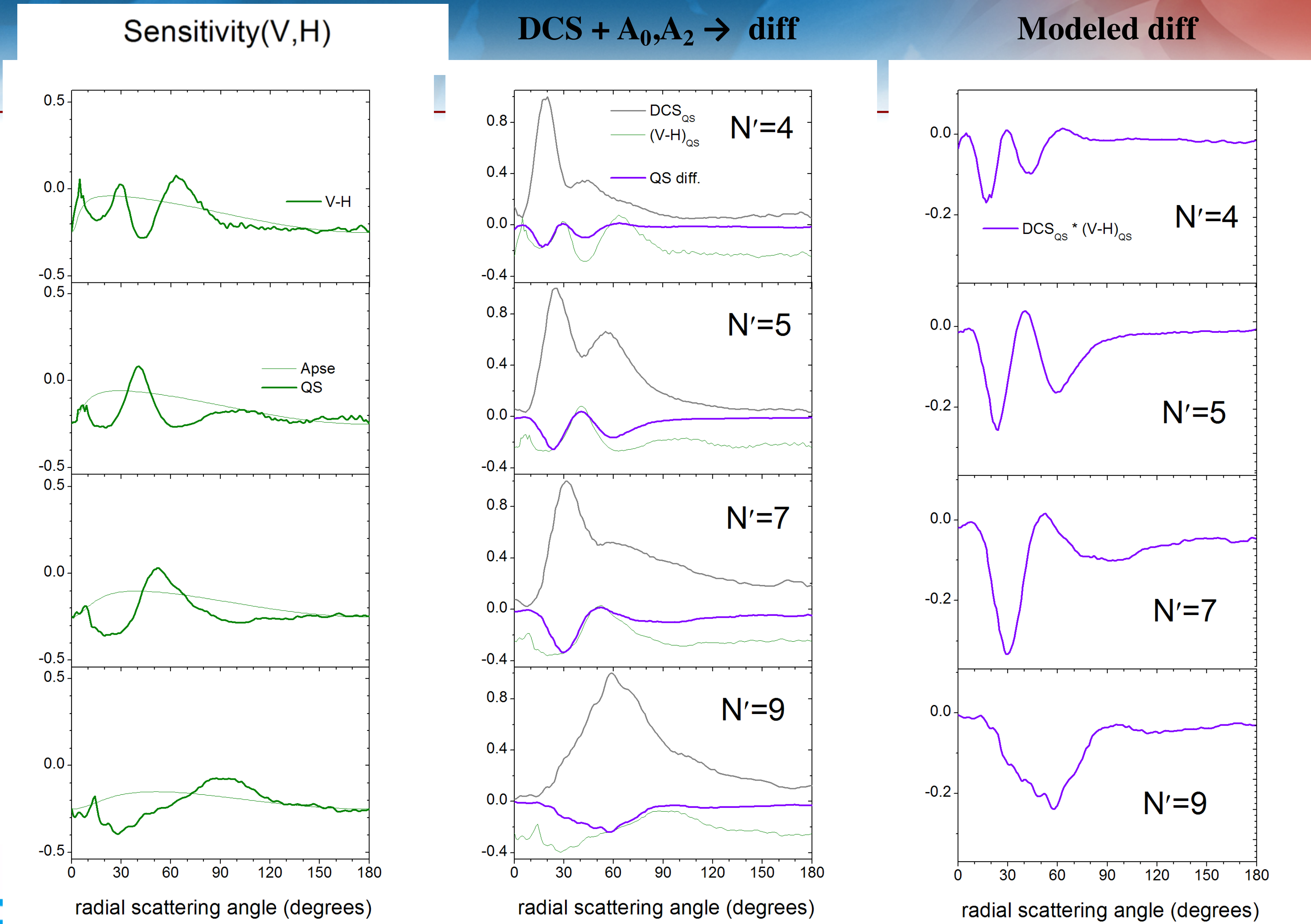
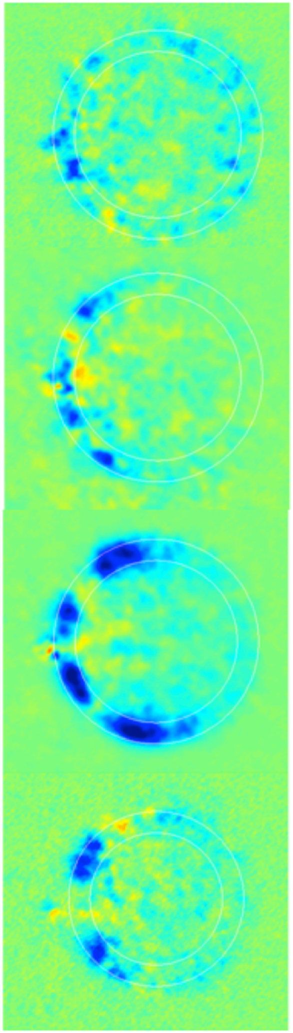
We can also combine the calculated DCS with the calculated alignment propensity to generate a theoretical "diff" (vertical - horizontal) for comparison of theory to experiment.

