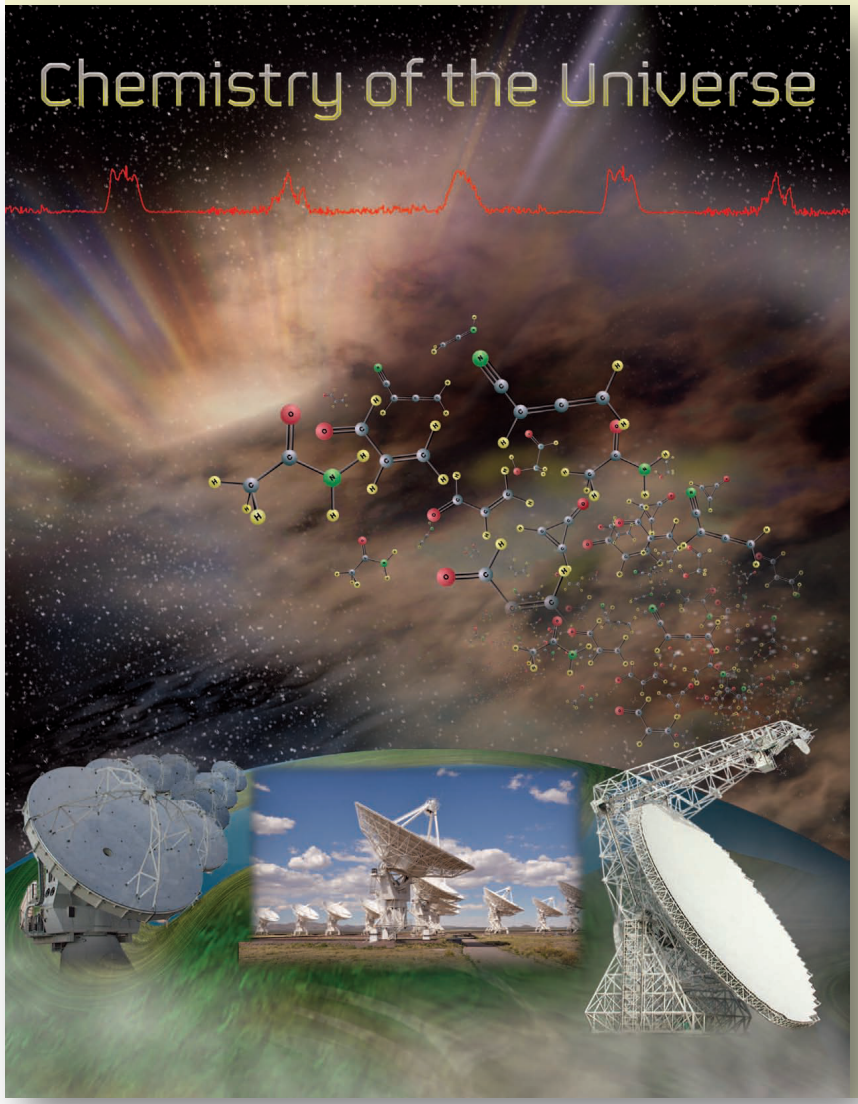
Opportunities for Spectroscopic Analysis with ALMA (and EVLA)

