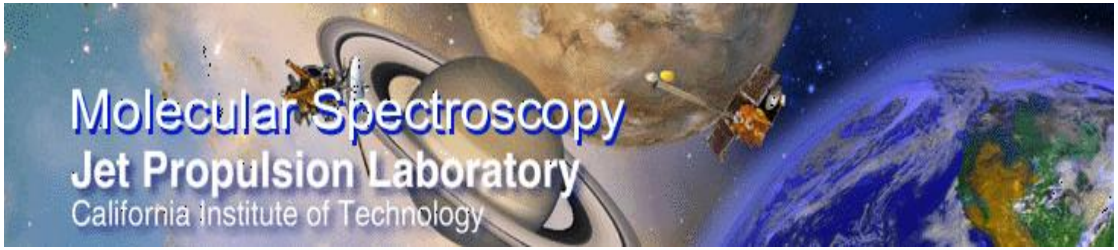
Millimeter-wave Chirality Spectrometer (ChiralSpec)

Shanshan Yu, Theodore Reck, John Pearson, Michael Malaska, Robert Hodyss

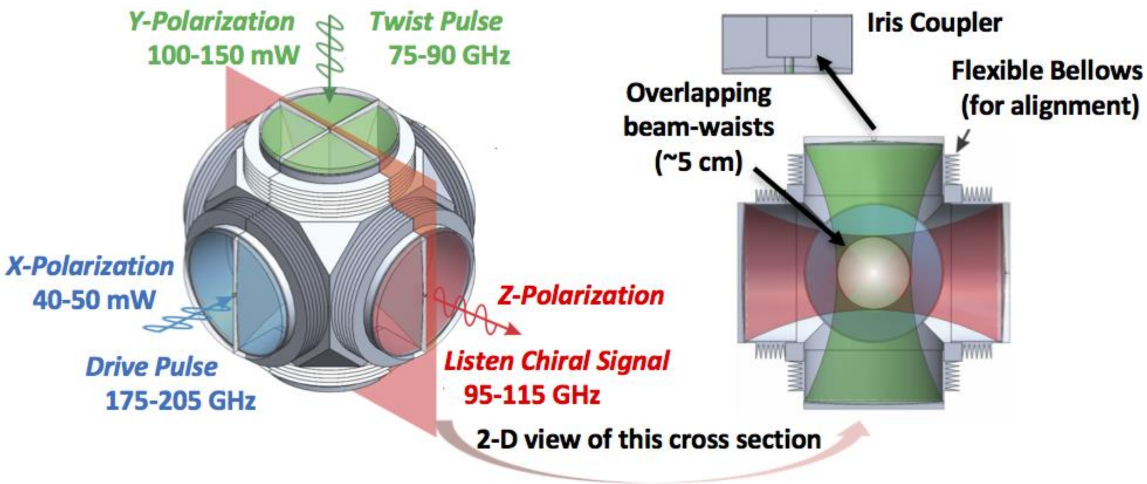
Jet Propulsion Laboratory, California Institute of Technology, USA

Brooks Pate

University of Virginia, Charlottesville, VA 22903, USA

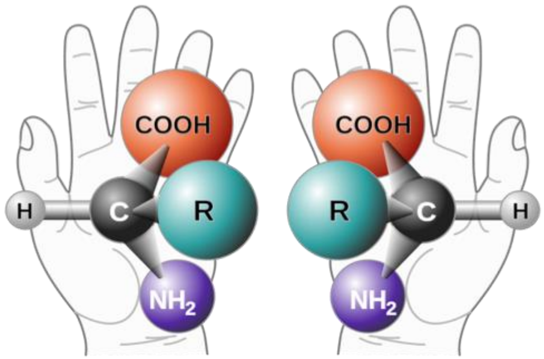


Overview of ChiralSpec



- A mm-wave 3-axis resonator spectrometer operated in two modes:
  - Chirality detection mode through 3-wave mixing principle
  - Survey mode as a traditional MW spectrometer for chemical composition analysis
- Funded by NASA Planetary Instrument Concepts for the Advancement of Solar System Observations (PICASSO)
- Chirality detection theory
  - Formulated in 2012 by Hirota
  - Demonstrated by the Patterson and Pate groups at 2-18 GHz
- Goal of this effort: experimental demonstration of chirality detection at 75-205 GHz where there is a path for instrument miniaturization.