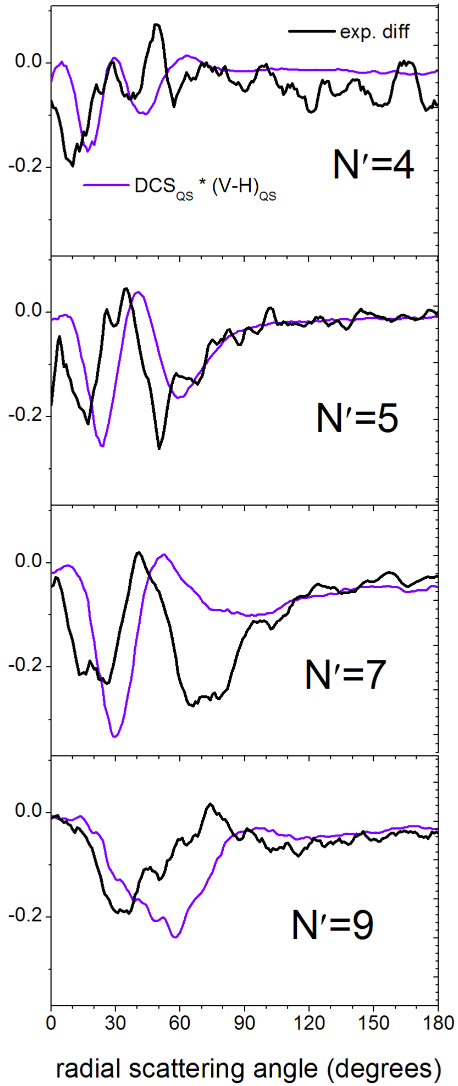


We Compare the Extracted Alignment Moments from the Theory Image and Moments extracted from the Experimental Image Using Difference (V-H) Images

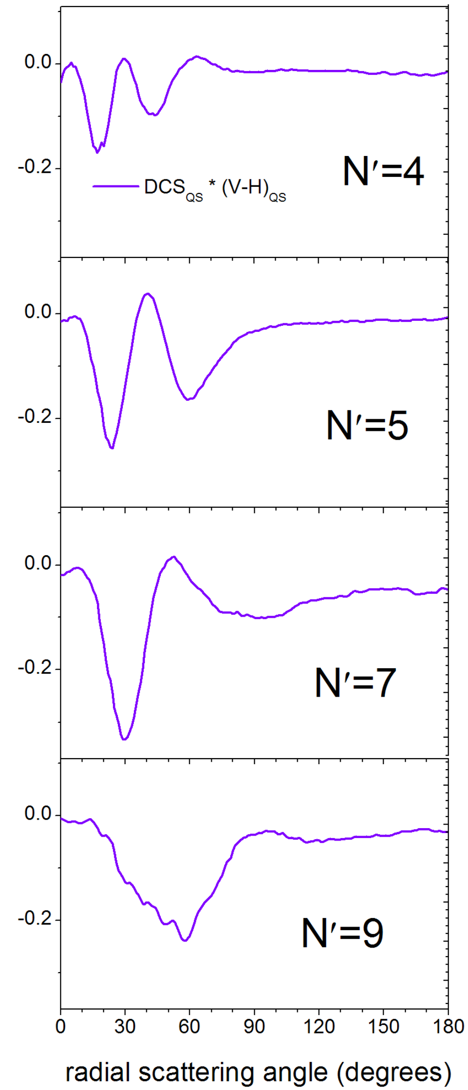
Expt. diff.



