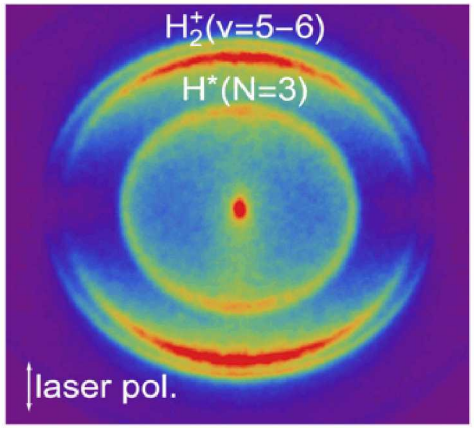
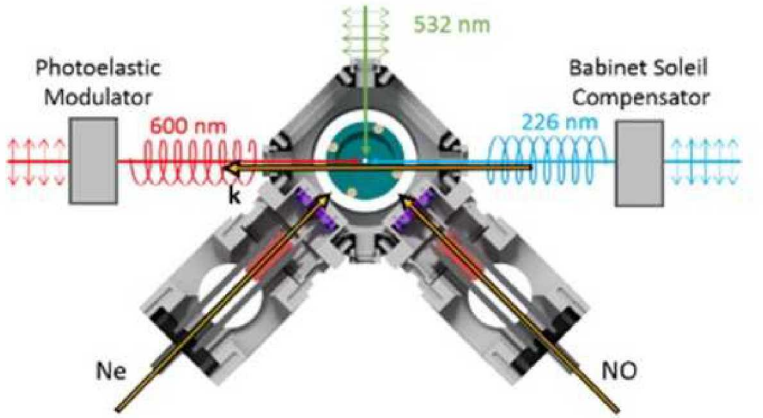
Chemical Dynamics of Aligned Excited Electronic States

SAND2018-9549C

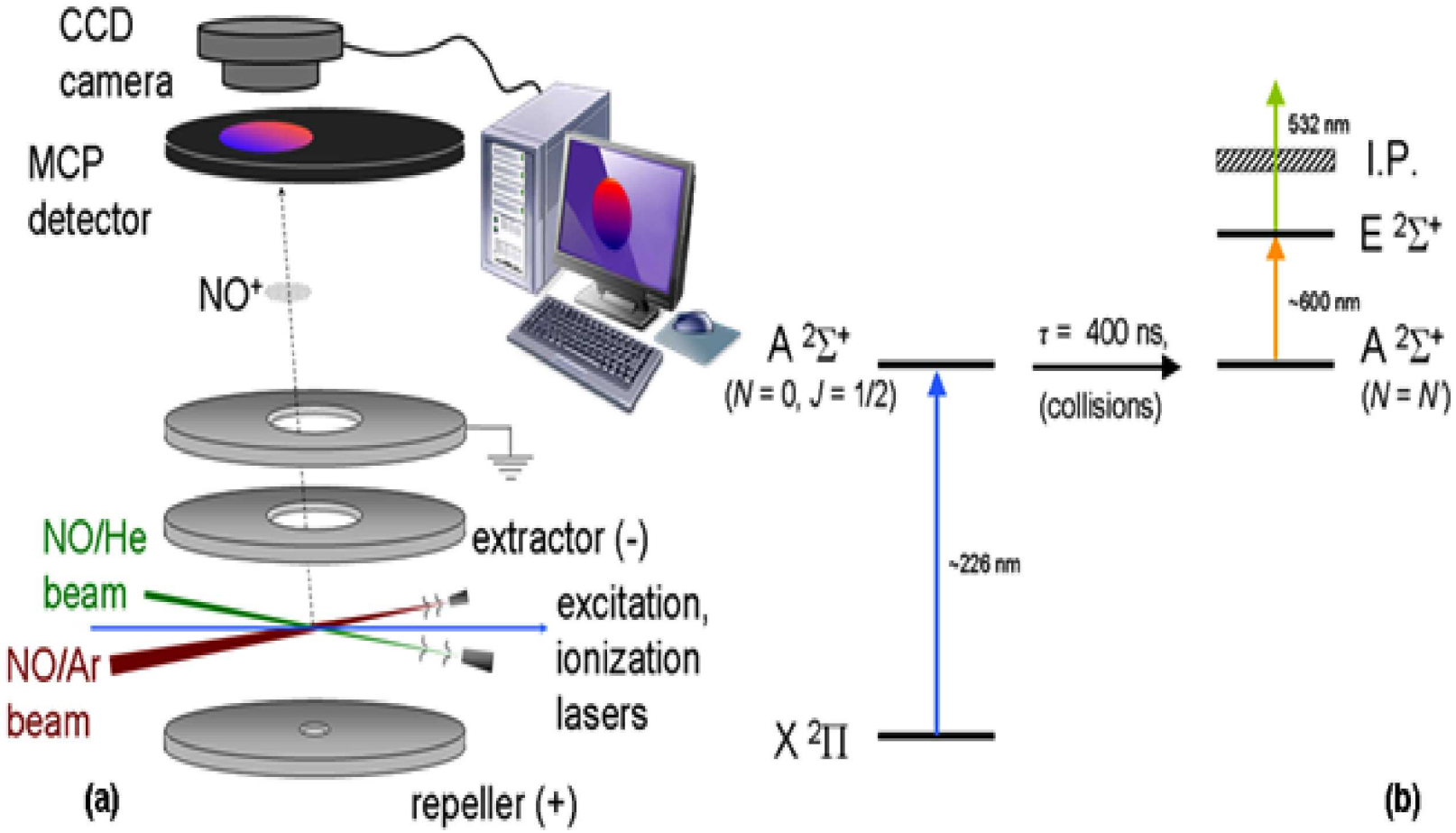
David W. Chandler
Sandia National Laboratory

Matt Costen Tom Sharples, Joe Leng, Ken McKendrick (Heriot Watt University)
Javier Aoiz (Cuidad, Madrid)
Justin Jankunis, Gary Lopez, Martin Fournier (Sandia)
Peter Rakitzis (University of Crete)

