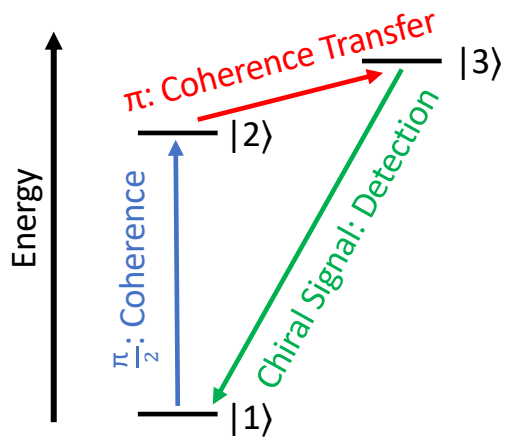
Progress on the Development of a Millimeter-Wave Chirality Spectrometer (ChiralSpec)

Martin Holdren

Shanshan Yu, Deacon Nemchick, John Pearson, Brooks Pate (UVa)



Jet Propulsion Laboratory
California Institute of Technology

PICASSO

ISMS, June 19, 2019

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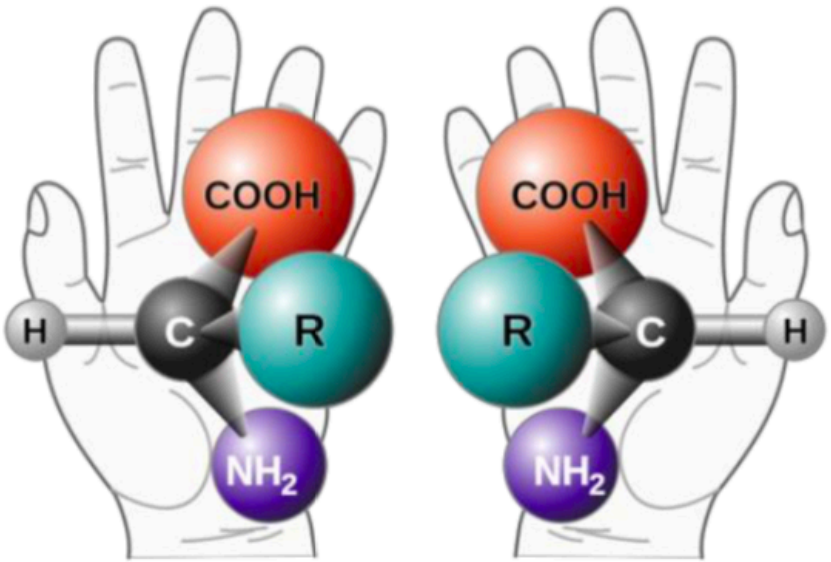
What Is Chirality?:

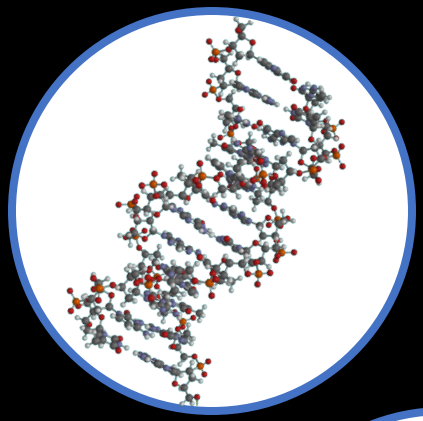


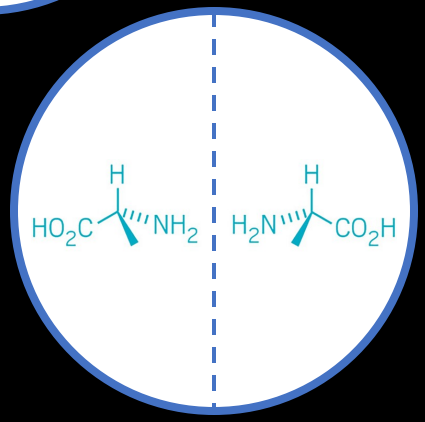
<u>Enantiomers:</u> Optical isomers that are mirror images of each other that are non-superimposable

- Same molecular weight
- Identical in many physical and chemical properties making them challenging to distinguish
- Only act differently in chiral environments

Image Source: https://en.wikipedia.org/wiki/Chirality_(chemistry)

Motivation:





Homochiral Origins of Life:

- In nature, chiral molecules used by organisms are predominately homochiral
- Can this be used as a chemical 'biomarker'?

Goal:

- Instrument for detecting and quantifying enantiomeric excess (**EE**) for use on a rover or probe mission.

1. https://www.khanacademy.org/test-prep/mcat/chemical-processes/stereochemistry/a/chiral-drugs
2. https://www.chem.ucla.edu/~harding/IGOC/D/dna.html
3. https://cen.acs.org/analytical-chemistry/separations/Magnetic-fields-fish-enantiomers/96/i20

Where to Look?:

REPORT

Radar evidence of subglacial liquid water on Mars

R. Orosei[1,*], S. E. Lauro[2], E. Pettinelli[2], A. Cicchetti[3], M. Coradini[4], B. Cosciotti[2], F. Di Paolo[1], E. Flamini[4], E. Mattei[3], M. Paj…
+ See all authors and affiliations

Science 03 Aug 2018:
Vol. 361, Issue 6401, pp. 490-493
DOI: 10.1126/science.aar7268

RESEARCH ARTICLE | ASTROBIOLOGY

ALMA detection and astrobiological potential of vinyl cyanide on Titan

Maureen Y. Palmer[1,2,3,*], Martin A. Cordiner[1,3], Conor A. Nixon[1], Steven B. Charnley[1], Nicholas A. Teanby[4], Zbigniew Kisiel[5]…
+ See all authors and affiliations

Science Advances 28 Jul 2017:
Vol. 3, no. 7, e1700022
DOI: 10.1126/sciadv.1700022

Organic compounds on comet 67P/Churyumov-Gerasimenko revealed by COSAC mass spectrometry

Fred Goesmann[1,*], Helmut Rosenbauer[1], Jan Hendrik Bredehöft[2], Michel Cabane[3], Pascale Ehrenfreund[4,5], Thomas Gautier[6]…
+ See all authors and affiliations

Science 31 Jul 2015:
Vol. 349, Issue 6247, aab0689
DOI: 10.1126/science.aab0689

Right: www.nasa.gov/image-feature/jpl/pia21904/contrasting-crescents
Left: https://www.bbc.com/news/science-environment-44952710
Middle: https://solarsystem.nasa.gov/moons/saturn-moons/enceladus/in-depth/
Bottom: https://europa.nasa.gov/resources/29/europas-stunning-surface/

Where to Look?:

letters to nature

Nature **296**, 837 - 840 (29 April 1982); doi:10.1038/296837a0

Distribution and enantiomeric composition of amino acids in the Murchison meteorite

MICHAEL H. ENGEL & BARTHOLOMEW NAGY

Laboratory of Organic Geochemistry, Department of Geosciences, The University of Arizona, Tucson, Arizona 85721, USA
*Present address: Geophysical Laboratory, Carnegie Institution of Washington, 2801 Upton St North-west, Washington, DC 20008, USA.

Discovery of the interstellar chiral molecule propylene oxide (CH_3CHCH_2O)

Brett A. McGuire[1,2,*,†], P. Brandon Carroll[2,*,†], Ryan A. Loomis[3], Ian A. Finneran[2], Philip R. Jewell[1], Anthony J. Remijan[1], Ge...
+ See all authors and affiliations

Science 17 Jun 2016:
Vol. 352, Issue 6292, pp. 1449-1452
DOI: 10.1126/science.aae0328

Peer Reviewed
← see details

Redox and pH gradients drive amino acid synthesis in iron oxyhydroxide mineral systems

Laura M. Barge, Erika Flores, Marc M. Baum, David G. VanderVelde, and Michael J. Russell

PNAS March 12, 2019 116 (11) 4828-4833; published ahead of print February 25, 2019
https://doi.org/10.1073/pnas.1812098116

Comparative Technologies for Planetary Science:

Technology	Methodology	Sensitivity	Comments
ChiralSpec	Rotational spectroscopy[a] Targets in gas phase	Gas[b]: 10^9 molecules/cm^3 with 1L volume Solid: ppm level with 0.2mg sample	Non-invasive Insensitive to non-polar molecules
GC-MS[c]	Gas chromatography Targets in gas phase	ppm	Need separating sample mixtures before measurements
MILA[d]	Laser induced fluorescence Targets in aqueous phase	Liquid: 100 pM (10^{-10} mol/L)	

[a] based on gaseous molecules absorbing or emitting light at fingerprint frequencies due to their free rotation

[b] Sensitivity varies with molecular line strength; The estimation was done with 1 minute INT time and typical line strengths in mm-wave

[c] Implemented in Rosetta/COSAC and Curiosity/SAM

[d] Microfluidic Life Analyzer, capillary electrophoresis based laser induced fluorescence

Three-Wave Mixing: Measurement Principle

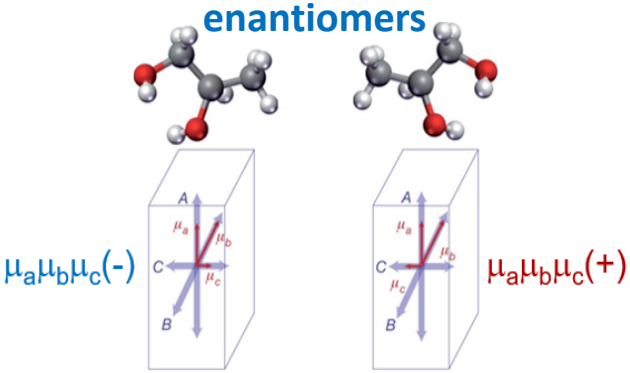
LETTER

doi:10.1038/nature12150

Enantiomer-specific detection of chiral molecules via microwave spectroscopy

David Patterson[1], Melanie Schnell[2,3] & John M. Doyle[1]