Expt. vs. modeled diff.



Modeled diff



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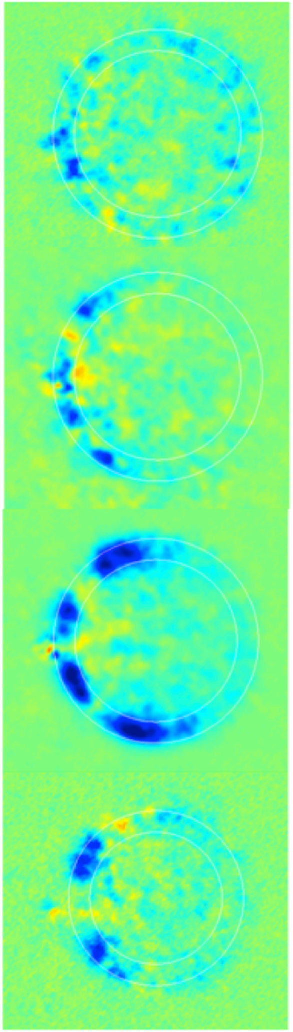
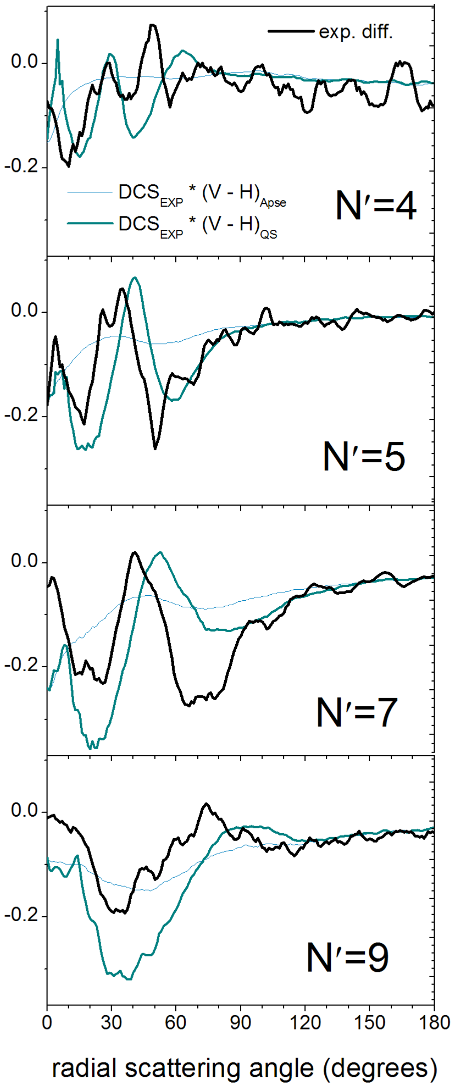
We Compare the Alignment Moments Using the Experimental DCS for Both Simulations.

$diff_{EXP}$

$diff_{EXP}$ vs. $diff_{Apse}(DCS_{EXP})$ & $diff_{QS}(DCS_{EXP})$

- **This difference image comparison shows qualitative agreement between experiment and the quantum scattering calculations that the simple Apse model cannot reproduce.**





- **Why do the Classical and QS model agree relatively closely for the sum but not**