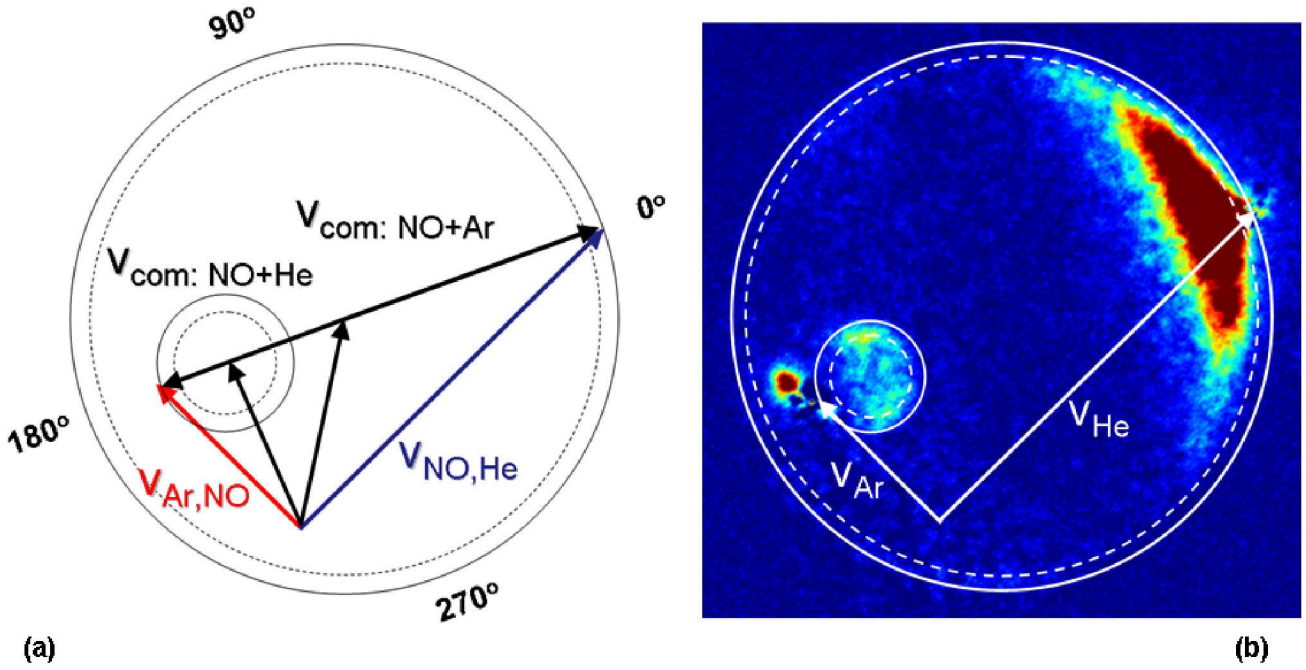




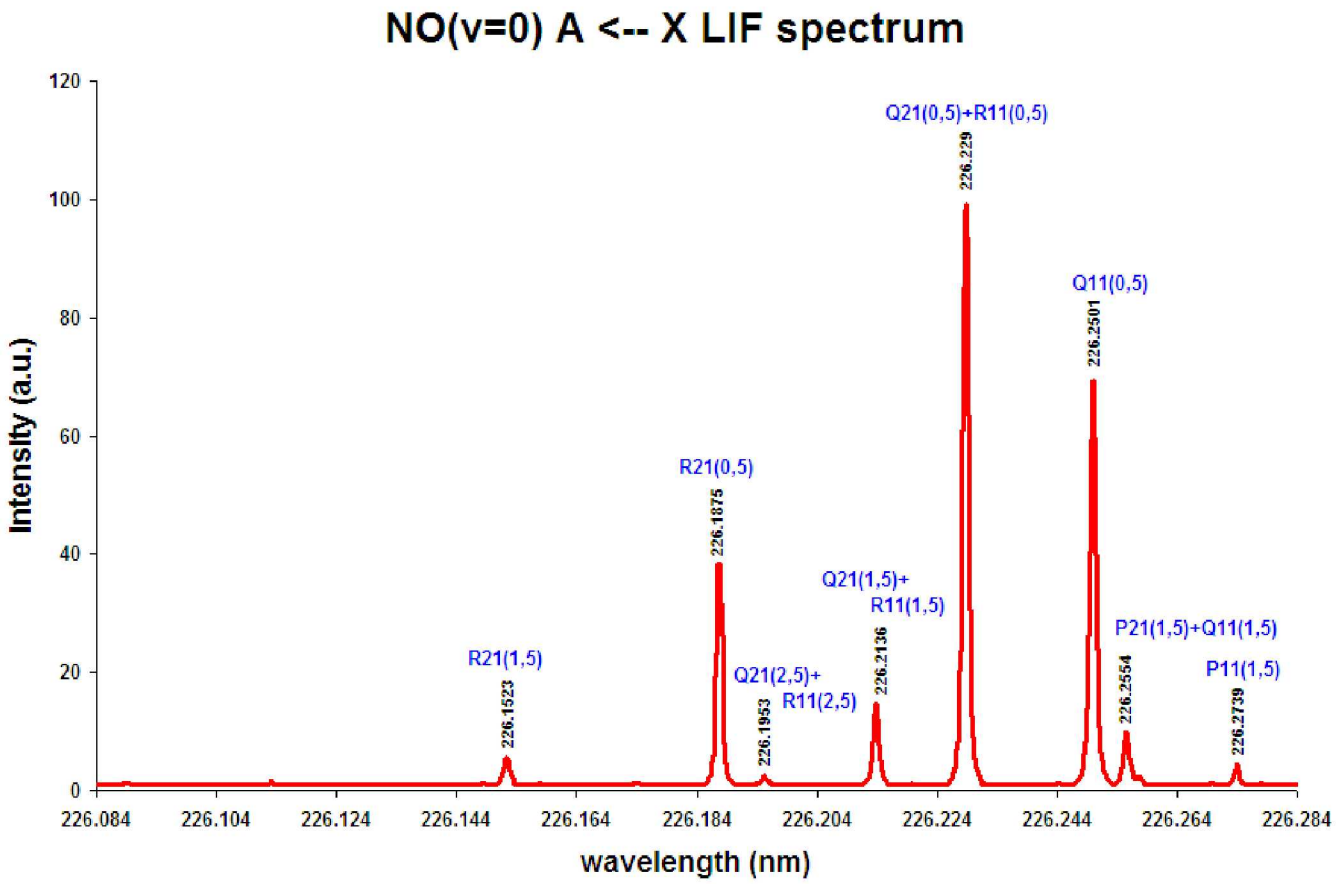
In the Past we Measured DCS and Alignment of NO(A) State Collisions.



Crossing two beam: NO/He with NO/Ar. NO is Scattered from Each Beam Simultaneously.

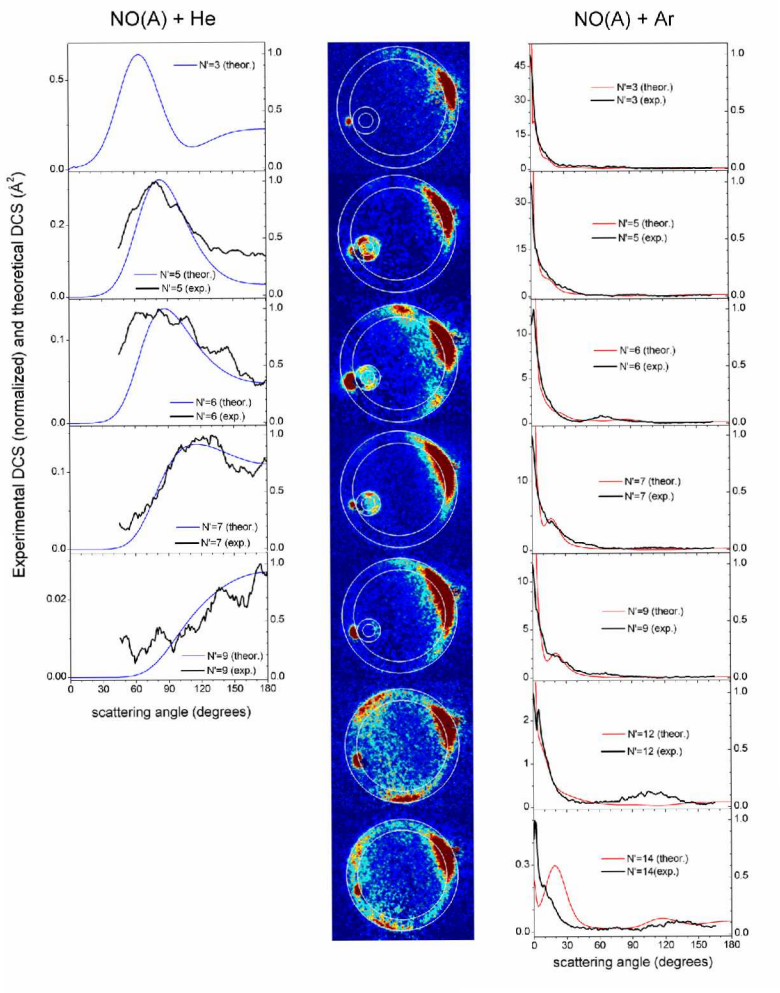


We Excite Different Rotational Levels of the A state Using Different Transitions.



Easier to Compare the Calculations of the NO He and NO Ar scattering when performed in this manner.

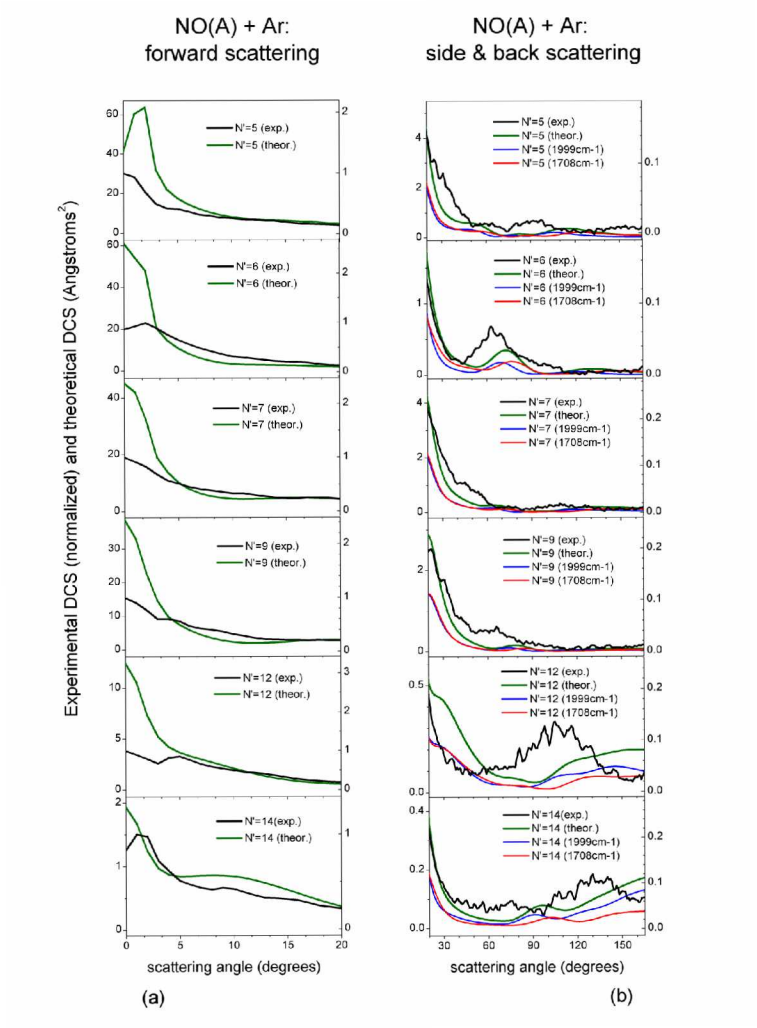
N=3
N=5
N=6
N=7
N=9



N=3
N=5
N=6
N=7
N=9
N=12
N=14

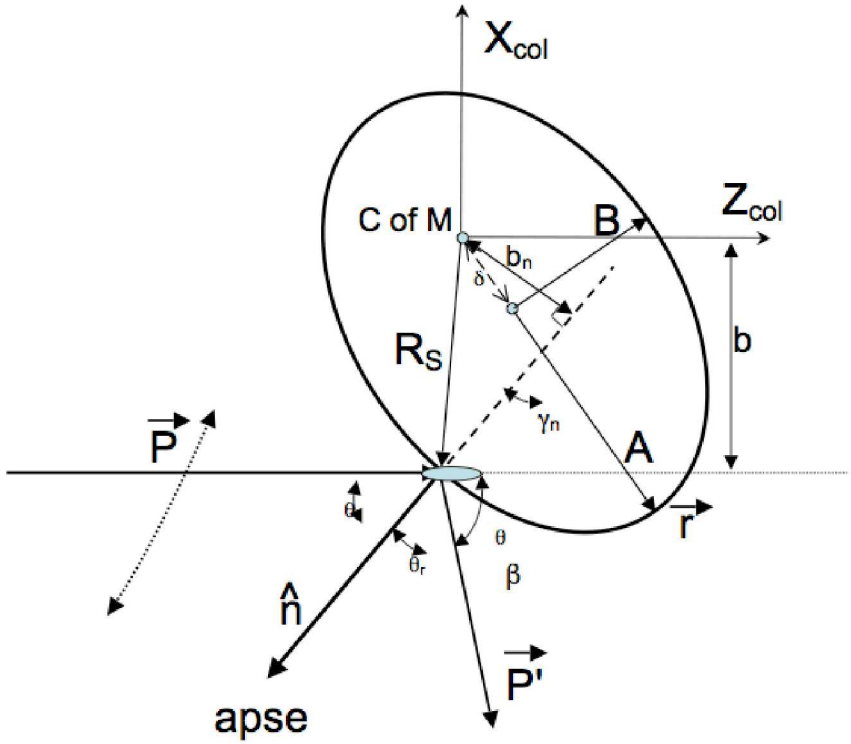
QM Scattering Calculations do not Reproduce Exactly the Results but Capture the Trends.