The sign of the product of dipole vector components are opposite for enantiomers



Three-Wave Mixing: Measurement Principle

LETTER

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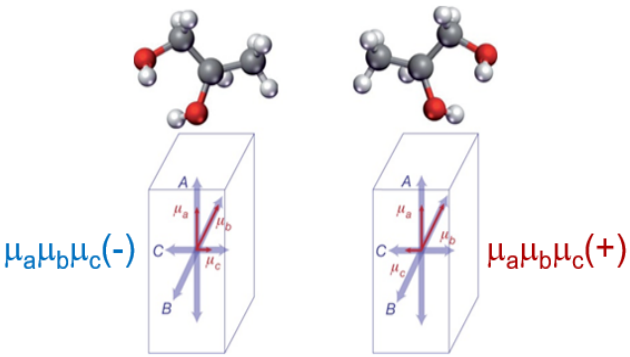
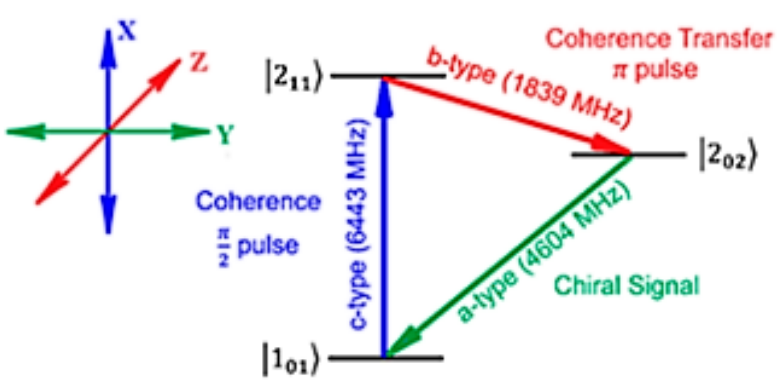
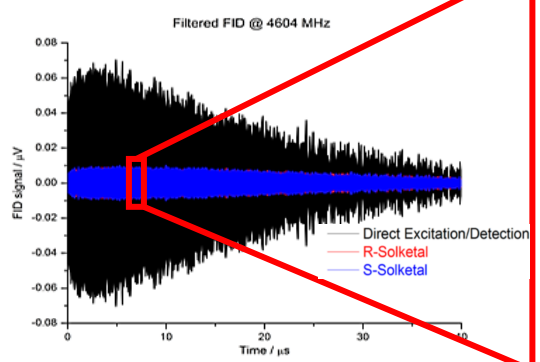
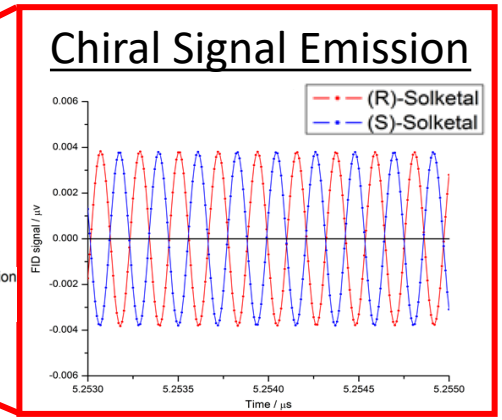


cm-Wave Regime Demonstration:







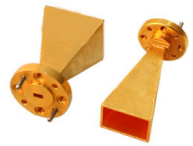
Differs in phase by π radians

Lobsiger, S.; Perez, C.; Evangelisti, L.; Lehmann, K. K.; Pate, B. H., Molecular Structure and Chirality Detection by Fourier Transform Microwave Spectroscopy. *J Phys Chem Lett* **2015,** *6* (1), 196-200.

SWaP Reduction - Centimeter-Wave to Millimeter-Wave:

Wave Antennae:

1-12GHz
~2kg
~ 11''x 6''x 9''

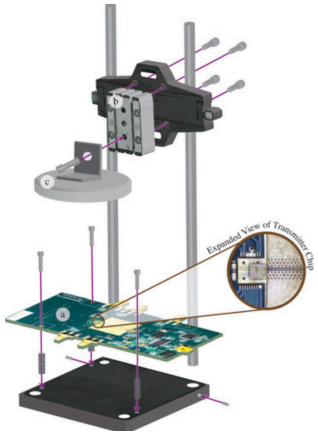


60.5-91.9GHz
~100g
~ 4''x 1''x 2''

Amplifiers:

0.8-2GHz, 10W
+28V, 5A

75-110GHz
+8V, 110mA

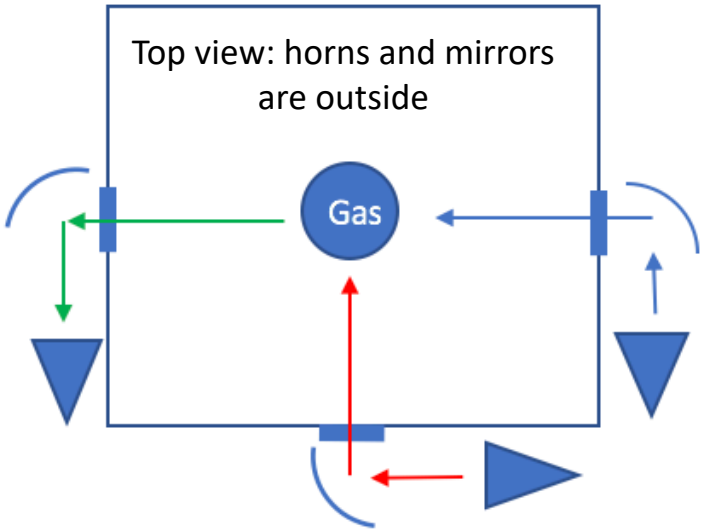


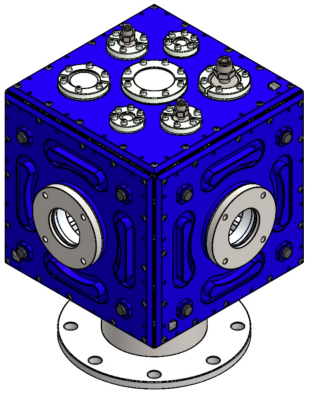
A 90-102 GHz CMOS based pulsed Fourier transform spectrometer: New approaches for *in situ* chemical detection and millimeter-wave cavity-based molecular spectroscopy

Review of Scientific Instruments **89**, 073109 (2018); https://doi.org/10.1063/1.5025729

Deacon J. Nemchick[1,a)], Brian J. Drouin[1,b)], Matthew J. Cich[1,c)], Timothy Crawford[1,d)], Adrian J. Tang[2,3,e)], Yanghyo Kim[2,f)], Theodore J. Reck[2,g)], Erich T. Schlecht[2,h)], M.-C. Frank Chang[3,i)], *and* Gabriel Virbila[3,j)]

ChiralSpec (without the resonators)

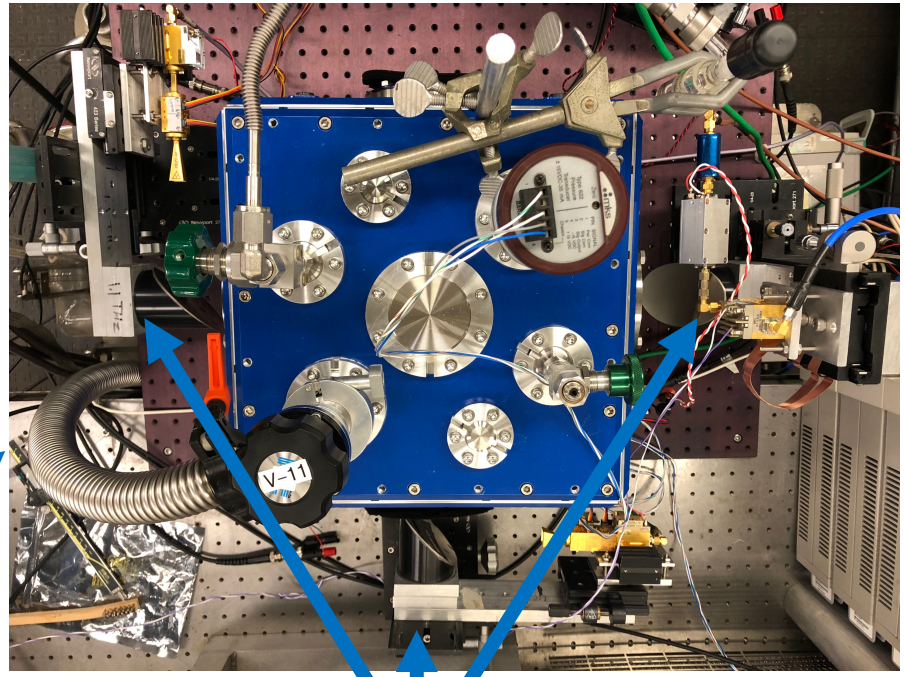




Chamber for gas

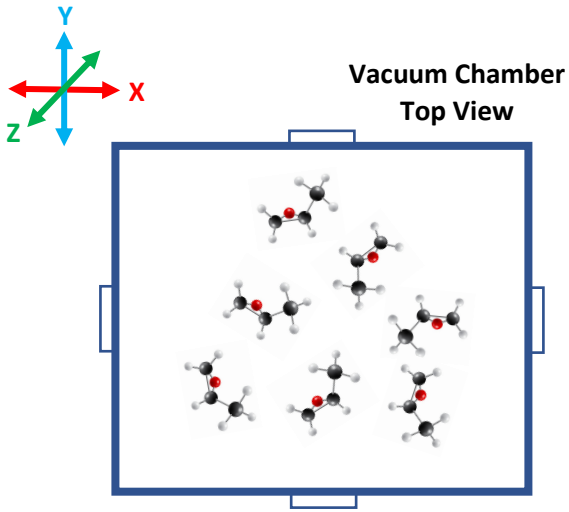
+

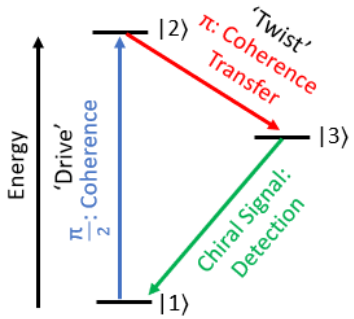
Transmitter and mirror mounted together



Use off-axis parabolic mirrors to have better control on beam sizes

ChiralSpec Measurement Scheme:





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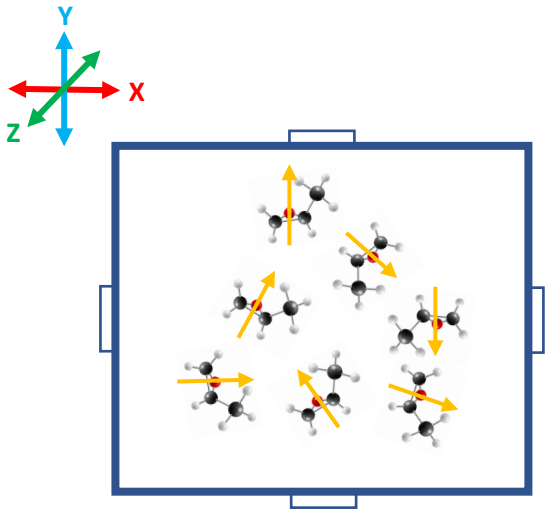

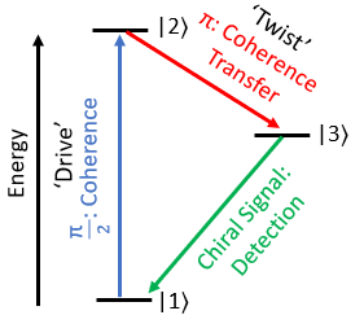

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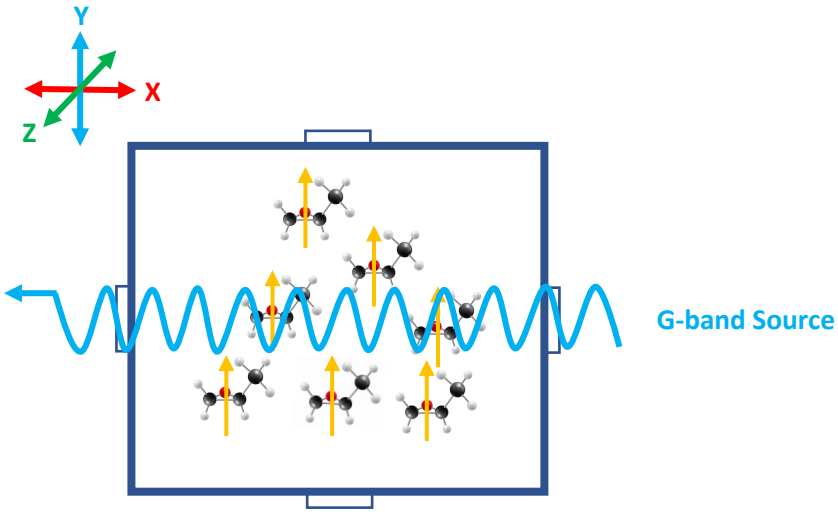

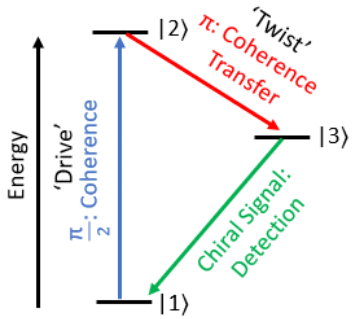

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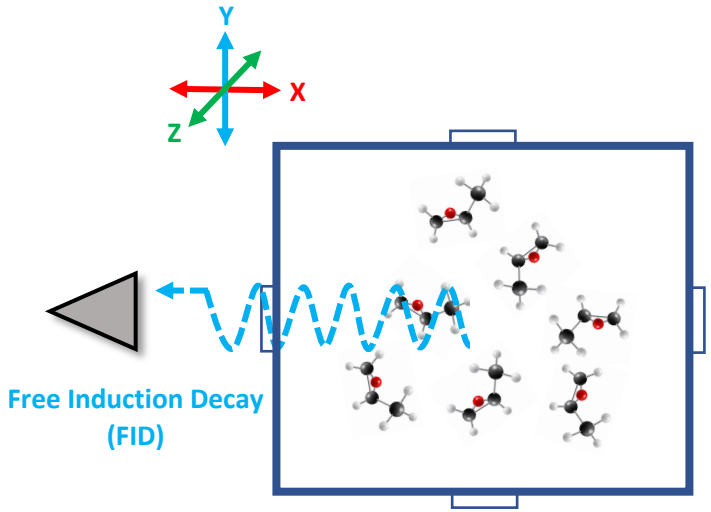

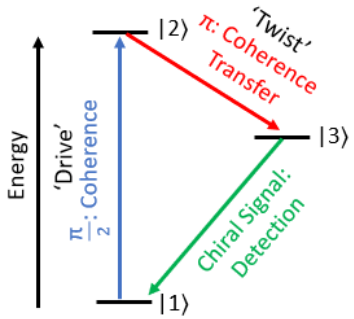

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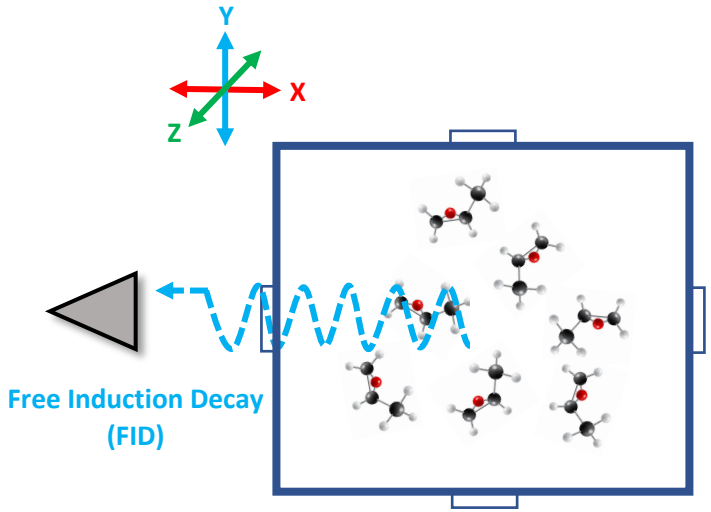

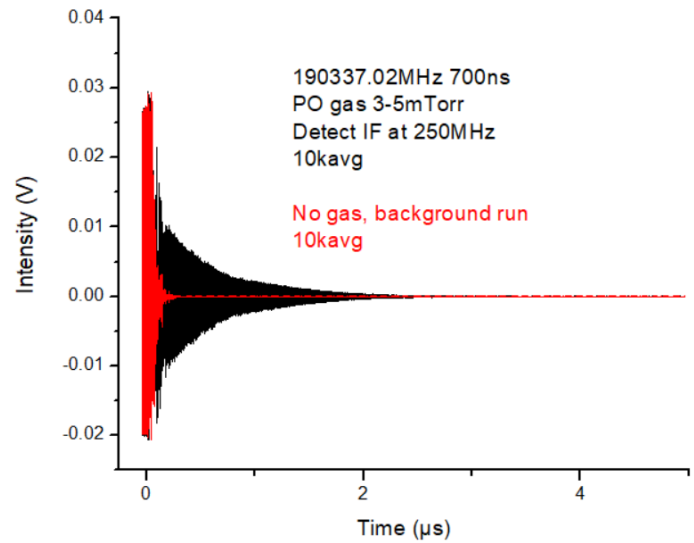

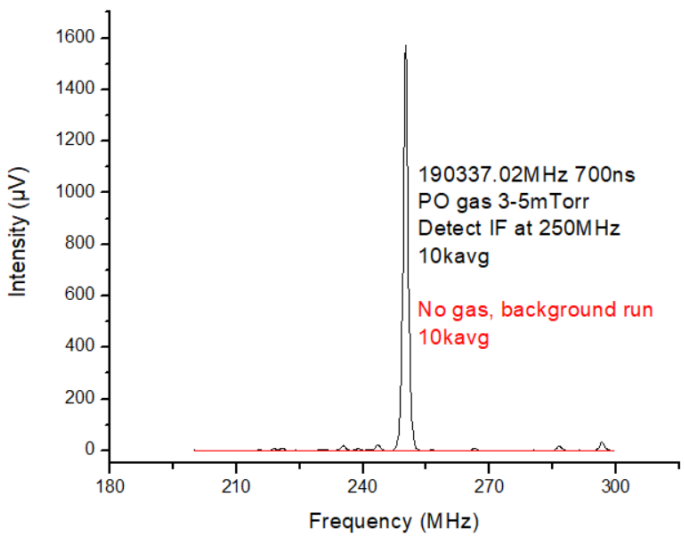

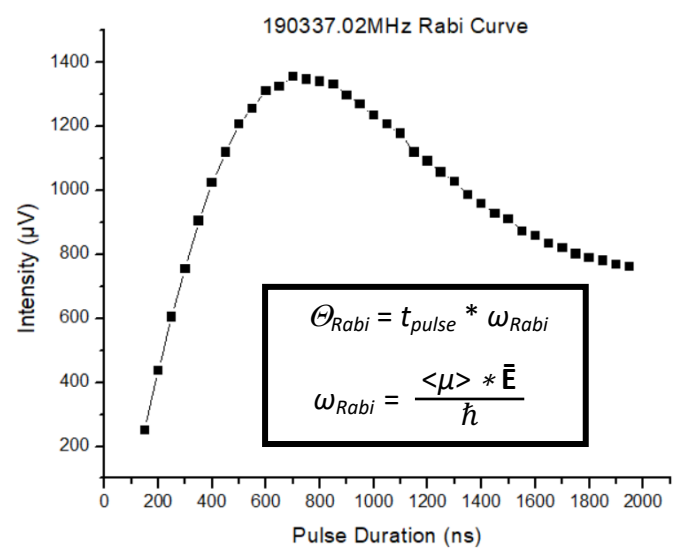

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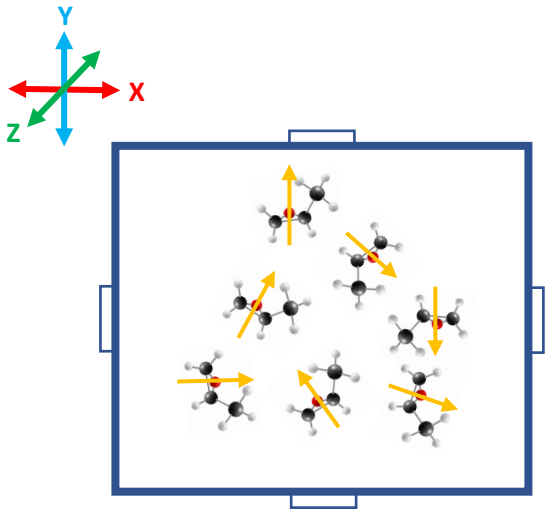