What is Chirality?



- A chiral molecule has four different groups bound to a single carbon atom, resulting in two unsuperposable chiral forms referred as enantiomers in terms of right- and left-handedness.
- One form predominates in life on earth; thus, chiral form detection can be used as evidence for a biological environment .
- Enantiomeric pairs are identical in many physical properties, such as mass, boiling/melting point, and molecular transition frequencies.
- They are indistinguishable by mass spectroscopy and traditional microwave spectroscopy.

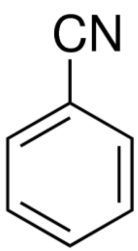
Image source: http://www.nai.arc.nasa.gov

Why ChiralSpec is Needed? (1)

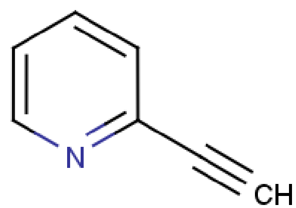
- Questions that can be answered by ChiralSpec:
  - Which amino acids are present?
  - What are the relative abundances of these amino acids?
  - Is a chiral excess present?
- Targets: Atmosphere, surface, and subsurface of Enceladus, Europa, Titan, and Mars; any bodies where amino acids, fatty acids, and other organic compounds are in gas phase or can be brought into gas phase
- Address a high-priority science objective - search for life, by looking for patterns consistent with biological synthesis, i.e., signatures of biological origin
  - Chirality of amino acids (preferred chirality in Life on Earth)
  - Amino acid distribution: biotic samples contain higher abundances of larger molecular weight amino acids - underrepresentation of glycine abundance relative to other amino acids

Why ChiralSpec is Needed? (2)

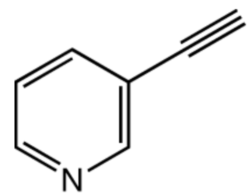
- Provide unique detection and identification capability of mixtures of structural isomers of the same molecular weight – which directly addressed three science objectives related to the history of organics, the existence of habitats beyond Earth, and search for life
- Mass spectrometers face challenges on discriminating these species
- Example: C_7H_5N, 103.124 Da, interesting to Titan, where is N inserted to?



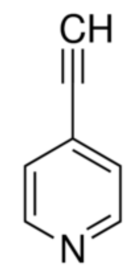
Benzonitrile



2-Ethynylpyridine



3-Ethynylpyridine



4-Ethynylpyridine

Body	Structural Isomers	Stereoisomers
Mars	PAHs, chlorinated aromatics	Amino acids
Titan	Small organics (cyclopropane v. propene), PAHs, heterocyclics	Amino acids, chiral nitriles, amines, alcohols
Europa	Fatty acids (double-bond position)	Amino acids, chiral alcohols
Enceladus	Fatty acids (double bond position)	Amino acids, chiral alcohols
Comets	Small organics (glycine v. methylcarbamic acid), PAHs	Amino acids, chiral alcohols