Experiment under Estimates the forward scattering due background subtraction procedure



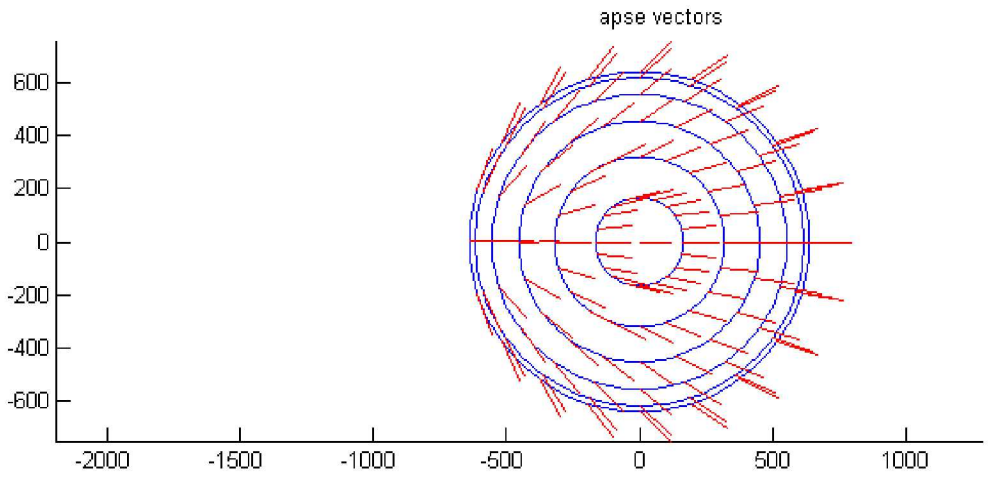
Theory to predict the position of the Rainbow Scattering at too large and angle.

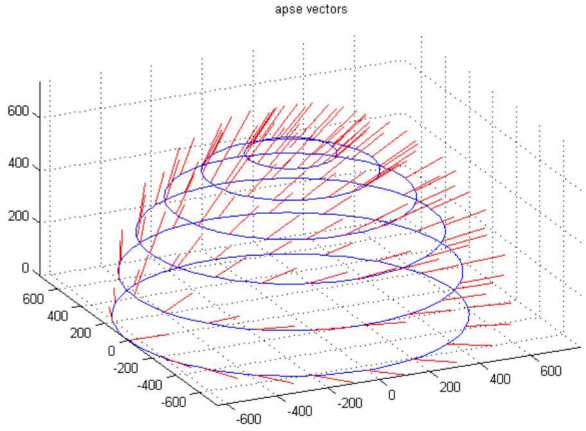
Collisions at High Collision Energy Can be Roughly Thought of as Hard and Sudden.



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

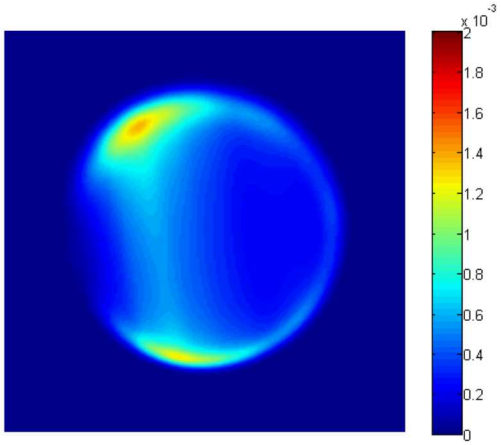
The Apse Model States That the Final J Vector Cannot Lie Along the Apse Vector



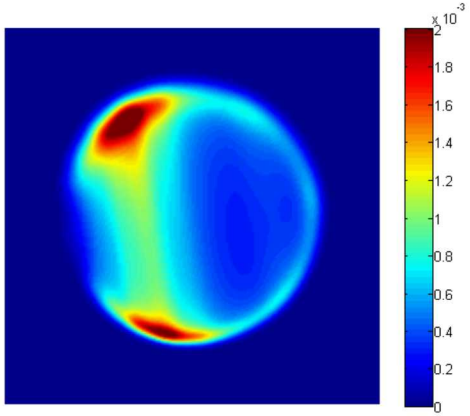


This Simple Rule Implies an Alignment to the Collisions

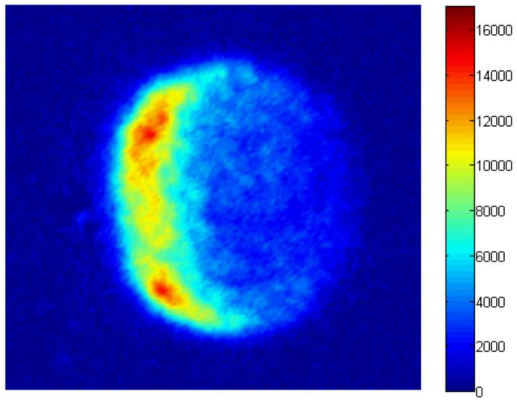
Detection with Linear Polarized Light Show the Alignment Inherent in the Images. NO(N=9)



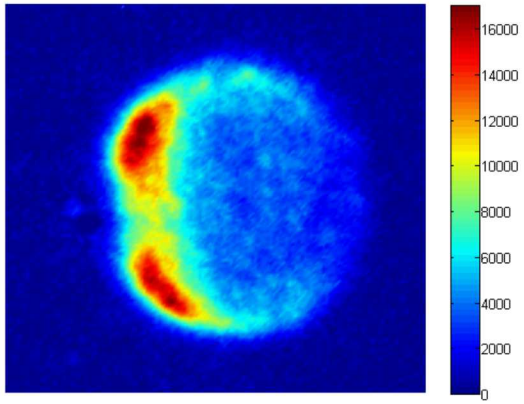
Exact model: V



Exact Model: H

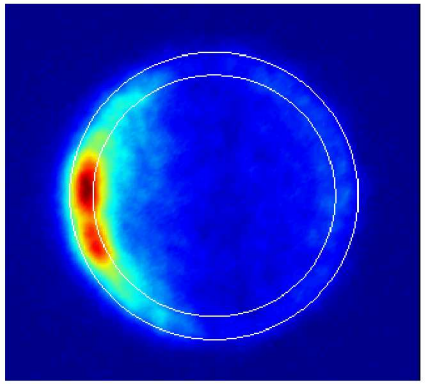


Experiment: V

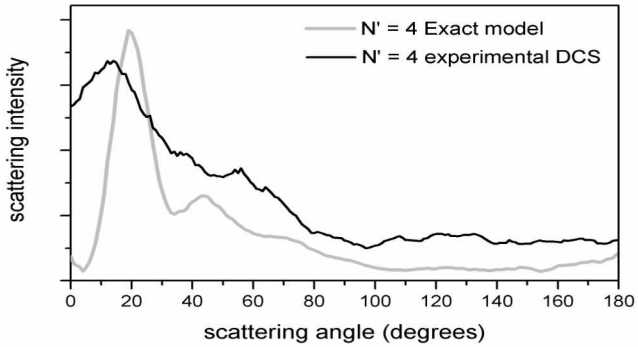


Experiment: H

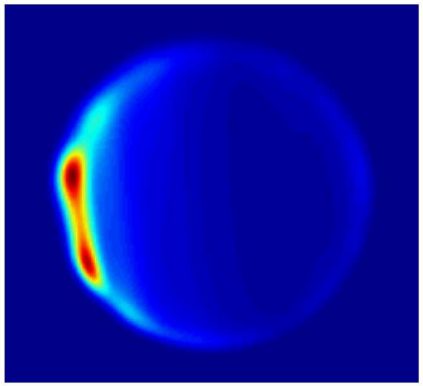
Calculated and Experimental Images are in Good Agreement.