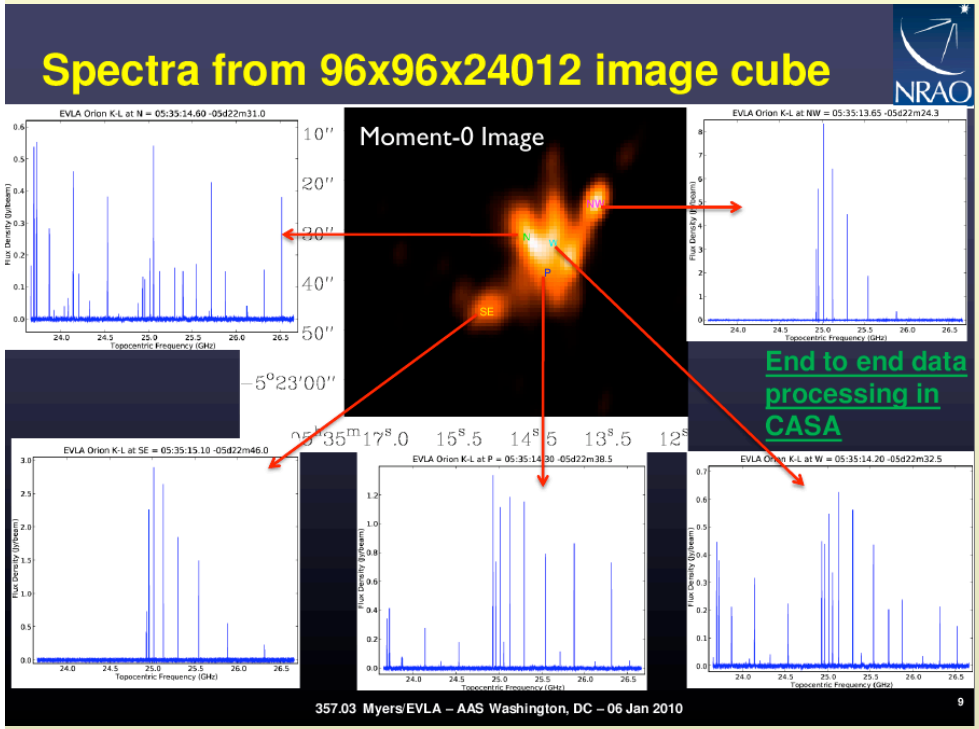


Brooks Pate
Department of Chemistry
University of Virginia

Tony Remijan (NRAO), Phil Jewel (NRAO), Mike McCarthy (CfA), Susanna Widicus Weaver (Emory), Frank Lovas (NRAO), David Plusquellic (NRAO), Eric Herbst (UVa), Kevin Lehmann (UVa)

Dan Zaleski, Brent Harris, Justin Neill, Amanda Steber, Ryan Loomis, Matt Muckle

What I Want Out of "My" Data Cube



- What molecules are present?

  Spectrum identification by broadband rotational spectroscopy (Mixture Analysis)

- What are their "concentrations"?

  Analysis of the intensity profile to determine the physical parameters

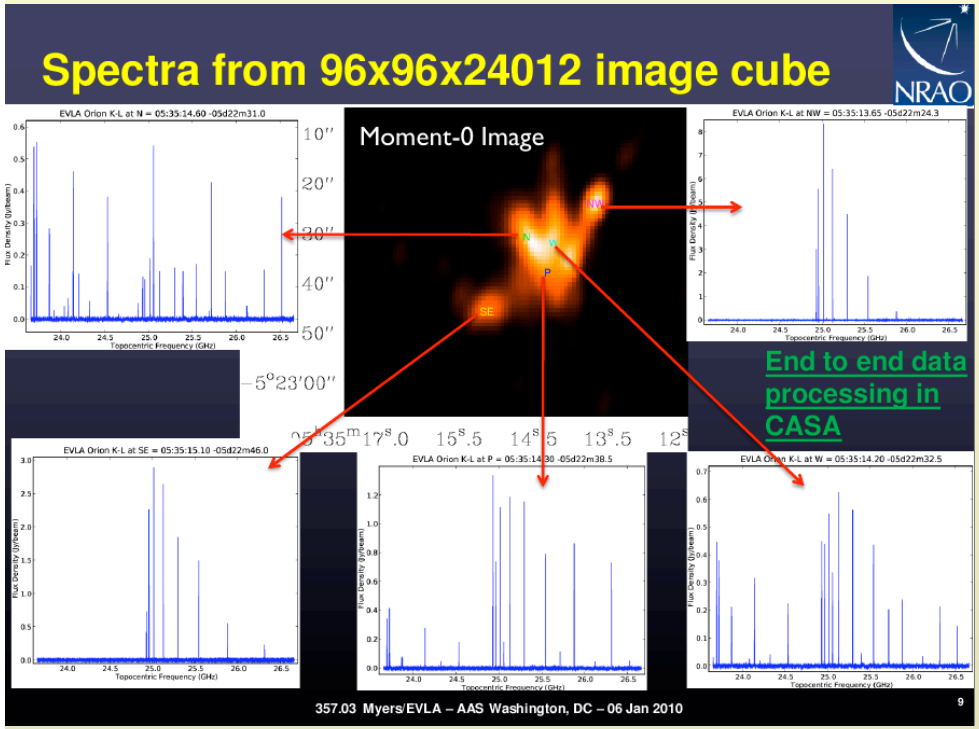
- The ability to make "chemical images"