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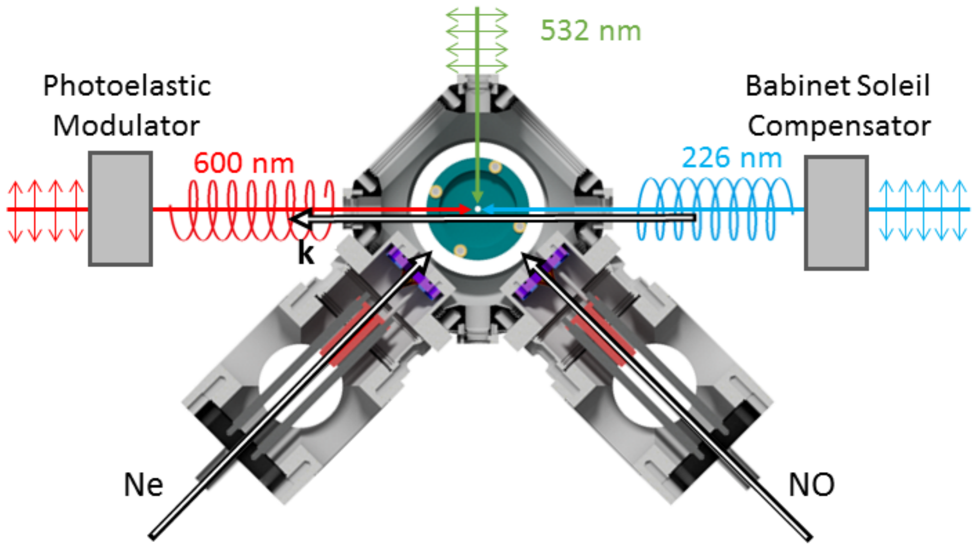
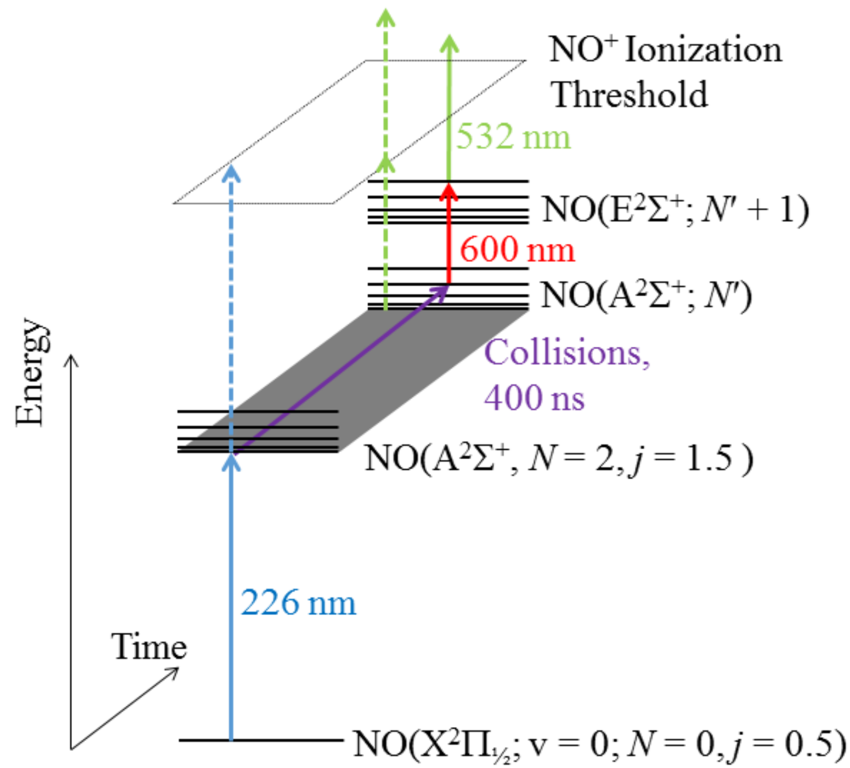
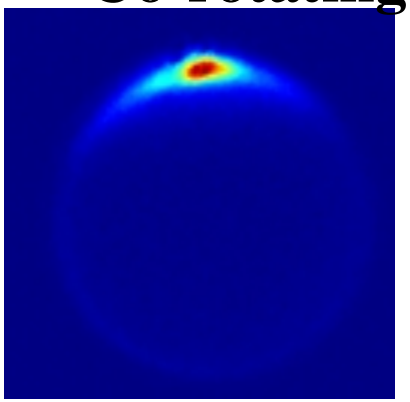