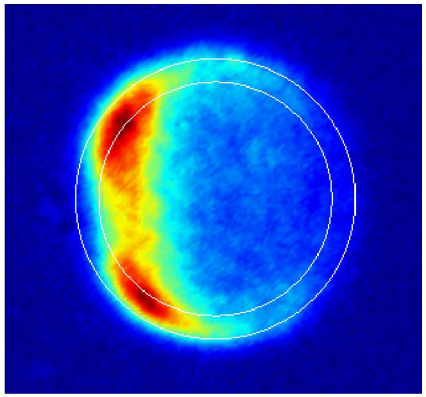
Experimental images

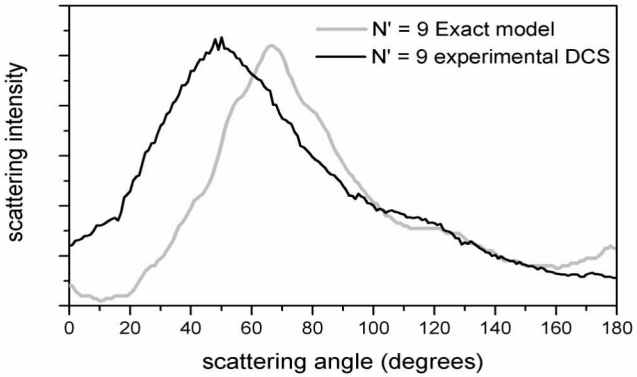


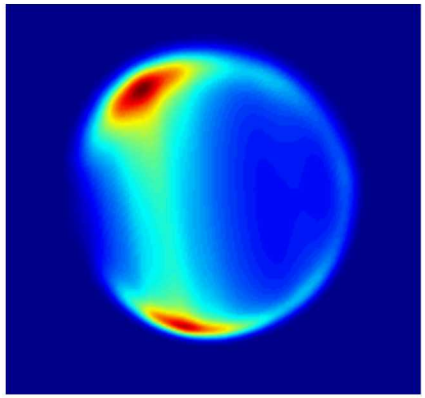
Annular profile comparison



Exact model

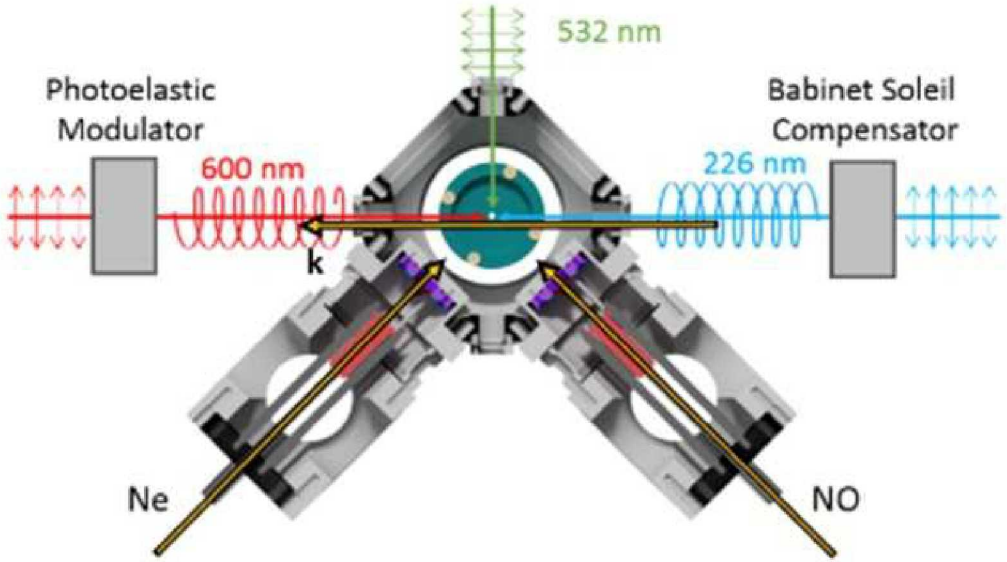




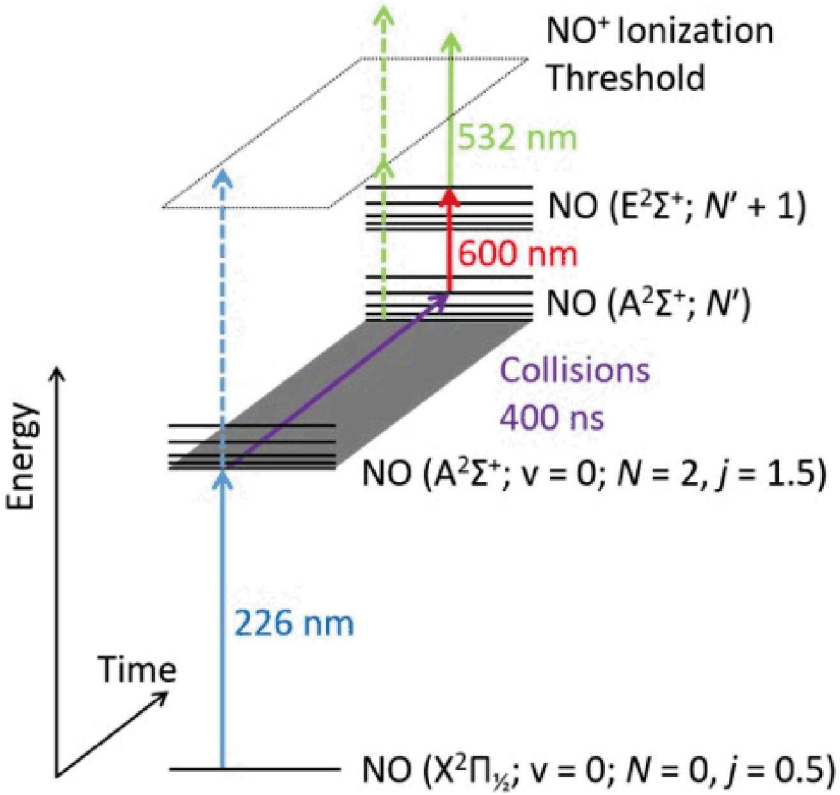


Collisional Energy Transfer of Oriented NO (A, v=0, N=2)

1) Prepare NO(A) with circularly polarized light at ~226 nm
2) Orient K vector with relative velocity vector of collision
3) Detect with circularly polarized light



Scheme for production of NO(A) and detection of NO (A).