  Images that examine the correlations of molecular column densities

EVLA Demonstration Science
Orion KL, 3100 MHz Bandwidth

PRIMOS Survey GBT
SgrB2(N) 6-40 GHz

What I Want Out of "My" Data Cube



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New Approaches for Molecular Discovery

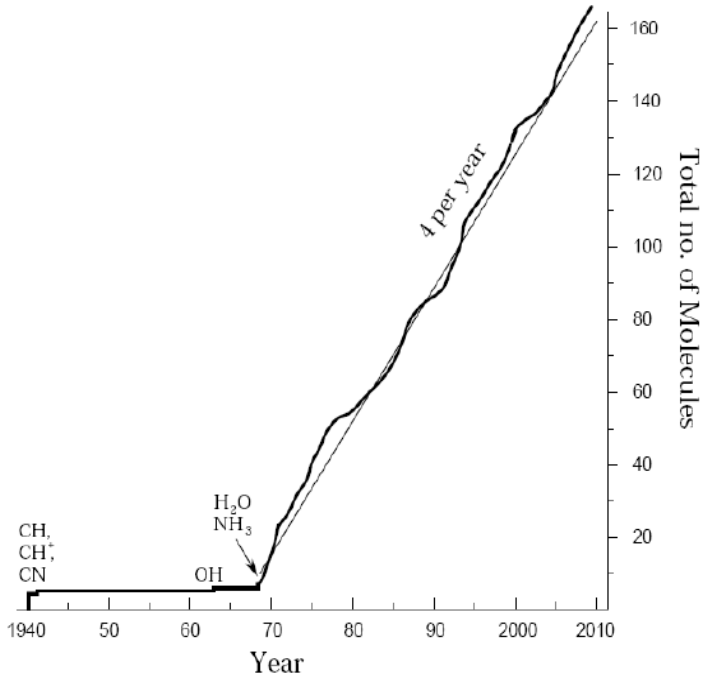


Fig. 1 Number of molecules detected in space with the historical rate of 4 new detections per year (see Ref. 40, updated to 2010).

Can we develop new approaches to Identifying new molecules in astronomical environments that can keep pace with and the explosion in data rates from ALMA and EVLA?

Are there new approaches to molecular discovery that exploit the unique properties of ALMA and EVLA data sets?

Broadband spectral coverage coupled with spatial resolution

Public interest in participating in science

Mike McCarthy (CfA)

The Old Model for Molecular Discovery

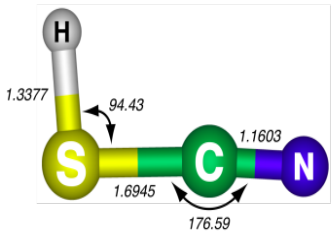
Molecule-by-Molecule Targeted Searches (Narrow Band Thinking)

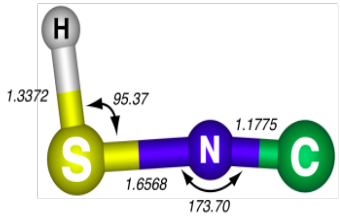
Idea for a Candidate Molecule in Space → Suggested Laboratory Synthesis → Laboratory Identification of Rotational Spectrum

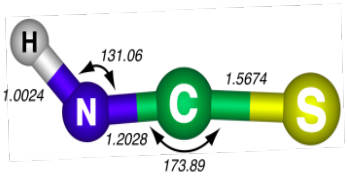
Application for Observing Time (Single Dish) → Targeted Search in Frequency Windows

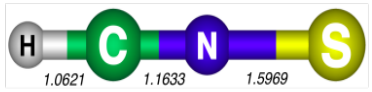
This model was imposed, in part, by the technical limitations on both laboratory spectrometers and radio telescope capabilities