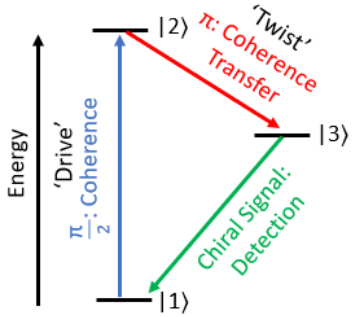

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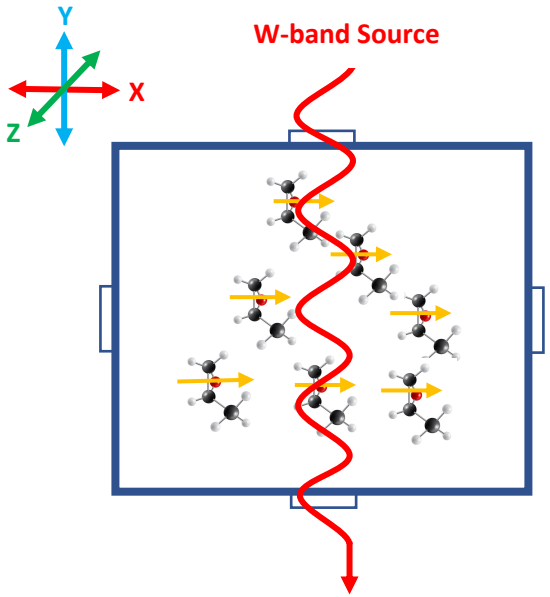

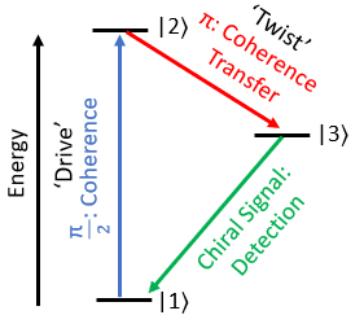

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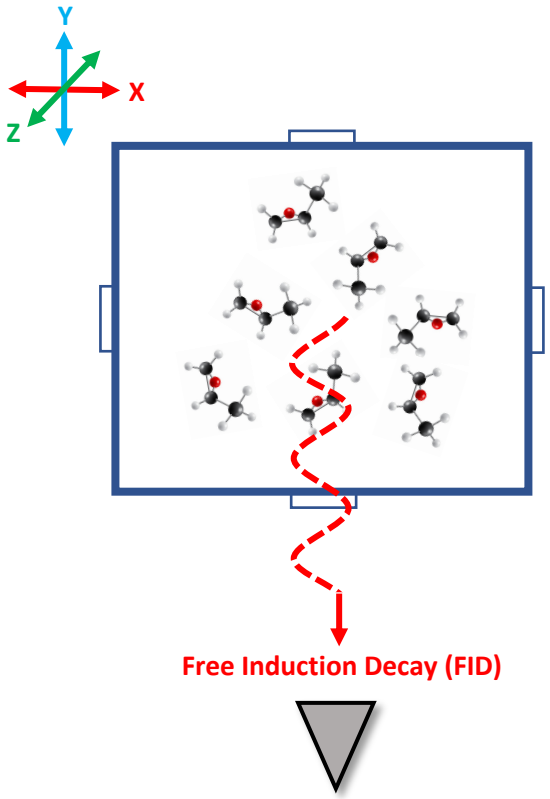

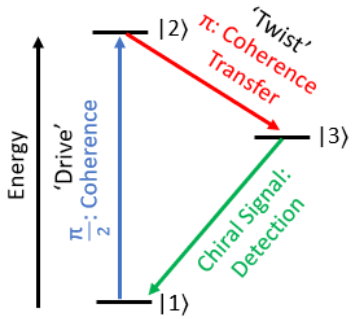

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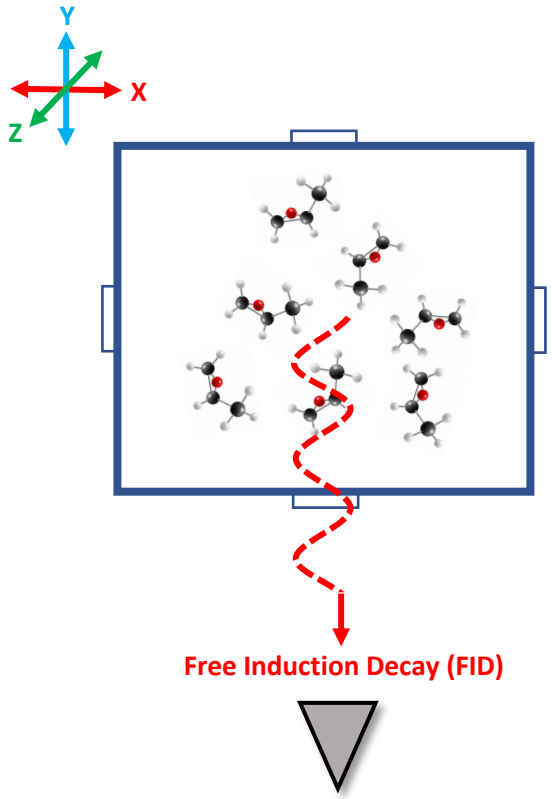
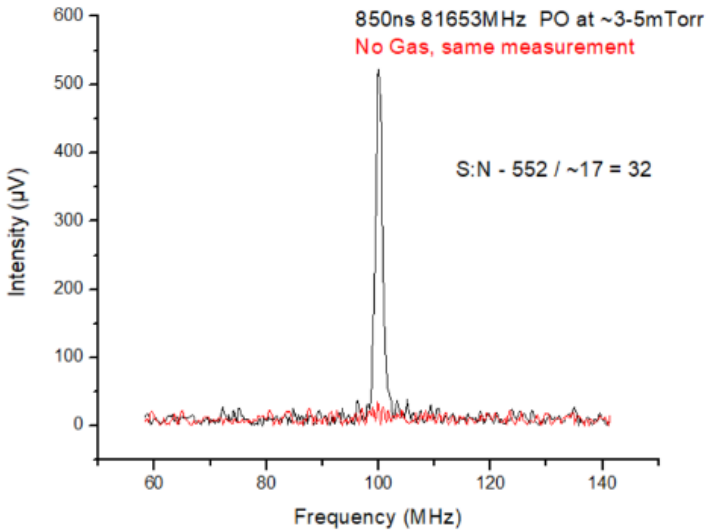
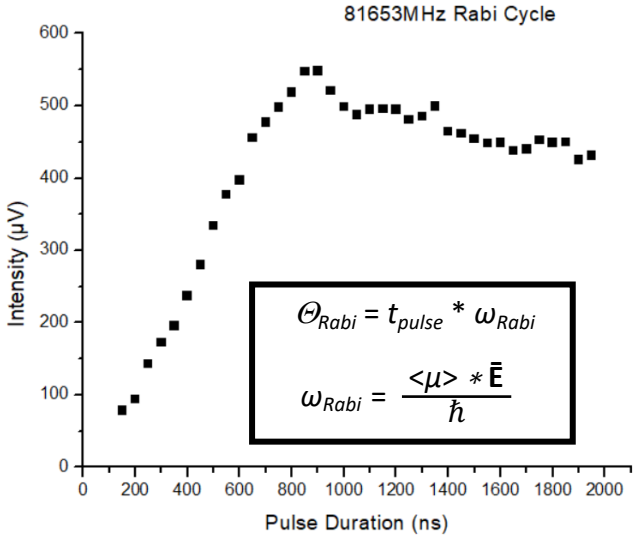