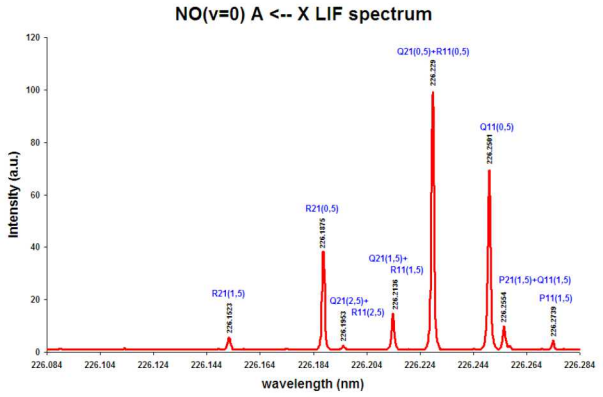


NO(A) has lifetime of 200ns

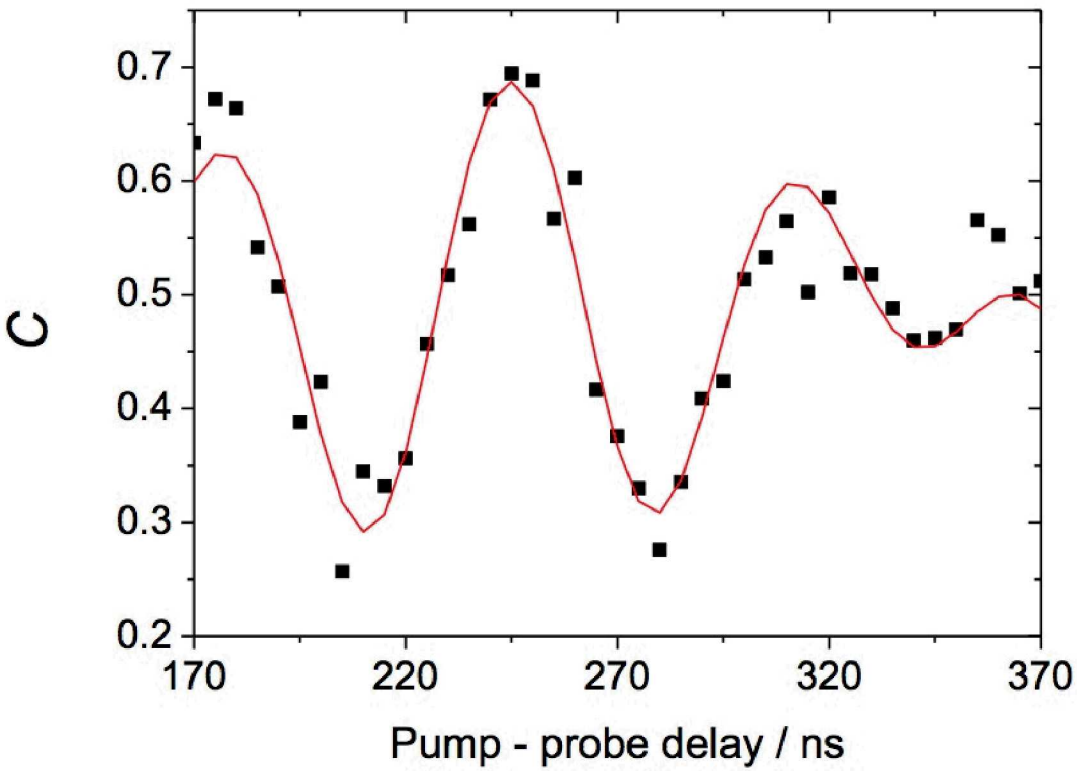
Detect NO (A) after 400 ns

Excite from N=0 j=0.5 to N=2 j=1.5

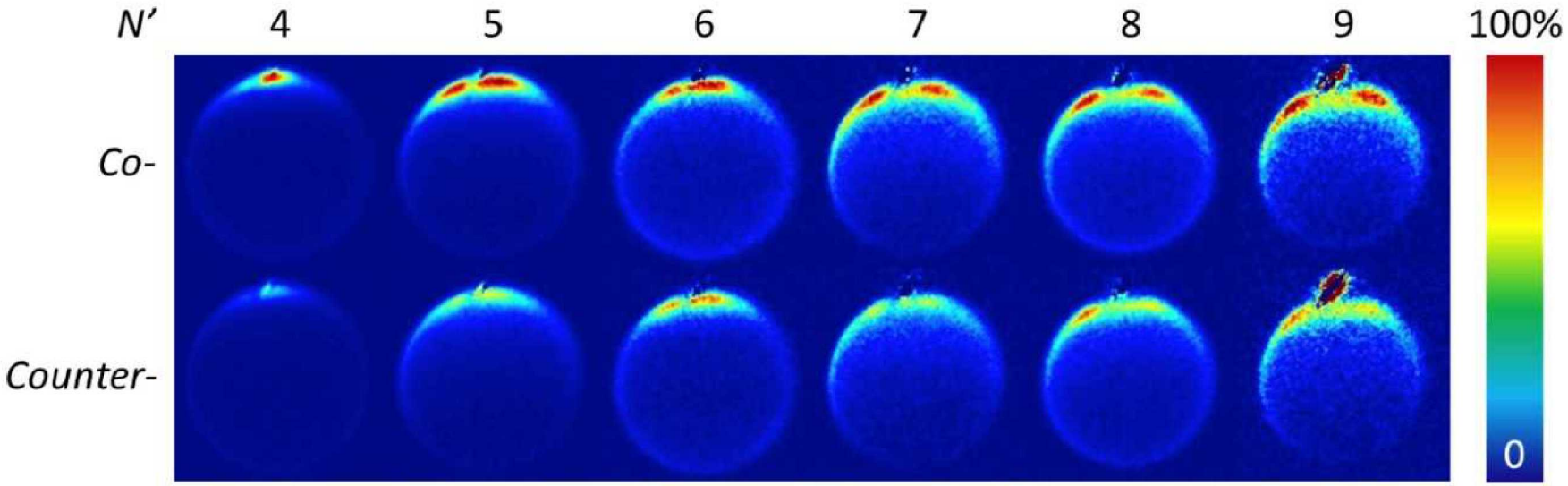
Detect different N states and compare
Co-rotating
versus
Counter rotating



Hyperfine Depolarization Makes the Orientation Oscillate but an Average Value of A10= 0.6 is Observed

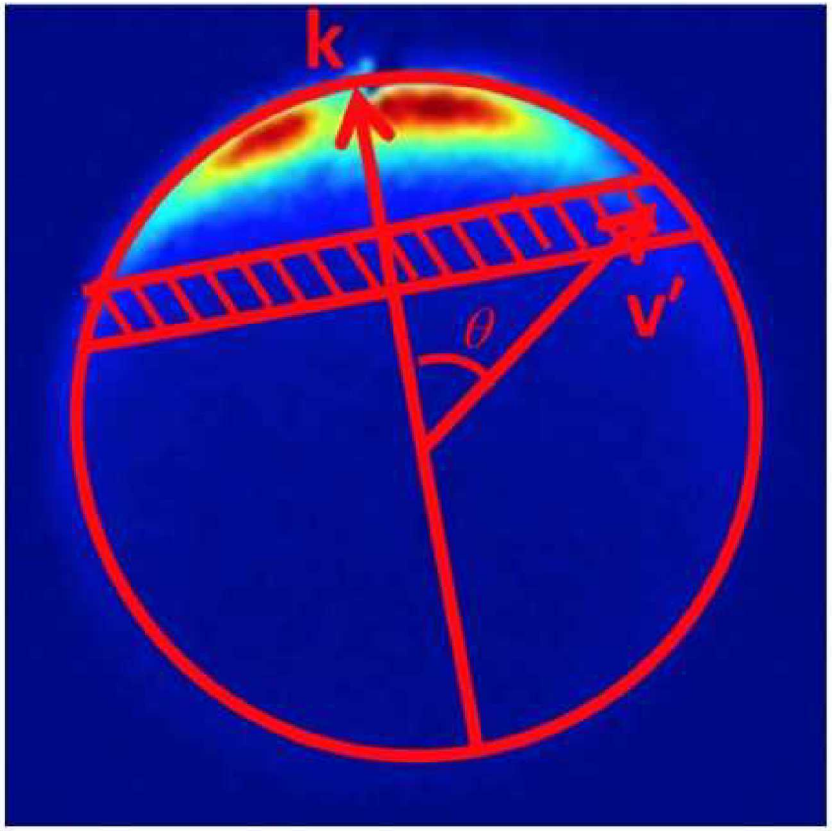


Images of Co- and Counter- Rotating NO After Collision With NO(N=2)



Scattering images for each final N' in the two geometries. Top row: co-rotating geometry, bottom row: counter-rotating geometry.

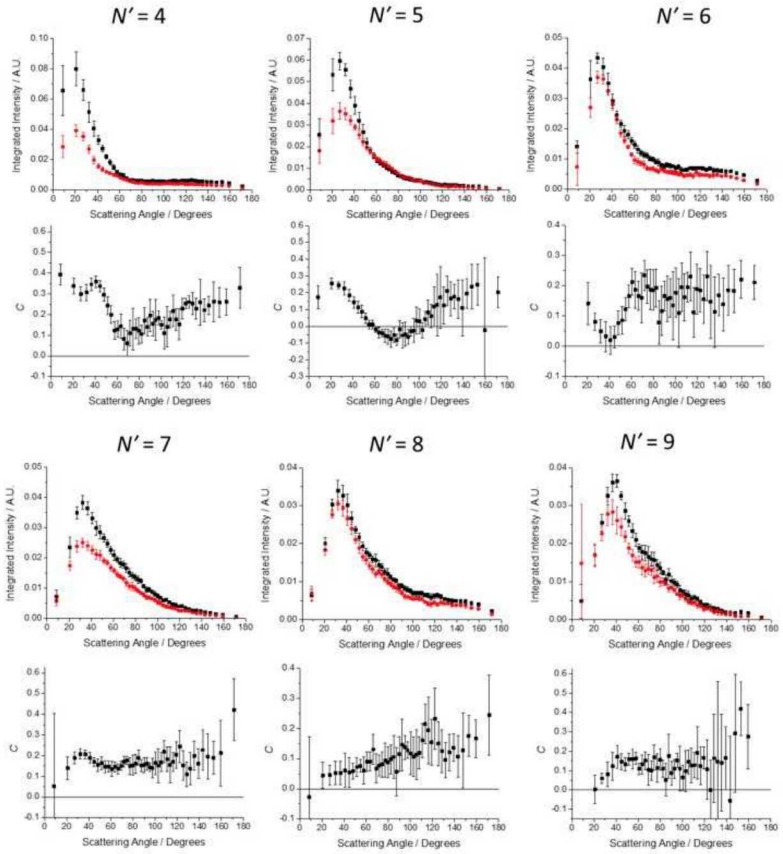
The intensity of the images as a function of azimuthal angle are recorded and compared

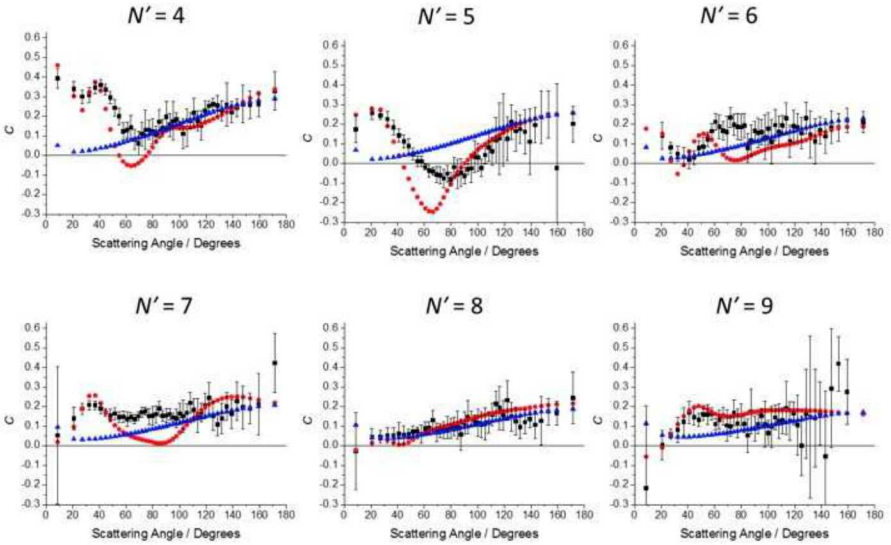


$$C = \frac{I_{co} - I_{counter}}{I_{co} + I_{counter}}$$

$$C = \frac{3h^{\{1\}}(j)g^{\{1\}}(j,t)A_0^{\{1\}}}{2 - h^{\{2\}}(j)g^{\{2\}}(j,t)A_0^{\{2\}}}$$

C is masured and compared to apse model and Quantum Calculations.