532 nm
Photoelastic Modulator
Babinet Soleil Compensator
600 nm
226 nm
k
Ne
NO



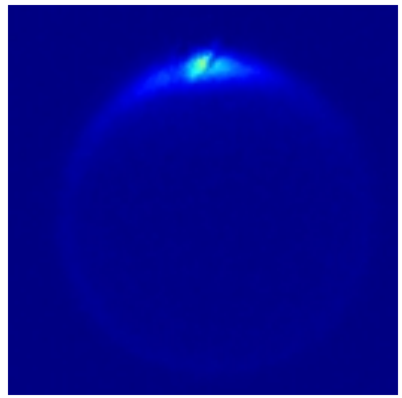
NO⁺ Ionization Threshold
532 nm
NO(E²Σ⁺; N′ + 1)
600 nm
NO(A²Σ⁺; N′)
Collisions, 400 ns
NO(A²Σ⁺, N = 2, j = 1.5)
Energy
226 nm
Time
NO(X²Π½; v = 0; N = 0, j = 0.5)

$N' = 4$

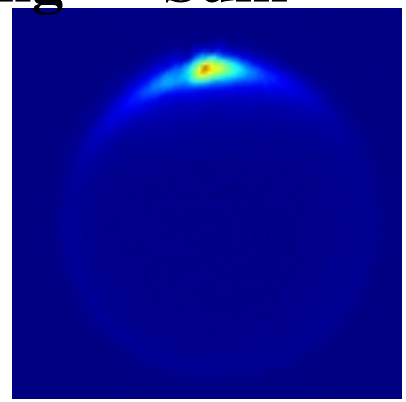
Co-rotating



Counter-rotating

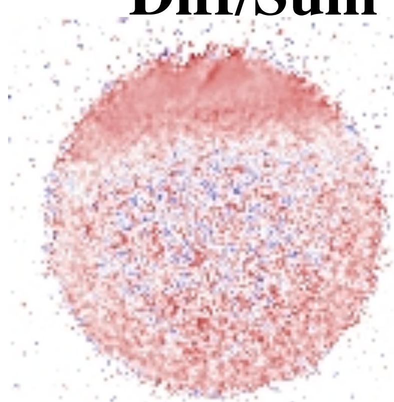


Sum



Difference

Diff/Sum



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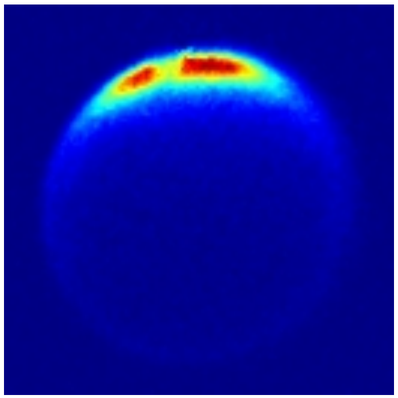
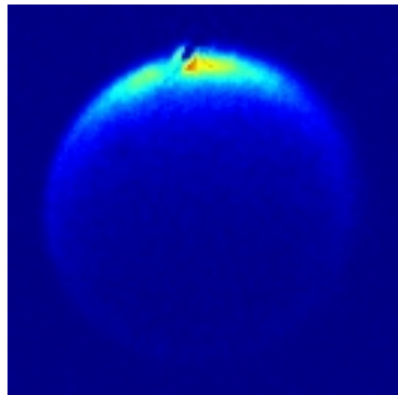
$N' = 5$