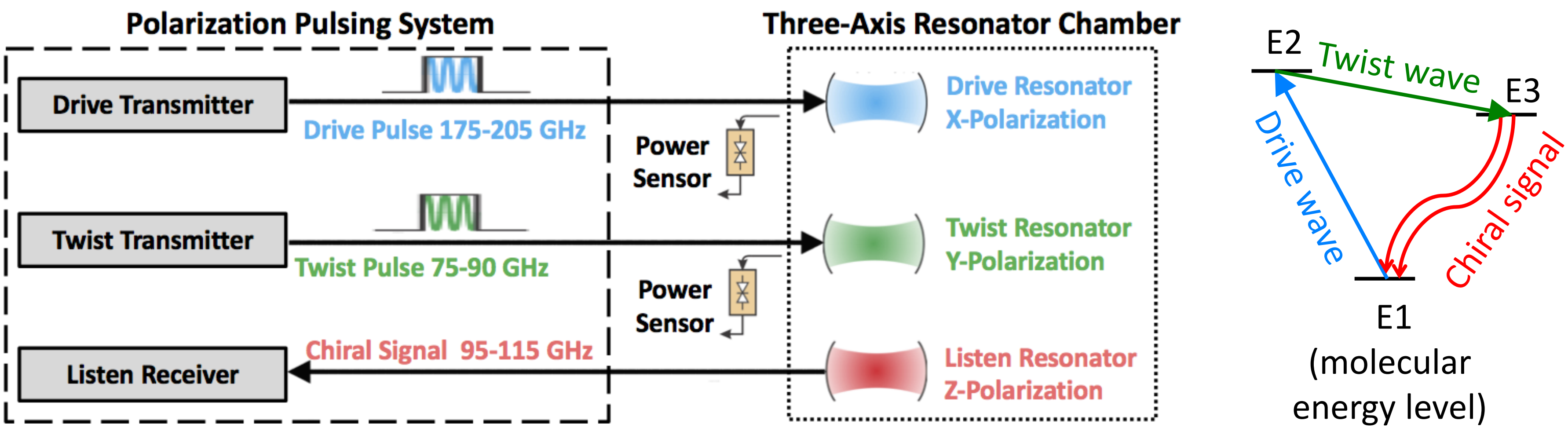
Comparative Technologies

Technology	Methodology	Sensitivity	Comments
ChiralSpec	Microwave spectroscopy Detects targets in gas phase	ppm	Provide unique isomer distinguish capability Does not require formal chemical bonding (derivatization) Insensitive to non-polar molecules Laser ablation proposed to get non-volatiles to gas phase
CE-LIF[a]	Laser induced fluorescence Detects targets in aqueous phase	sub-ppm	Limited isomer distinguish capability Liquid (CE-LIF)/gas (GCMS) handling Requires derivatization
GC-MS[b]	Gas chromatography Detects targets in gas phase	ppm	

[a] Capillary electrophoresis (CE) based laser induced fluorescence (LIF), under development (PI Peter Willis). [b] Gas chromatography (GC), implemented in Rosetta/COSAC and Curiosity/SAM.

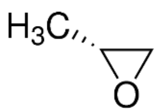
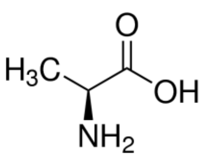
Schematic of ChiralSpec Instrument

Two subsystems: a polarization pulsing system and a three-axis resonator chamber



- ✓ ChiralSpec generates a time-domain chiral signal via exciting targeted species with two excitation pulses.
- ✓ Chiral signal of the right-handed enantiomers has an opposite phase to that of the left-handed enantiomers.
- ✓ It is this phase difference that allows enantiomer differentiation.