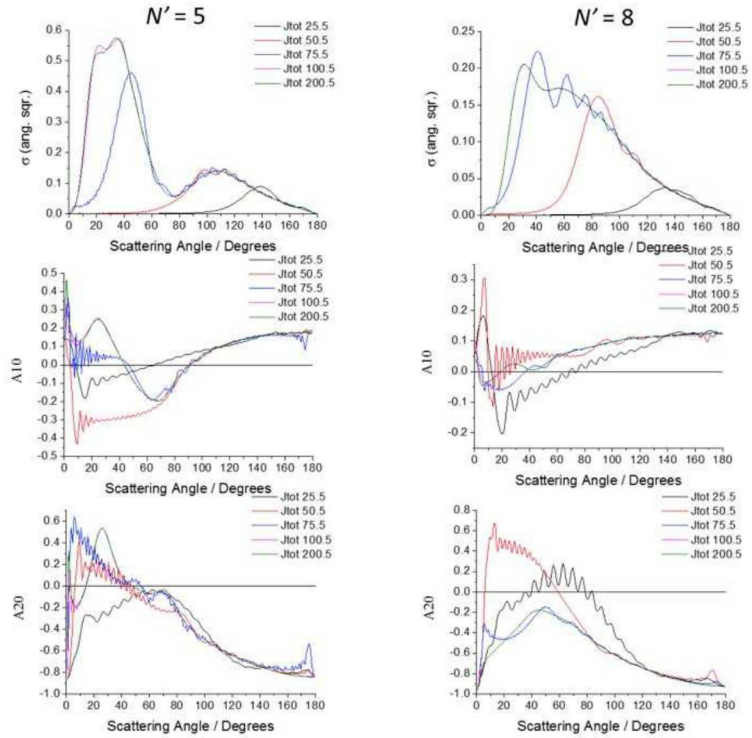


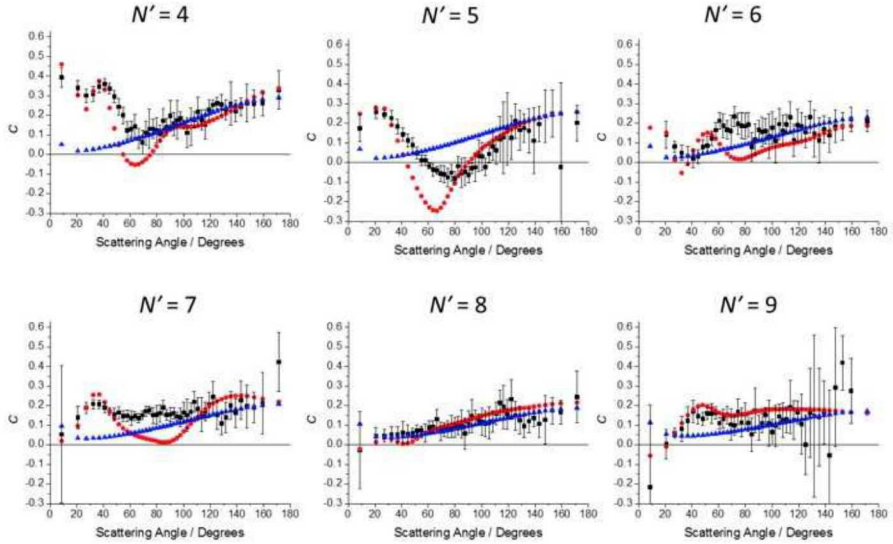


$$C = \frac{I_{co} - I_{counter}}{I_{co} + I_{counter}}$$

Figure 6: *Integrals and values of C for each quantum state . For each quantum state the integrals for the co- and counter rotating geometries are shown in the upper plot, in black and red, respectively. The values of C are plotted in the lower plot.*

C values are seen to be dominated by the A10 moments.





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$$C = \frac{I_{co} - I_{counter}}{I_{co} + I_{counter}}$$

Conclusions

Oriented collisions allow one to test the details of the potential energy surfaces
And inform the scattering calculations.

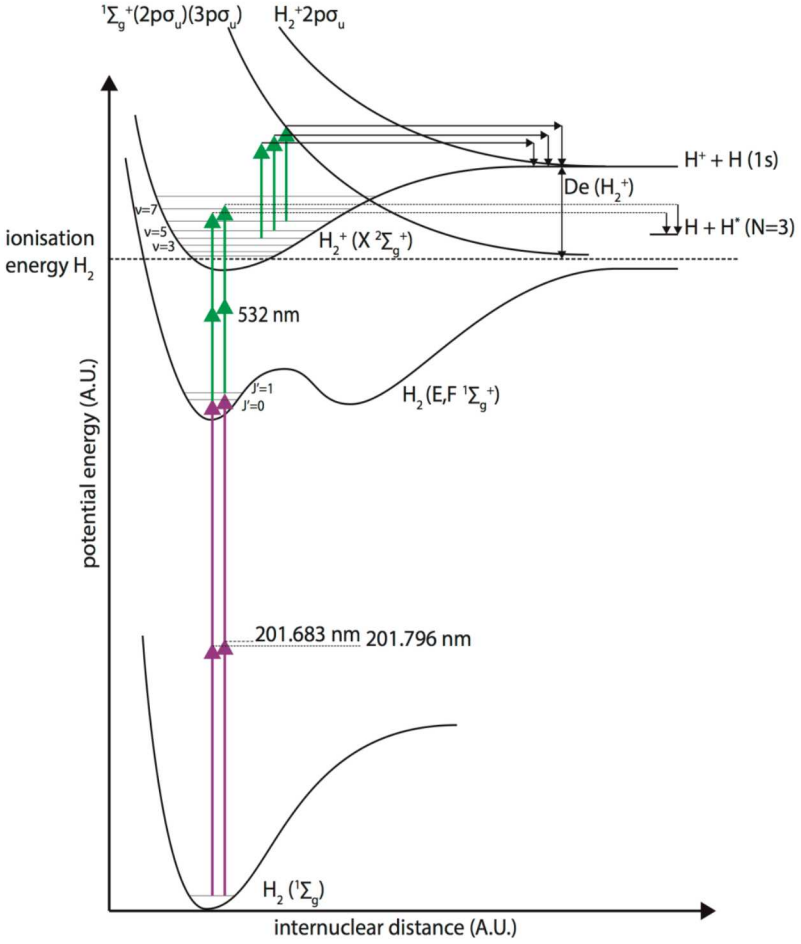
Co-rotating products are more probable than counter-rotating for low values of N.

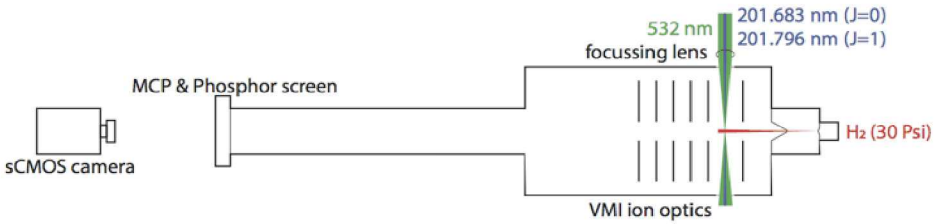
This is a four vector correlation.

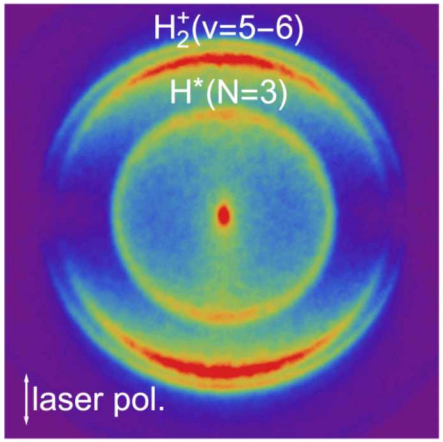
H_2 Alignment utilizing double resonance and studied with Velocity-mapped imaging of photo-dissociation products

- The distribution of products VMI imaging provides a measurement of the degree of molecular alignment prior to photodissociation.
- Even as the simplest molecule, H_2 in strong laser fields remains a challenge for high level quantum theory.
- Single quantum states may be excited with narrowband tunable lasers, providing a high level of control, minimizing the number of coupled rotational states, and thus simplifying the analysis of data.

To measure the alignment of the H_2 (E,F) we use a 201.7-nm laser beam to produce the ro-vibrational state we desire, then align and detect with 532-nm light.