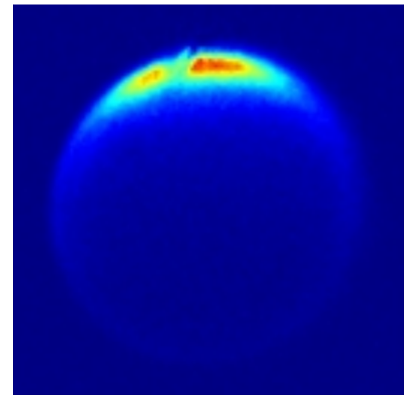
Co-rotating



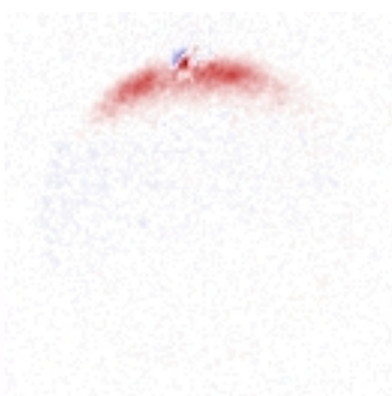
Counter-rotating



Sum



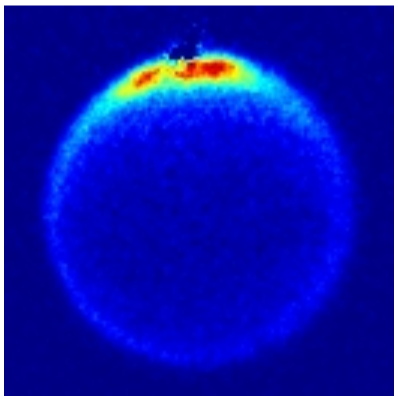
Difference

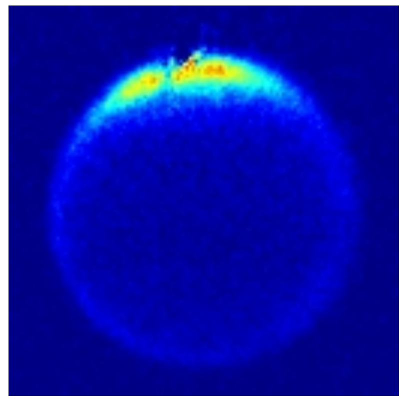


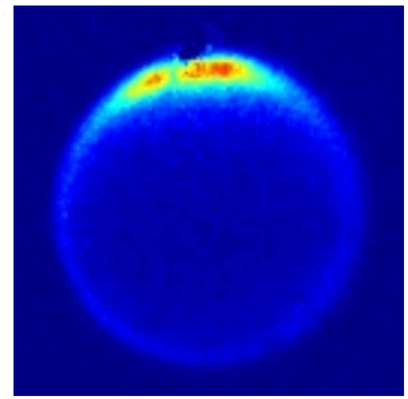
Diff/Sum

$N' = 6$

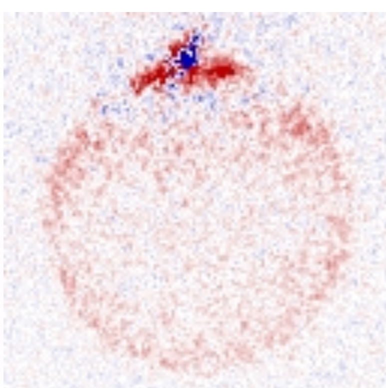
Co-rotating | **Counter-rotating** | **Sum**