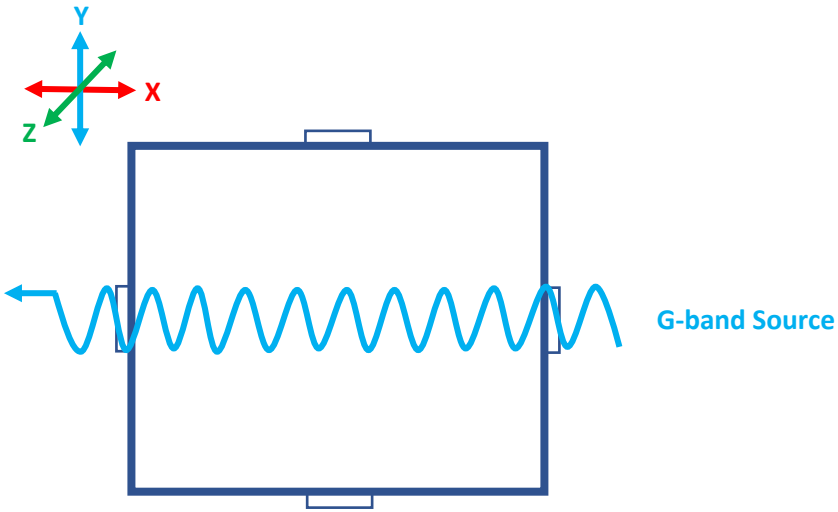


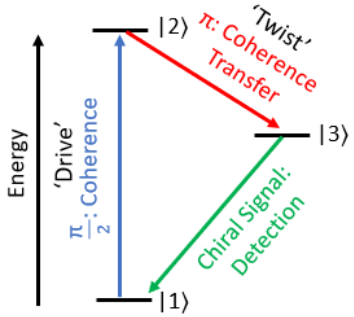


$$\Theta_{Rabi} = t_{pulse} * \omega_{Rabi}$$

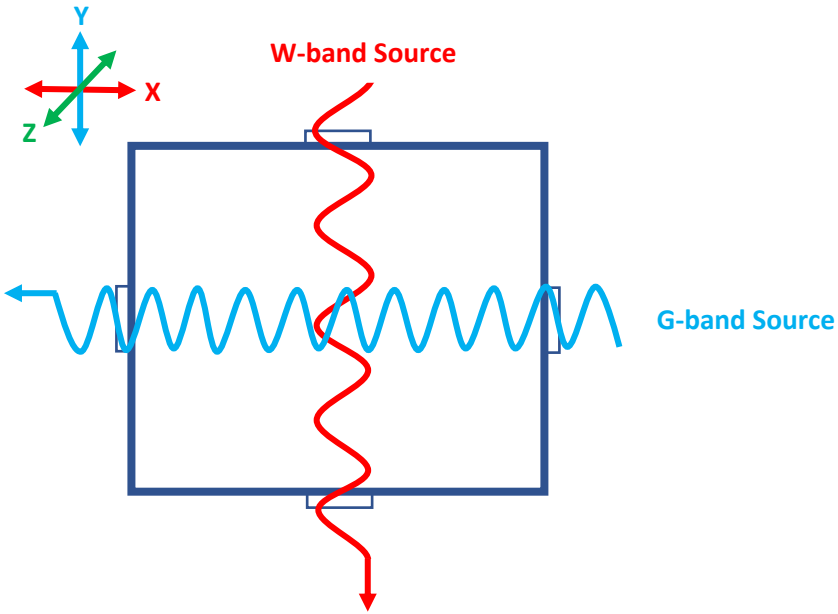
$$\omega_{Rabi} = \frac{\langle\mu\rangle * \bar{E}}{\hbar}$$

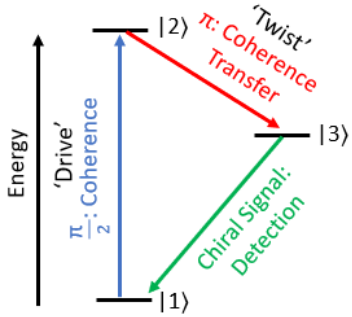
ChiralSpec Three-Wave Mixing:



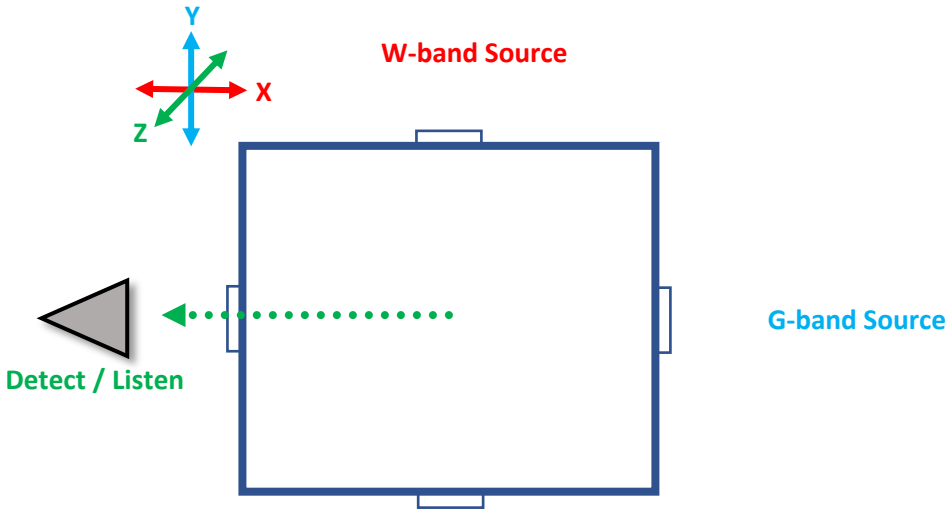


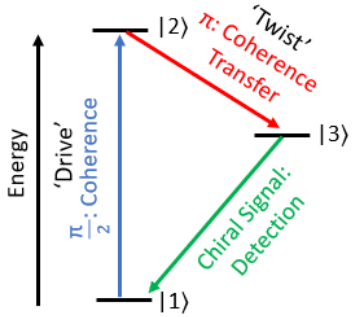
ChiralSpec Three-Wave Mixing:





ChiralSpec Three-Wave Mixing:

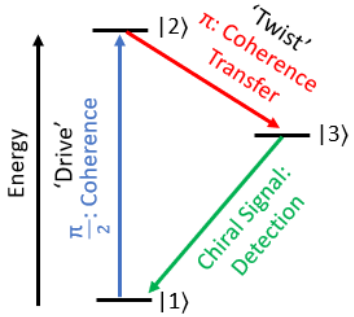




The chiral signal is:

- Proportional to enantiomeric excess
- Proportional to population difference in states of first excitation
- Proportional to its transition dipole component
- Has mutually orthogonal polarization to the excitation pulses
- 'Background-free'

ChiralSpec Instrument Progress:



G-band (175-200GHz) set up and tested:

- 50-80mW

W-band (75-90GHz) set up and tested:

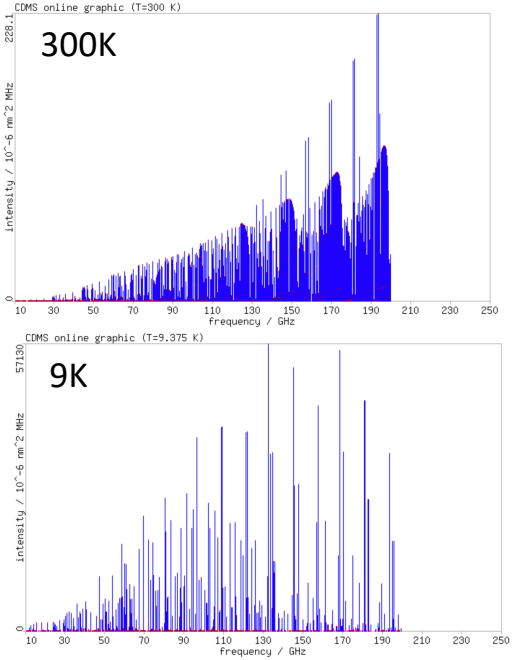
- 150-200mW

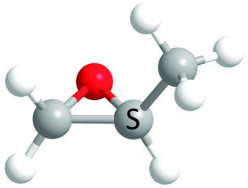
Detection W-band set up and tested:

- Low noise amplifier, low noise figure mixer, filters

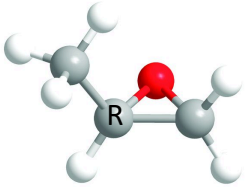
Test case molecule:

- Propylene Oxide, 3-5mTorr vapor pressure, room temperature

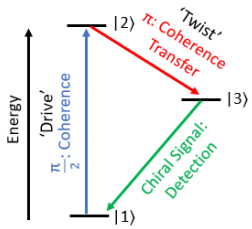




Propylene Oxide
$|\mu_a|$: 0.95D
$|\mu_b|$: 1.67D
$|\mu_c|$: 0.56D



ChiralSpec Measured Transitions:



G-Band:

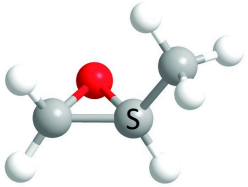
***Multiple lines here*

Frequency (MHz)	Type	Pulse Length (ns)	Signal to Noise
181168.31**	b	600	12
182844.28	b	700	12
182856.21	c	700	3
183051.37	c	1000	7
190337.02	a	700	2200
191226.31	a	700	1000
193804.41**	b	1000	50
193805.50**	c	1400	4
195257.60	b	700	12

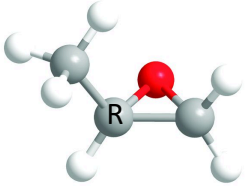
W-Band:

***Multiple lines here*

Frequency (MHz)	Type	Pulse Length (ns)	Signal to Noise
81653.37	b	850	32
81695.88	b	600	----
101298.26	a	800	2
101306.20	a	700	2
101355.49	a	500	13
101599.36	a	600	12
102268.05	c	600	3
105253.48**	c	900	5