Benchmark Molecules

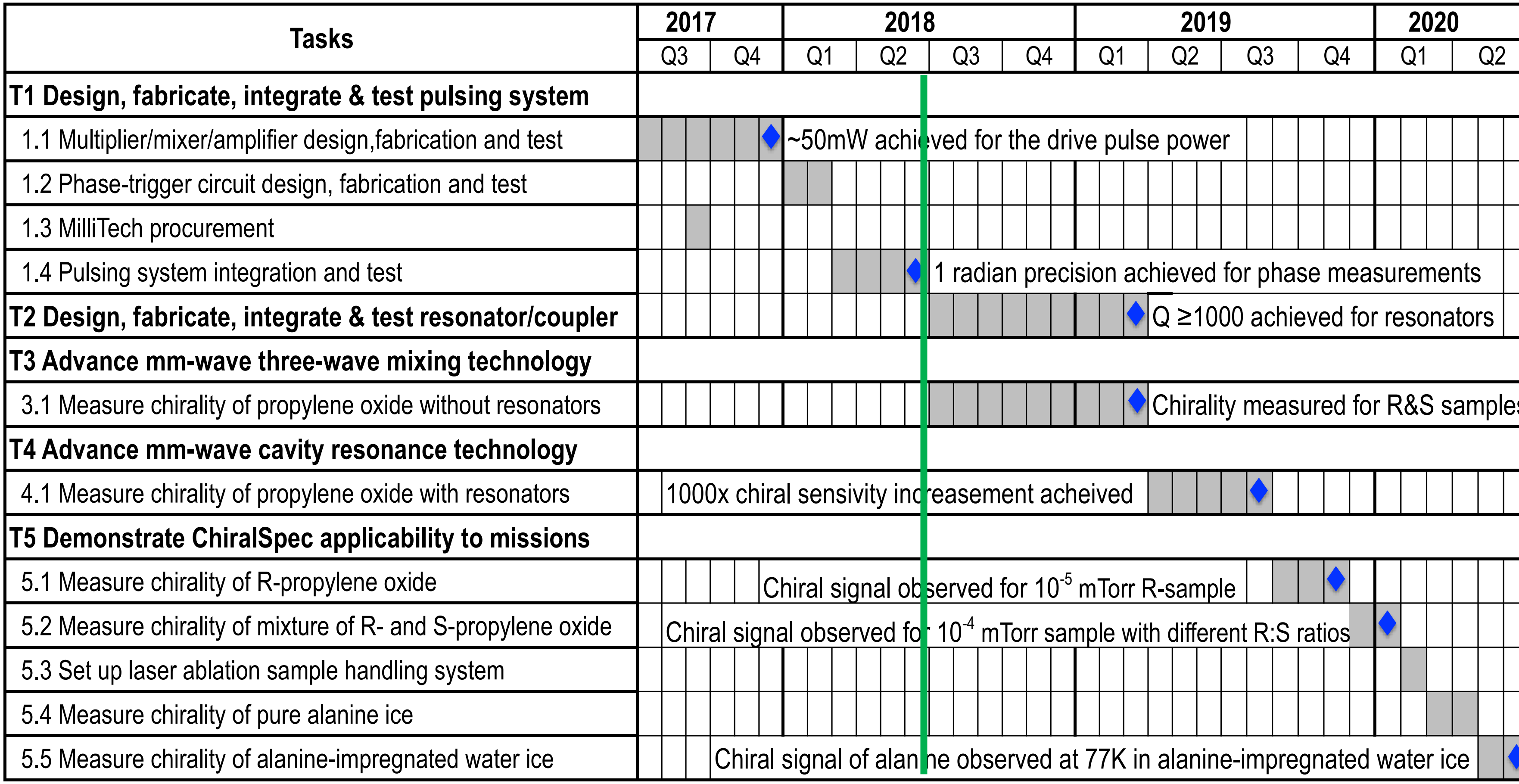
Molecule[a]	Cycle	Pulse	Transition[a]	Freq. (GHz)[a]	*P* (mW)[b]	τ (ns)[b]
Propylene Oxide (CH_3CHCH_2O) MW=58 g/mol μ_a, μ_b, μ_c =0.95,1.67, 0.56 Debye	1	Drive	$8_{4,4} \leftarrow 7_{3,4}$	182.856	50	65
		Twist	$8_{3,5} \leftarrow 8_{4,4}$	81.256	150	24
		Listen	$7_{3,4} \leftarrow 8_{3,5}$	101.599	-	-
	2	Drive	$15_{4,11} \leftarrow 14_{4,10}$	191.226	50	21
		Twist	$14_{5,10} \leftarrow 15_{4,11}$	88.069	150	35
		Listen	$14_{4,10} \leftarrow 14_{5,10}$	103.157	-	-
Alanine (CH_3CHNH_2COOH) MW=89 g/mol μ_a, μ_b, μ_c =0.62, 1.33, 0.34 Debye	1	Drive	$21_{17,4} \leftarrow 20_{16,4}$	191.590	50	31
		Twist	$21_{16,5} \leftarrow 21_{17,4}$	76.855	150	15
		Listen	$20_{16,4} \leftarrow 21_{16,5}$	114.735	-	-
	2	Drive	$20_{19,1} \leftarrow 19_{18,1}$	195.558	50	30
		Twist	$20_{18,2} \leftarrow 20_{19,1}$	86.643	150	23
		Listen	$19_{18,1} \leftarrow 20_{18,2}$	108.915	-	-

[a] *Spectroscopic data obtained from the Cologne Database for Molecular Spectroscopy(CDMS) [10].*

[b] *Estimated pulse power and length that meet the requirements for the drive and twist pulses to become the $\pi/2$ and π pulses.*

- Propylene oxide is the first chiral molecule observed in ISM (McGuire et al 2016), is volatile and easier for sampling handling (vapor pressure of 450 Torr at 300K).
- We will use laser ablation to bring alanine into gas phase.

Schedule and Milestones



Sensitivity on the order of 10^9 molecules/cm^3

Acknowledgements

Part of this research was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.