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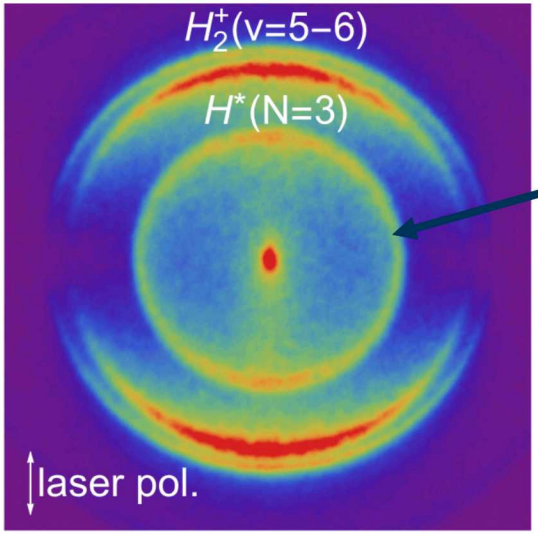
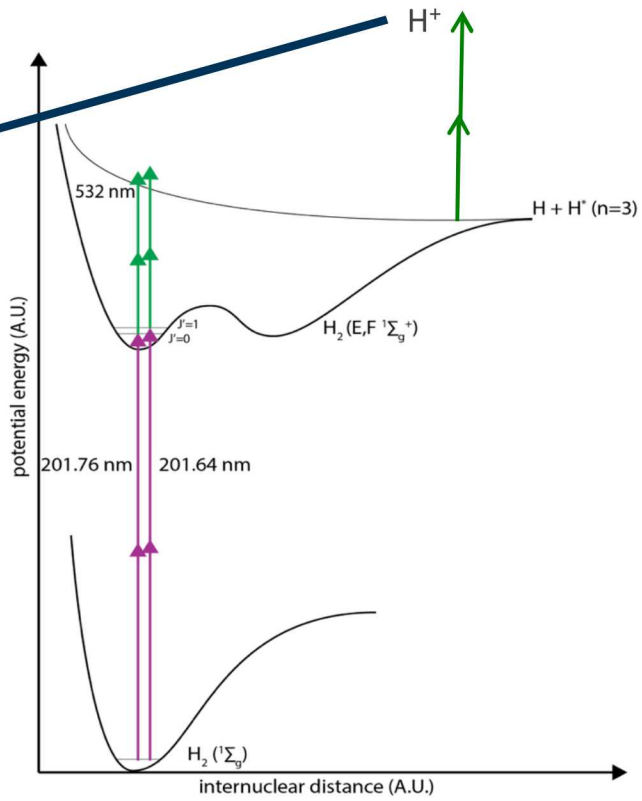


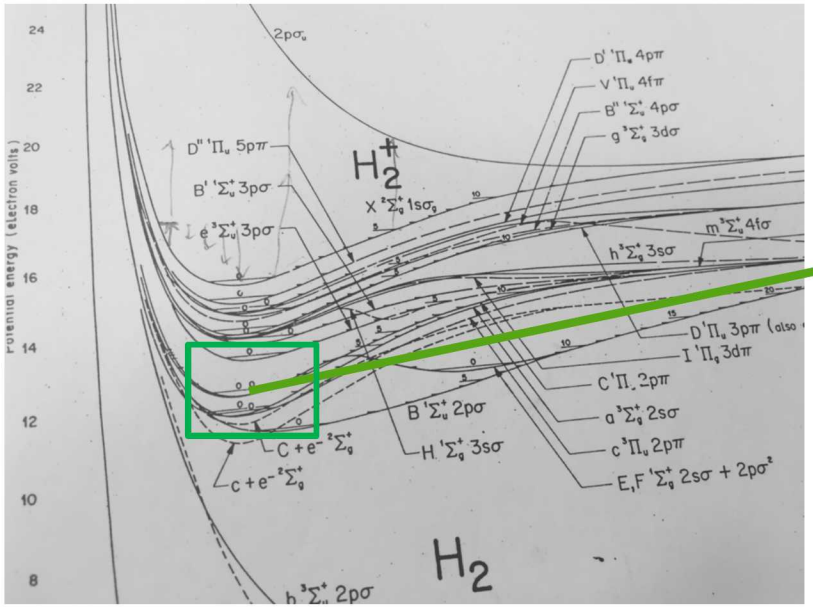
This is the image you obtain of H^+ coming from 532-nm Photo-dissociation of the H_2 EF (v=0, j=0) quantum state.

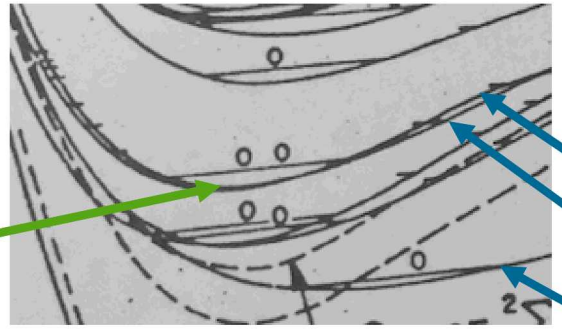


GAS PHASE CHEMICAL PHYSICS

The E,F state lies on top of the B and C states. Those States Couple to the E,F state via the Electronic Dipole Operator.

Coupling to the B state is along the molecular axis and to the C state is perpendicular to molecular axis

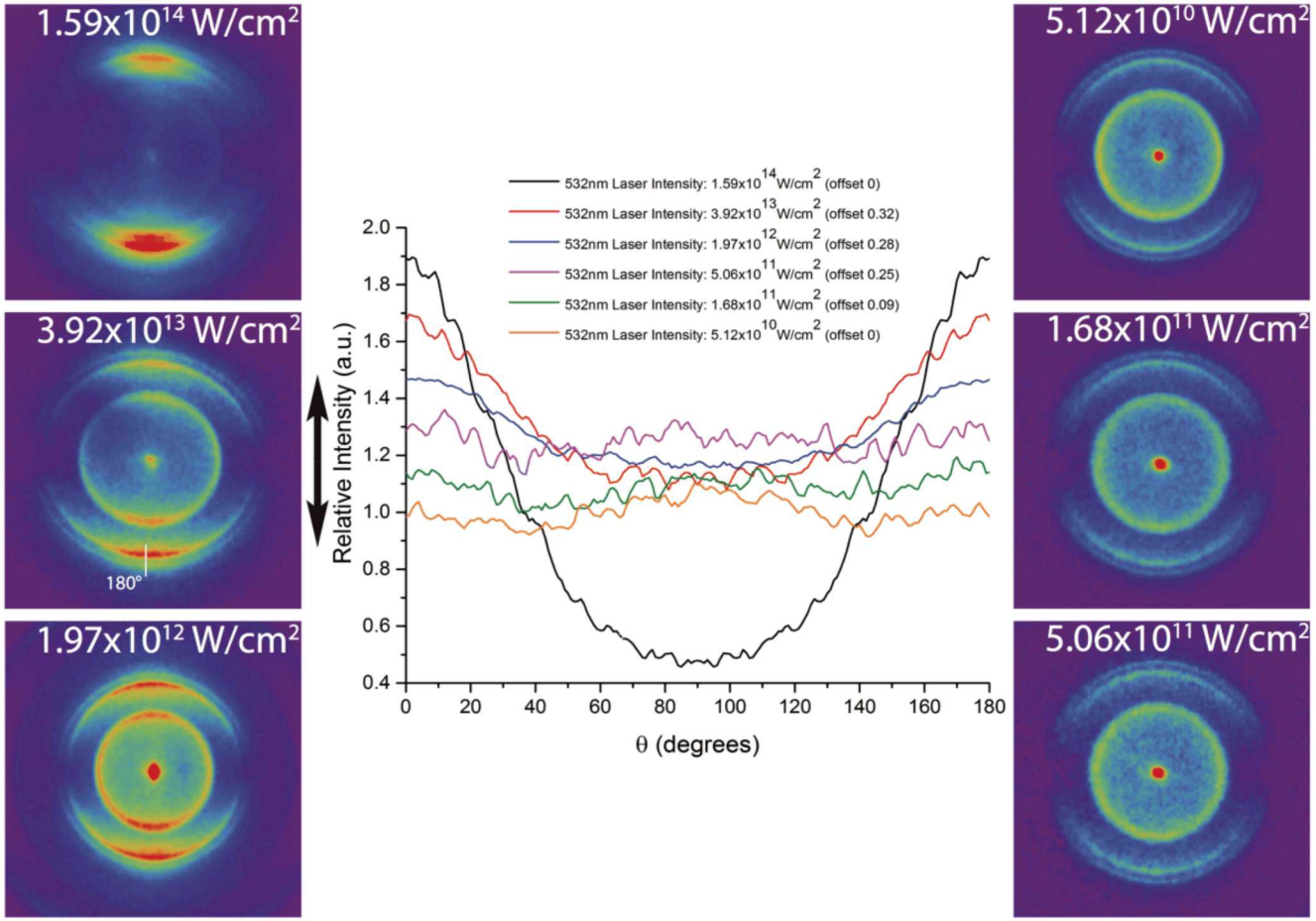




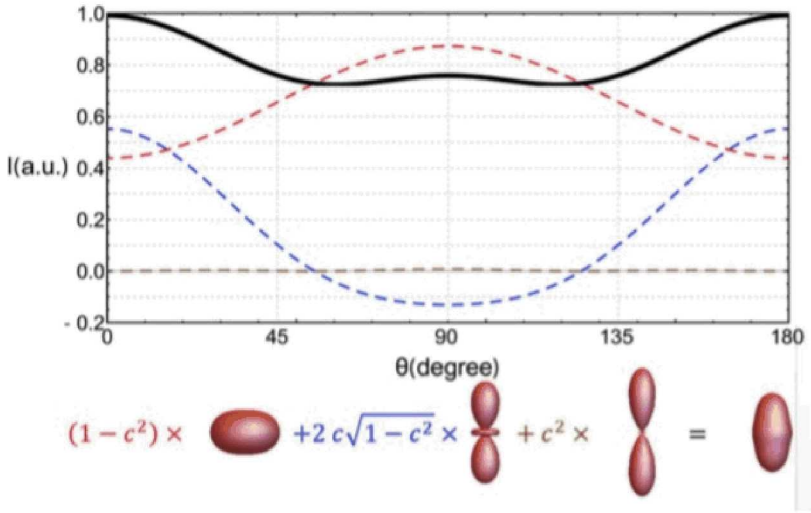
The Electric field of the laser beam mixes the EF, B and C states creating a superposition state That has 100 times higher polarizibility difference than ground state H_2