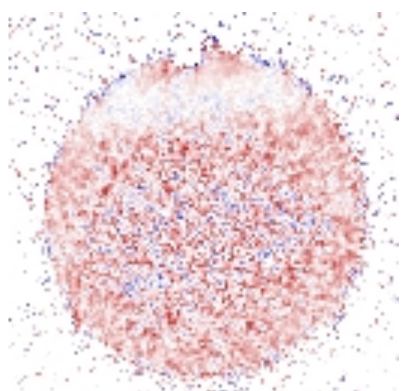






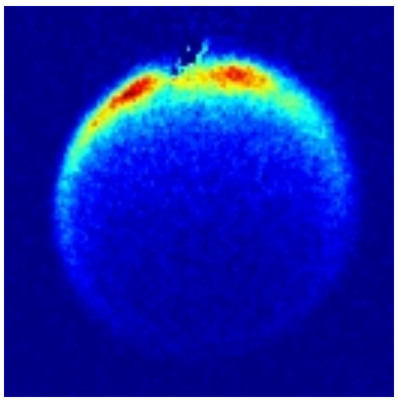
Difference | **Diff/Sum**



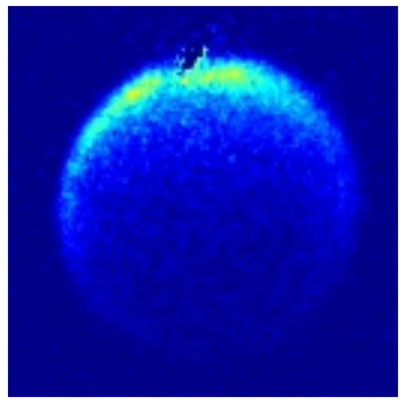


$N' = 7$

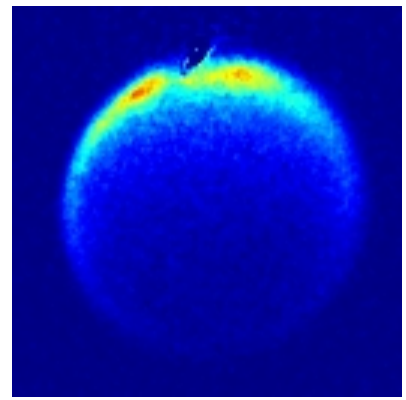
Co-rotating



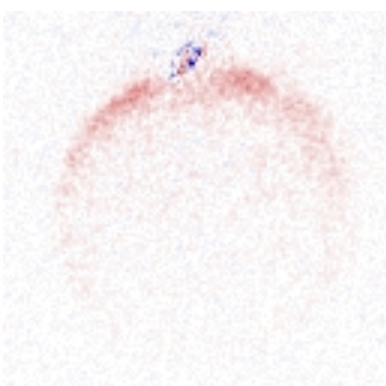
Counter-rotating



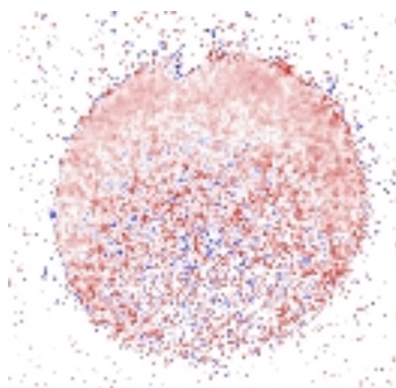
Sum



Difference

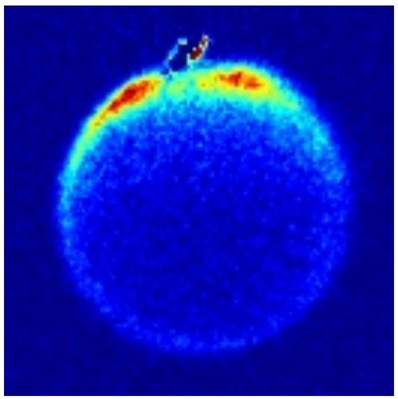


Diff/Sum

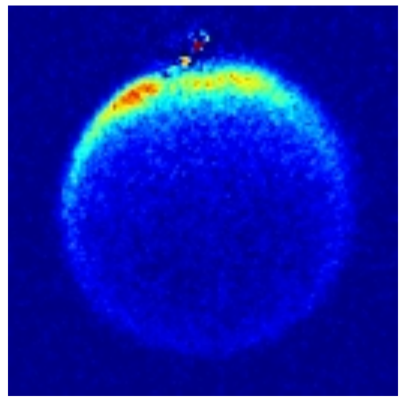


$N' = 8$

Co-rotating



Counter-rotating



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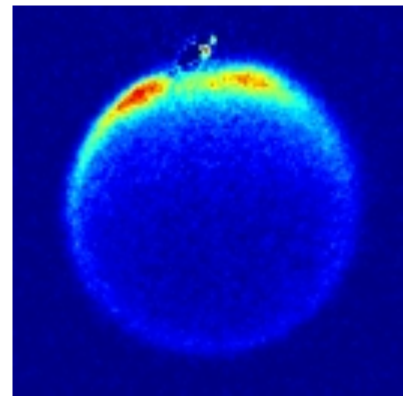
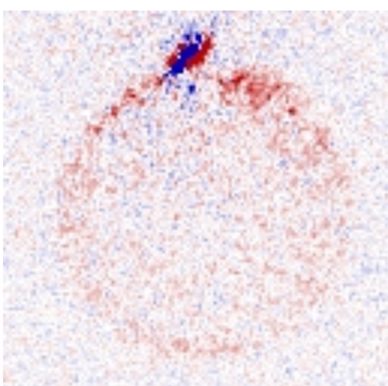
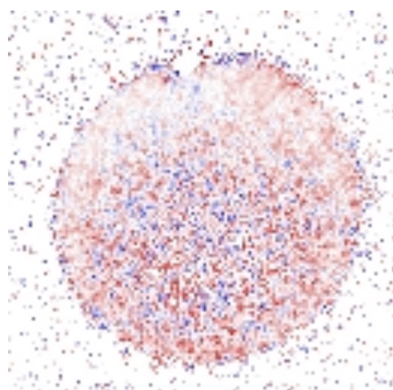