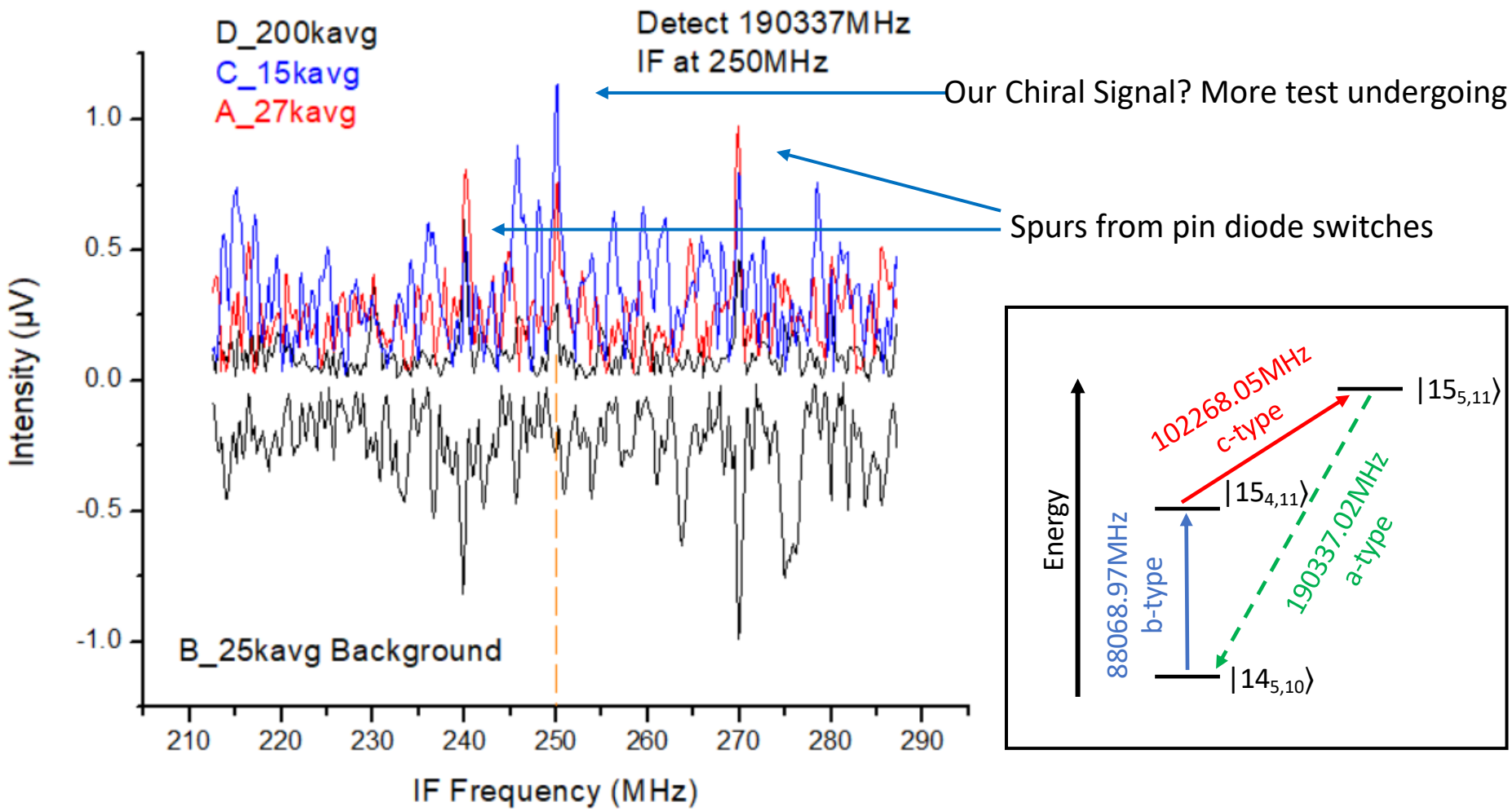
Propylene Oxide
$|\mu_a|$: 0.95D
$|\mu_b|$: 1.67D
$|\mu_c|$: 0.56D



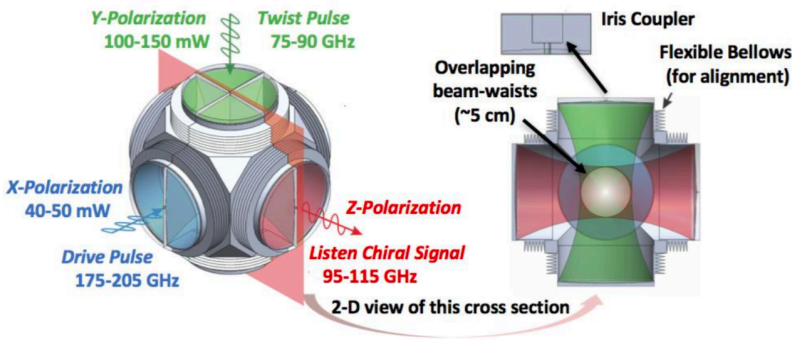
Three-wave Mixing Trials:

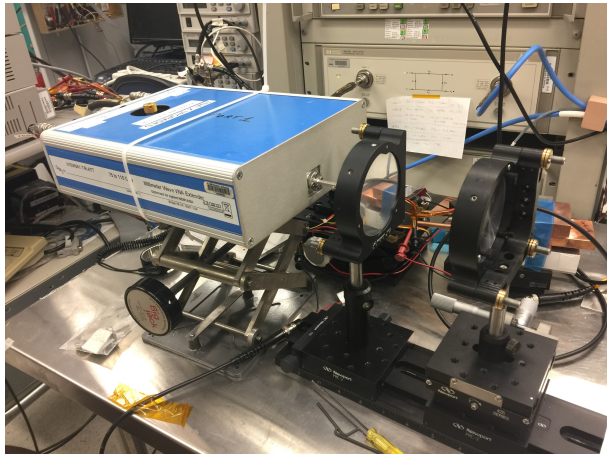
Frequency (MHz)	Type	Pulse Length (ns)
183051.37	c	1000ns
81695.88	b	Vary
101355.49	a	
195257.60	b	900
80764.80	c	Vary
114492.80	a	
182844.28	b	750
81244.93	c	Vary
101599.36	a	
190337.02	a	700
102268.05	c	Vary
88068.97	b	
183051.37	c	700
101298.26	a	Vary
81753.11	b	
88068.97	b	700
102268.05	c	Vary
190337.02	a	
101599.36	a	700
81244.93	c	Vary
182844.28	b	
103157.33	c	700
88068.97	b	Vary
191226.31	a	

Three-Wave Mixing Experiment:



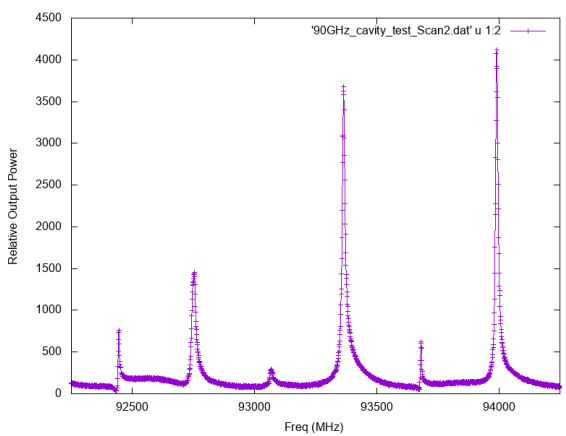
Cavity Enhancement

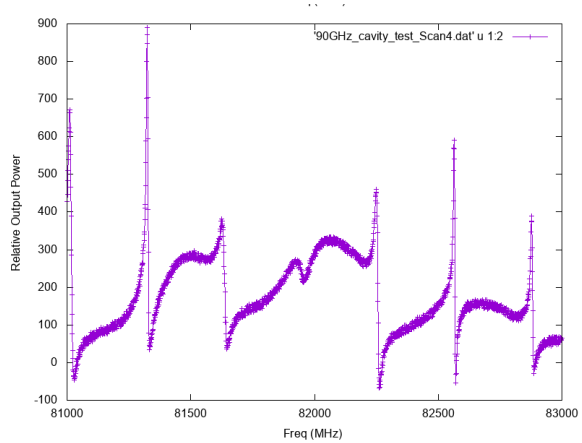


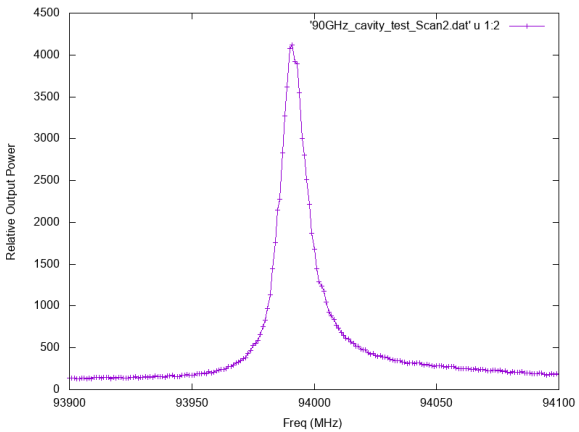


- Combines three-wave mixing with cavity resonance for signal enhancement in a three axis resonator
- Challenges due to higher frequencies and the need to down convert signals

W-Band Cavity Testing: Cavity mirrors fixed at ~80mm and frequency scanned to find modes – the mode at ~94GHz has a Q-factor of ~6800







Conclusion and Future Work:

- W-band (75-100GHz) and G-band sources (175-200GHz) as well as detection chains have been designed, tested, and optimized
- ChiralSpec is currently underway to detect chiral signals
- Improving signal to noise with new synthesizers, quieter mixers, and new signal processing in future work

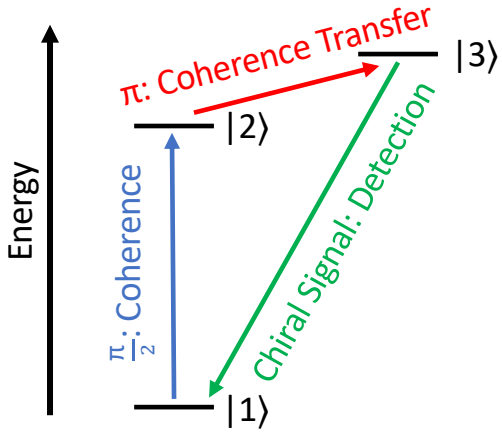
Acknowledgements:

- Special thanks to the Education Office and the JPL Year-Round Internship Program
- Thanks to everyone in the lab at JPL for all their help!
- The research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Prime Contract NNN12AA01C issued through the PICASSO Program by the National Aeronautics and Space Administration.