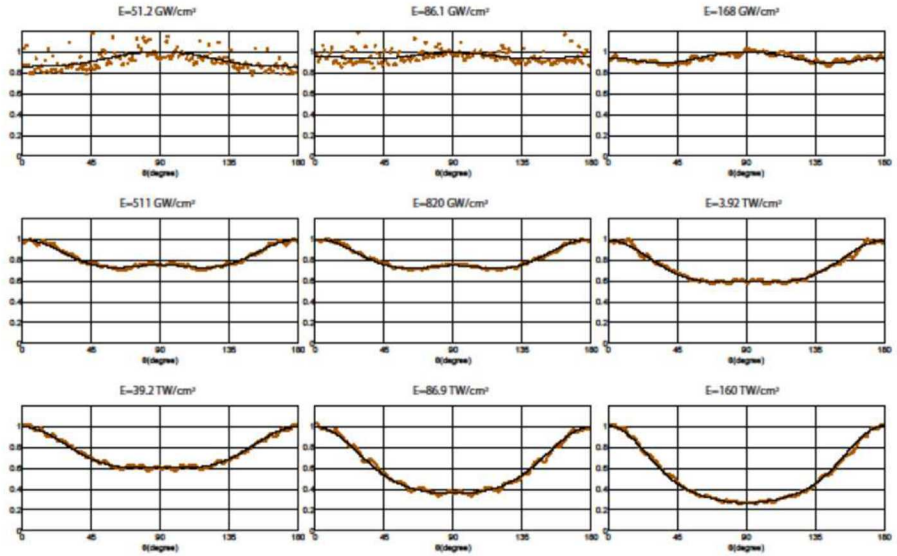
The alignment of the H_2 by intense 532-nm light is quantified by taking images at different 532-nm intensities.

H_2 (E,F; J = 0)



The alignment of the H2 (E,F J=0) as a function of 532-nm laser intensity is plotted and fitted using an Adiabatic Alignment model Employing J=0, J=2 and a cross term.

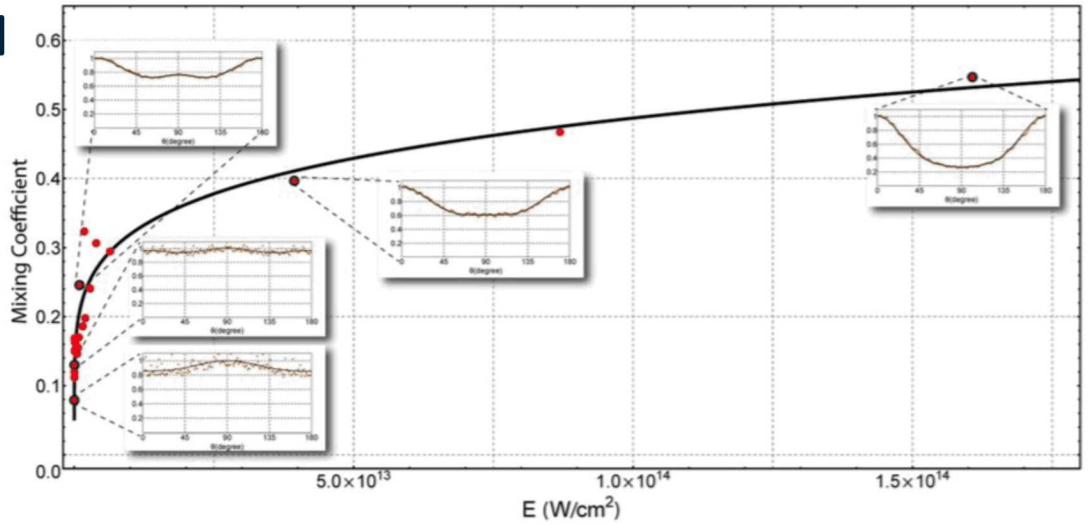




The angular distribution of the inner ring can be well fit with a model that involves mixing of rotational wave functions as a function of laser intensity. At the lowest laser power at which we observe signal we can see evidence of H2(E,F J=2) quantum state mixing

GAS PHASE CHEMICAL PHYSICS

Analysis of the alignment of the H2 (E,F J=0 and J=1) as a function of 532-nm laser intensity resulted in polarizability measurement

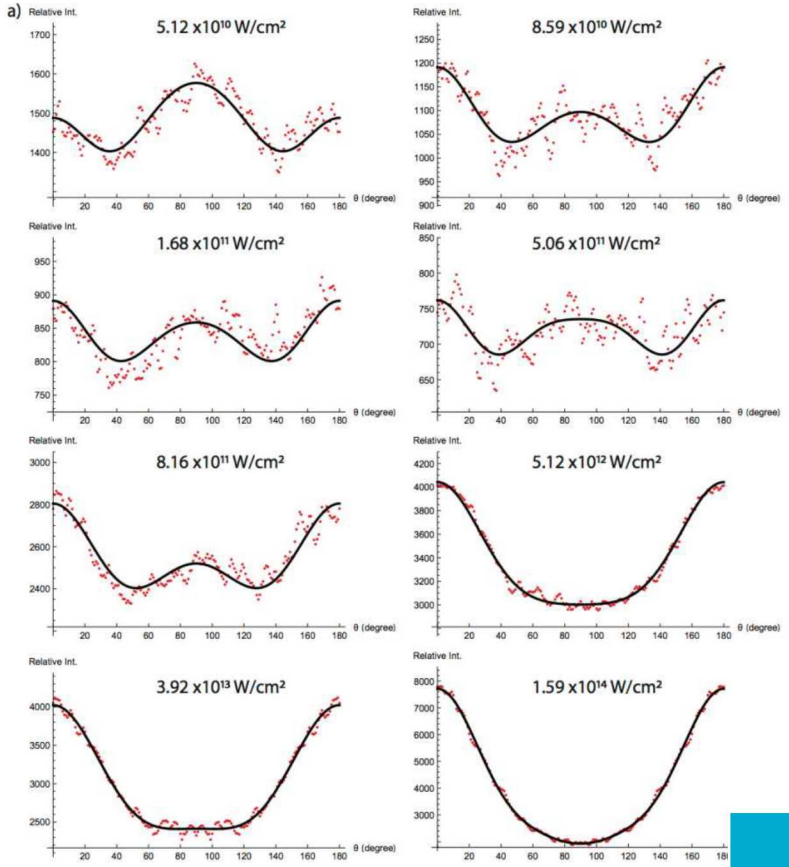


Mixing coefficient is measure of the mixing between the different rotational states of the H_2 molecule. From the slope of this line at low laser intensity we extract the polarizability

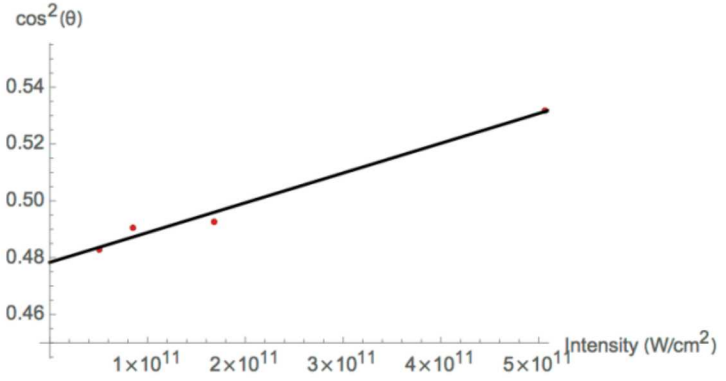
Proposed Work: To remove ambiguity for comparison to simulations, two different wavelengths will be used to prepare and probe the molecular alignment.

GAS PHASE CHEMICAL PHYSICS

By modeling the data, one can extract the polarizability anisotropy of H_2(E,F) state when irradiated with 532-nm light.



$$\langle \mathrm{Cos}^2(\theta) \rangle_{\Delta\omega} = \frac{1}{3} + \frac{10^{13}\,\delta\alpha}{135\,B}\,\mathrm{I}$$



J state	Linear Fit		Anisotropy (a.u.)
	Intercept	slope	
J0	0.5325	1.032E-13	312 ± 82

How Polarizable is the H2(E,F) state?

J state	Linear Fit		Anisotropy (a.u.)
	Intercept	slope	
J0	0.5325	1.032E-13	312 ± 82

Theoretical values in static fields:
$\delta\alpha$ ground state = 1.9 a.u.*
$\delta\alpha$ E,F state = -9600 a.u.+

* E. Ishiguro, et al; Proc. Phys. Soc. A 65, 178 (1951)
+ Komasa, J.; Adv. Quant. Chem. 48, 151 (2005).

- Anisotropy ($\delta\alpha$) values of 312 a.u. is almost 46, Å^3, respectively.
- By comparison CS_2 has 10 Å^3, I_2 has 7 Å^3 and 1,4 diiodobenzene has about 18 Å^3.
- The most polarizable state of any molecule to date.

Conclusions

Doing dynamics on transient excited states allows
one to have better preparation of the initial conditions.

We have demonstrated this preparation for NO(A) and H2 (EF)
both having 200 ns lifetimes.

Dynamics not observed on the ground state are studied. In Hydrogen
he mixing with nearby electronic states creates superposition states
with strange characteristics. For NO (A) an oscillating orientation of the J vector
is observed and utilized for collisional studies.