Difference

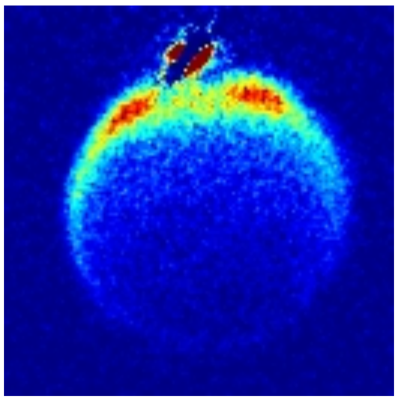


Diff/Sum

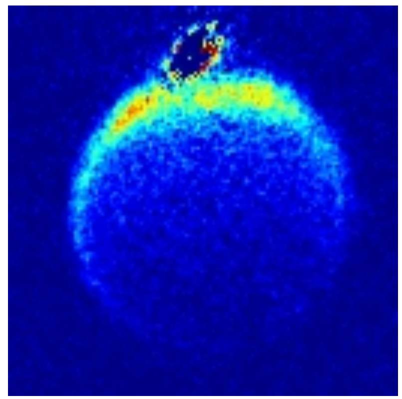


$N' = 9$

Co-rotating



Counter-rotating



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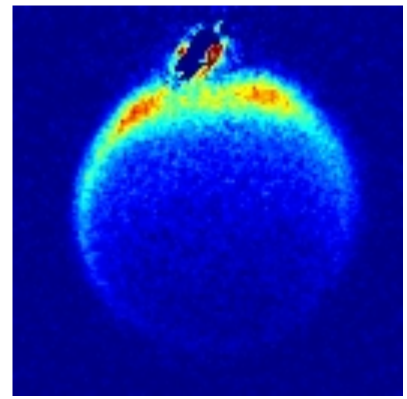
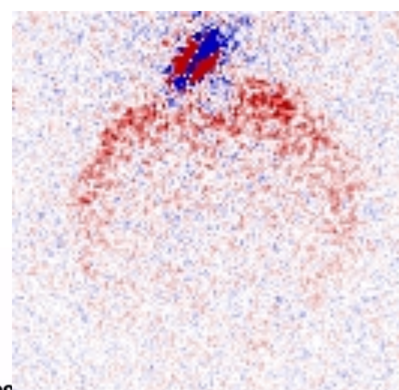
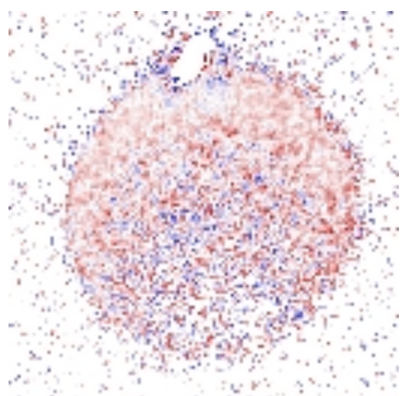


Difference



Diff/Sum



Kinematic Cooling and the Study of Chemical Dynamics with Ultracold Molecules

Outline:
Tutorial on what it means to be ultracold
and why you care about cold molecules

Using photodissociation to study cold half collisions

Recent progress in our lab on Kinematic cooling

A New Molecular Beam Machine Design