Targeted Detection of HSCN









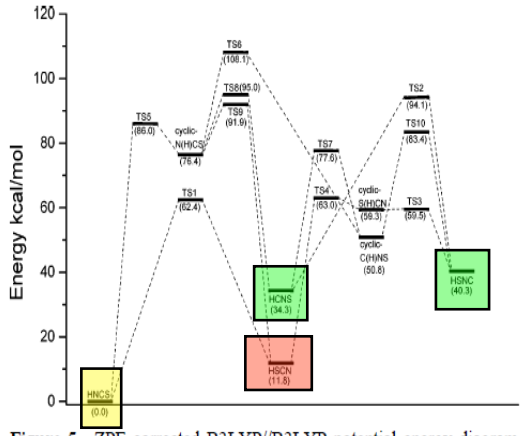
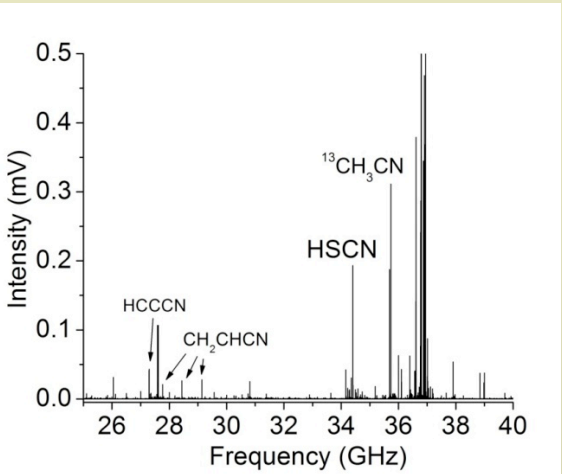
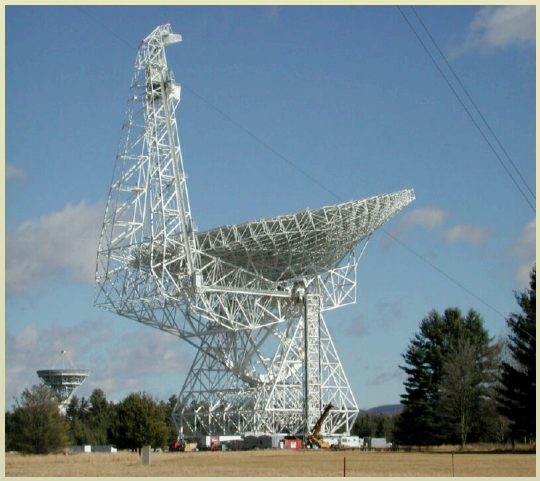


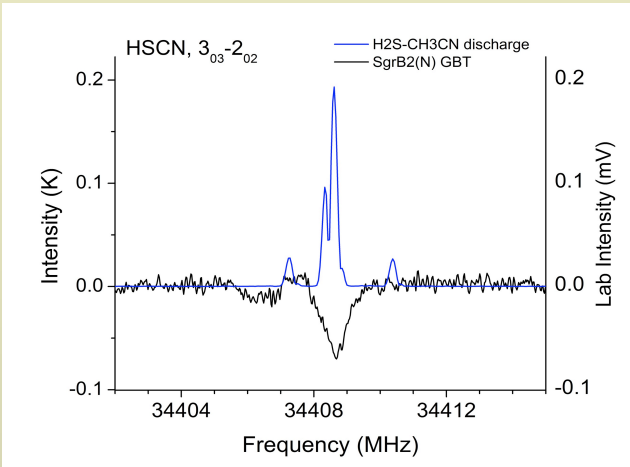
Figure 5. ZPE corrected B3LYP//B3LYP potential energy diagram for isomerization of singlet CHNS.