Image Source: www.nasa.gov/image-feature/jpl/pia21904/contrasting-crescents

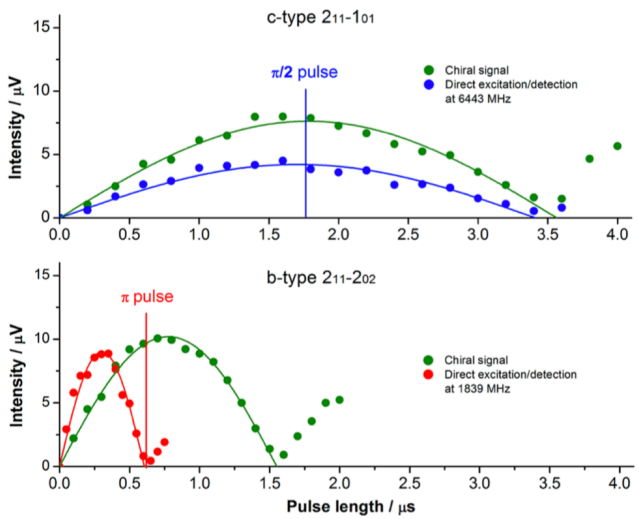
Appendix - Measuring Enantiomeric Excess (EE):

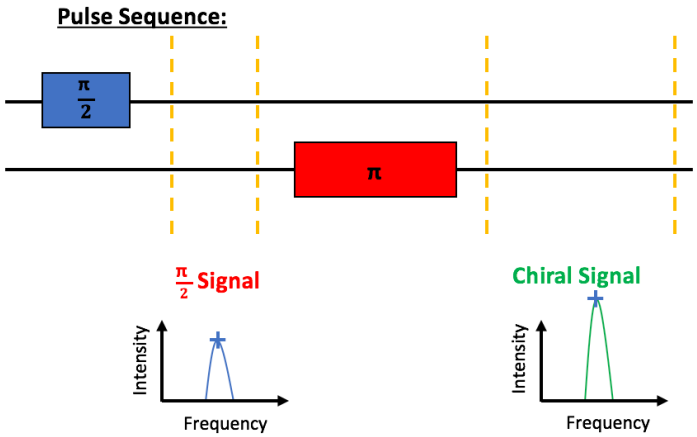
$$EE = \frac{N_L - N_R}{N_L + N_R} = C * \frac{Chiral\ Signal}{\frac{\pi}{2}\ Signal}$$



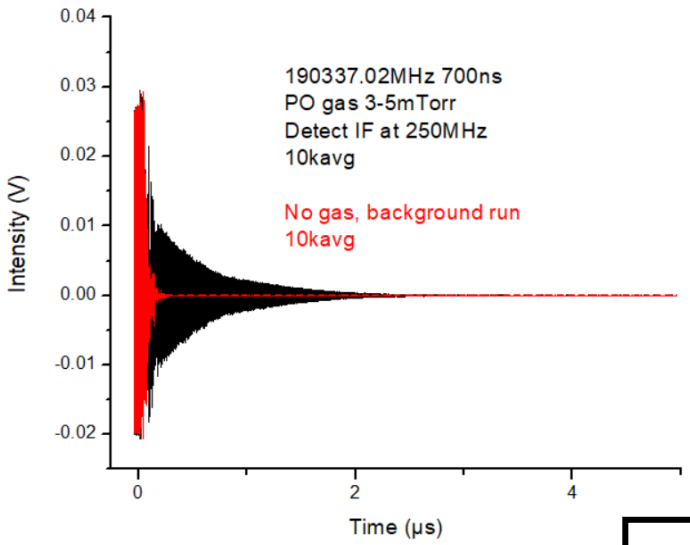
Optimization:

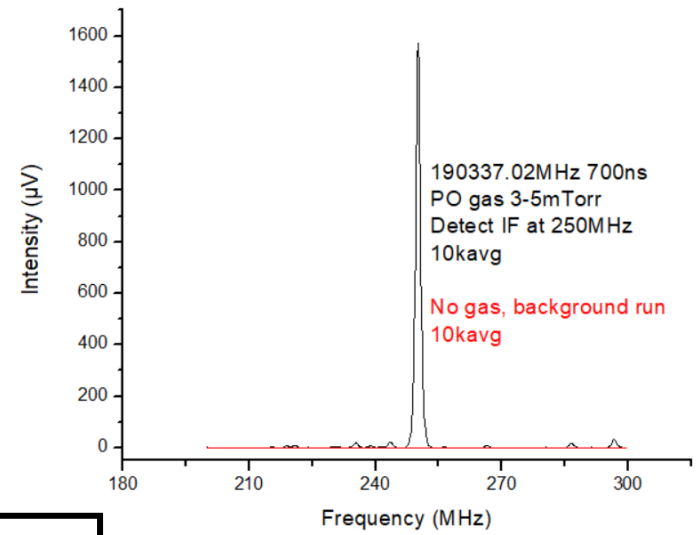
- Vary pulse duration for optimal π/2-pulse condition
- Vary second pulse for optimal π-pulse condition by monitoring chiral signal while keeping π/2 pulse duration fixed





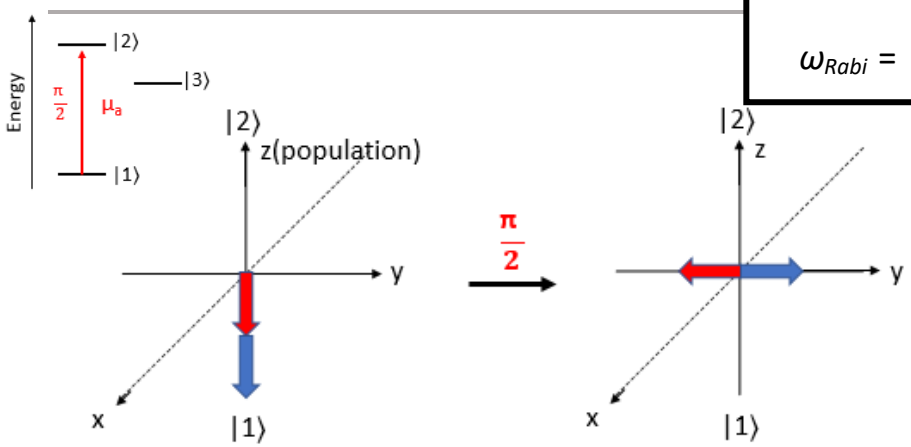
Appendix - Optimizing Cycles – Rabi Curves:

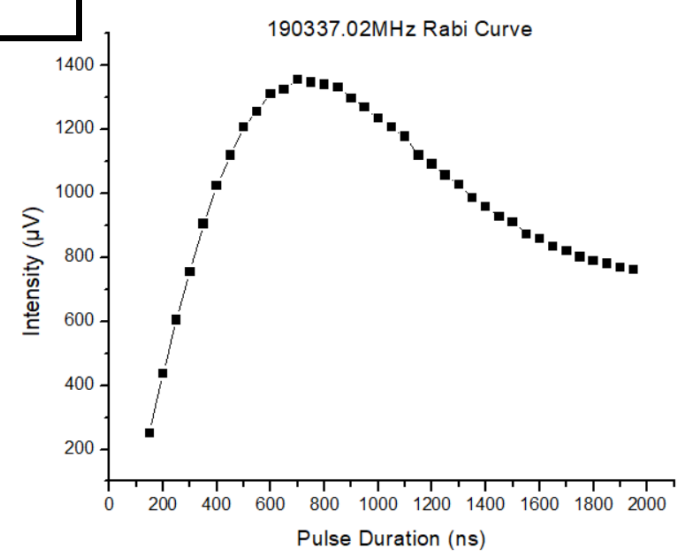




$$\Theta_{Rabi} = t_{pulse} * \omega_{Rabi}$$

$$\omega_{Rabi} = \frac{\langle\mu\rangle * \bar{E}}{\hbar}$$





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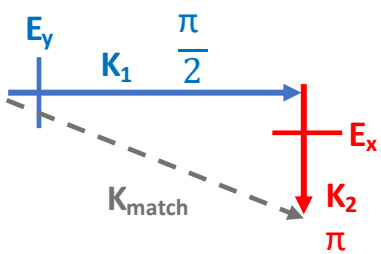
J.-U. Grabow, *Angew. Chem. Int. Ed.* **2013**, 52, 11698-11700; *Angew. Chem.* **2013**, *125*, 11914-11916; J.-U. Grabow, *International Symposium on Molecular Spectroscopy*, Plenary Lecture, **2015**.

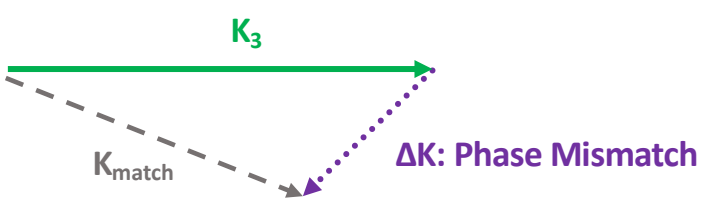
Appendix - Challenges for ChiralSpec:

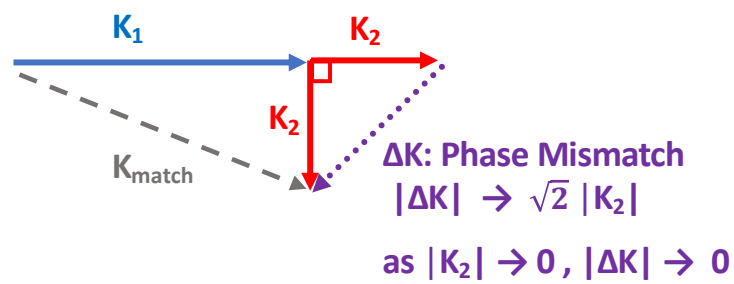
- **Phase matching**

$\bar{K} \perp \bar{B} \perp \bar{E}$

$|\bar{K}|$ is proportional to ω_{light}

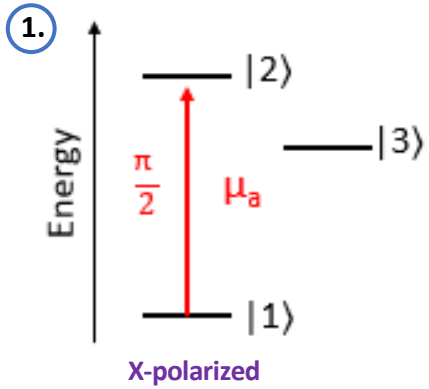




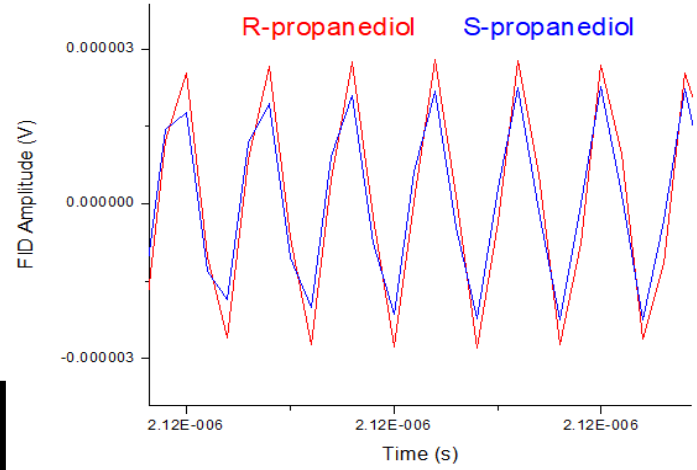


Appendix - Step by Step 3WM:

S:	R:
$-\mu_a$	μ_a
μ_b	μ_b
μ_c	μ_c

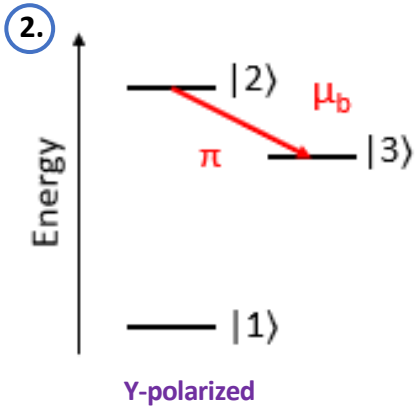


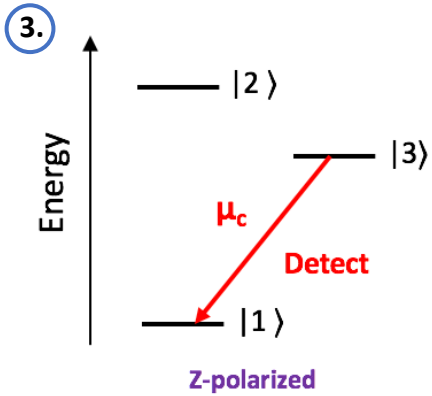
Traditional Rotational Spectroscopy



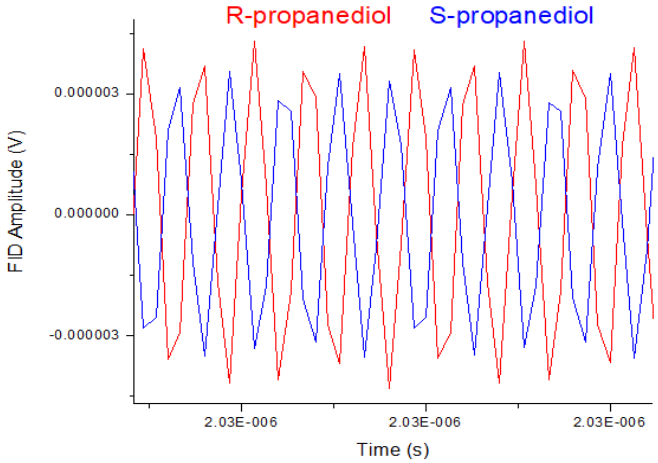
$$\Theta_{Rabi} = t_{pulse} * \omega_{Rabi}$$

$$\omega_{Rabi} = \frac{\langle\mu\rangle * \bar{E}}{\hbar}$$





Three-Wave Mixing



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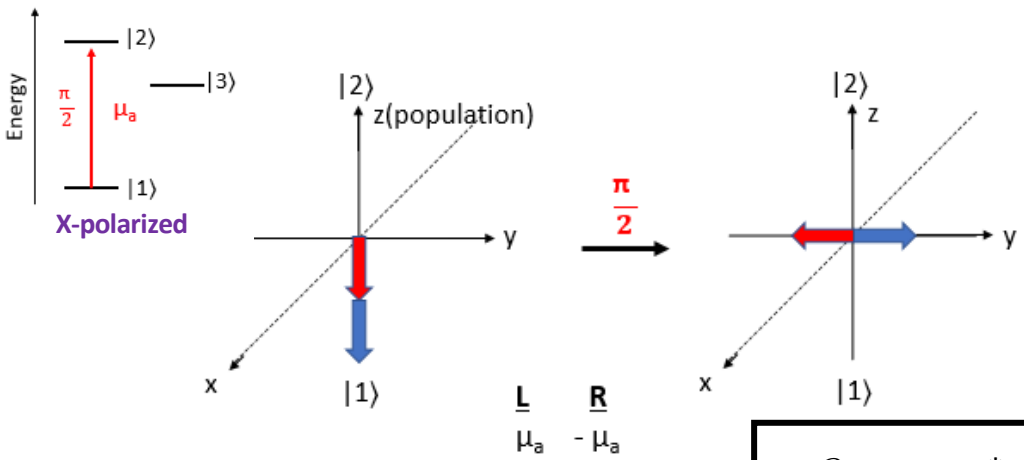
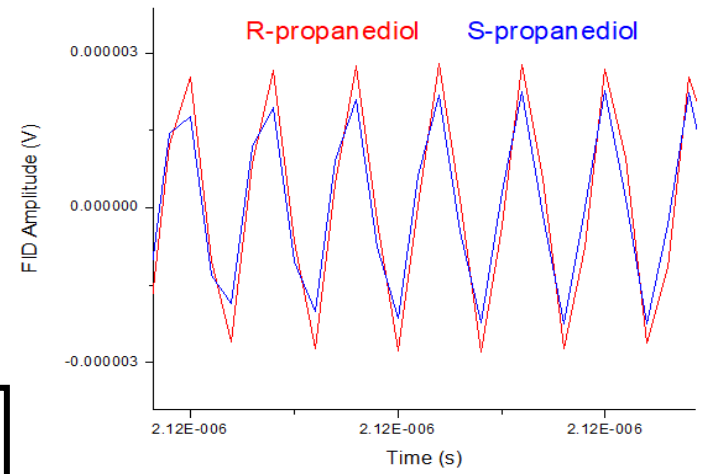
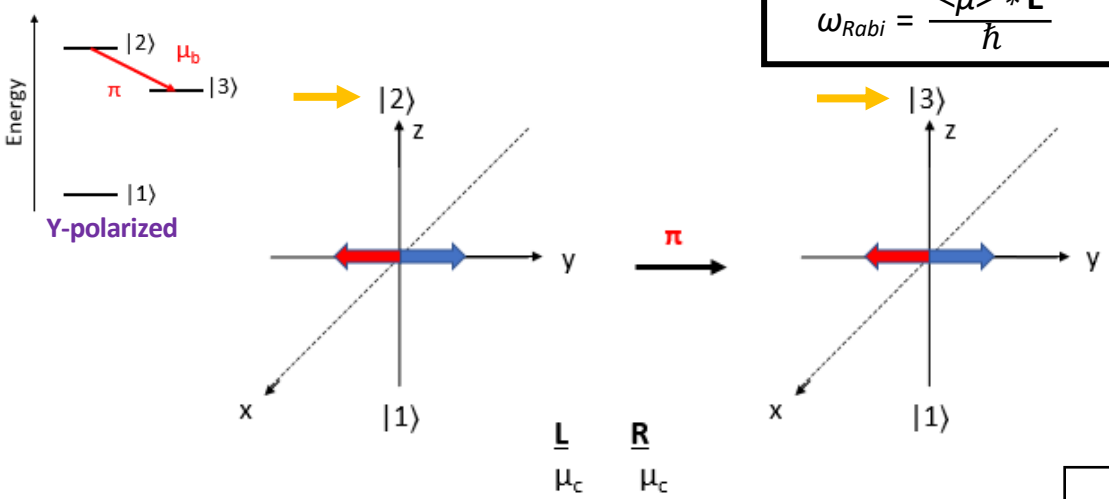
Appendix - Bloch Sphere Diagrams:

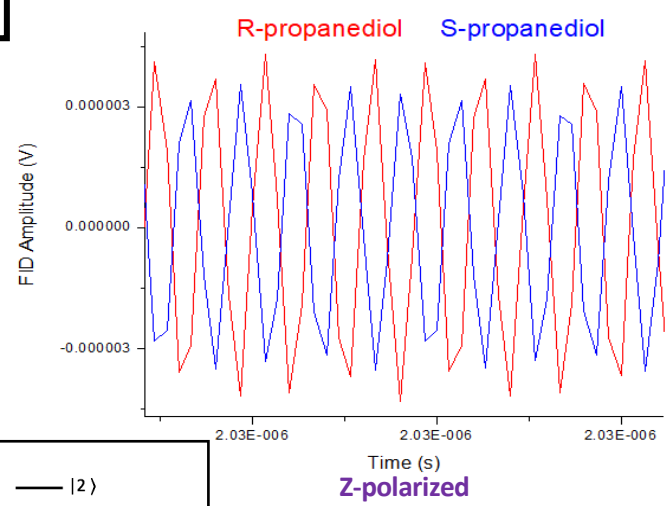


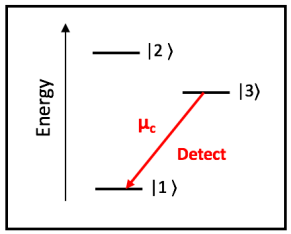


$$\Theta_{Rabi} = t_{pulse} * \omega_{Rabi}$$

$$\omega_{Rabi} = \frac{\langle\mu\rangle * \bar{E}}{\hbar}$$







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J.-U. Grabow, *Angew. Chem. Int. Ed.* **2013**, 52, 11698-11700; *Angew. Chem.* **2013**, *125*, 11914-11916; J.-U. Grabow, *International Symposium on Molecular Spectroscopy*, Plenary Lecture, **2015**.