Laboratory Chemistry: H_2S + CH_3CN in an Electric Discharge

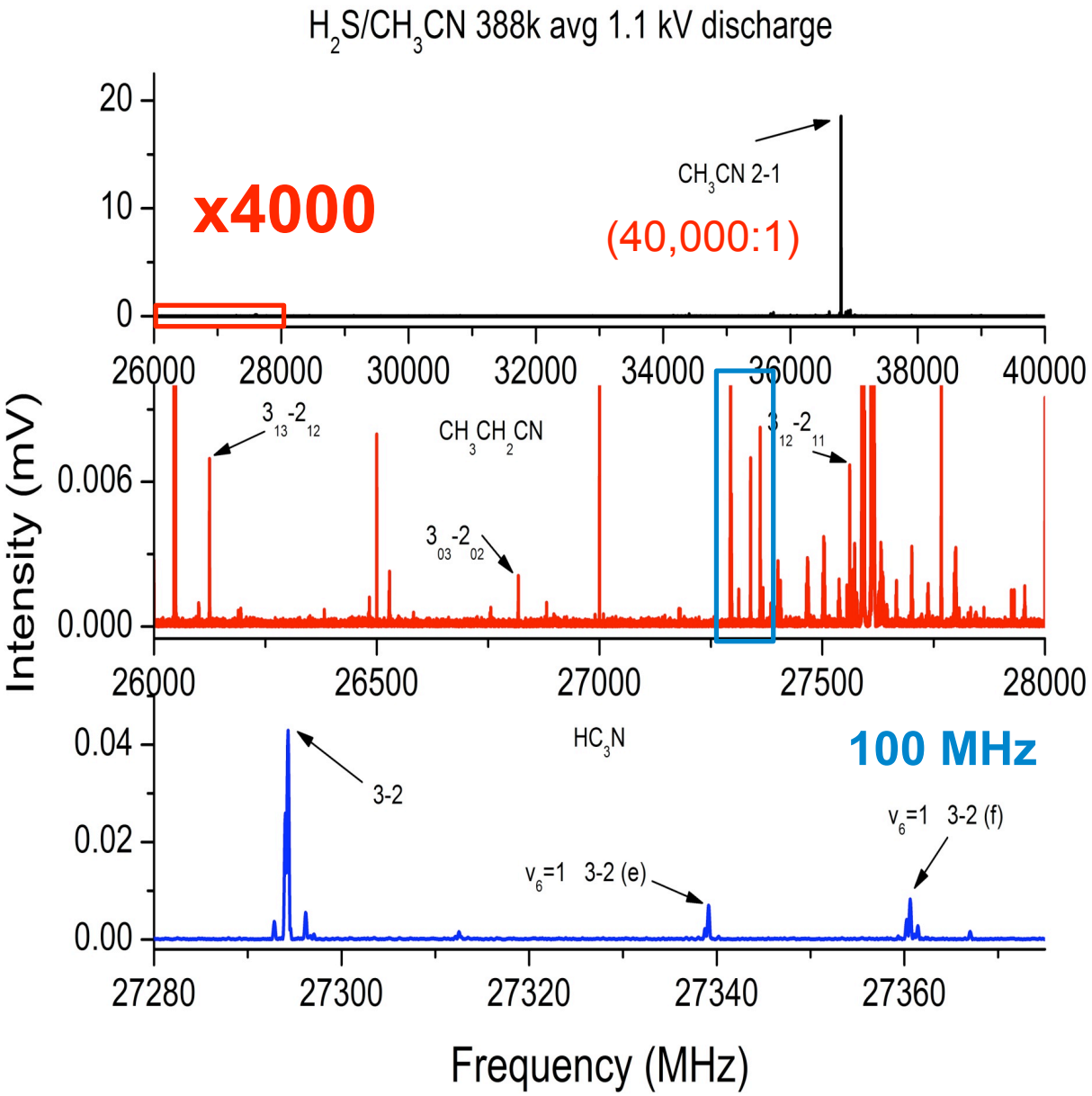




Interstellar Detection



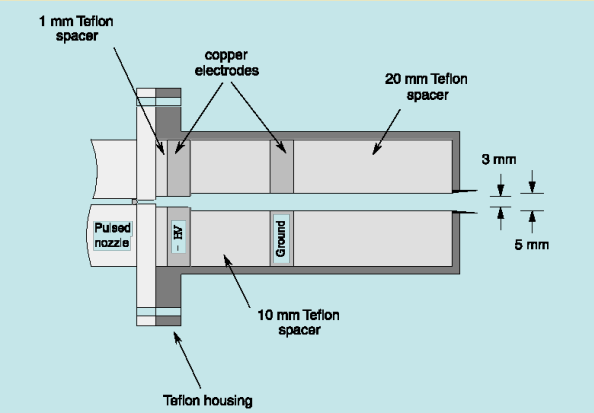
Combinatorial Astrochemistry: Broadband Spectroscopy



$CH_3CN + H_2S$

(0.4%, 0.4% in neon, 1.1 kV)

388,000 spectrum averages
38,800 sample injections
(1 hour: Jan 2012)



M.C. McCarthy, W. Chen, M.J. Travers, and P. Thaddeus, Ap. J. Supp. Series, 129, 611-623 (2000).

How do we identify molecules in a complex mixture?

- Spectral Libraries of Known Molecules (Splatalogue)

*Compare known **spectra** with the broadband spectrum*

*21 Previously Known **and Catalogued** Molecules Identified*
17 Previously Identified in the ISM

Less than 50% of all transitions with S/N Ratio greater than 3:1 are "assigned" to a molecular structure

How do we identify molecules in a complex mixture?

- Screen Laboratory Broadband Spectra with Astronomical Broadband Spectra

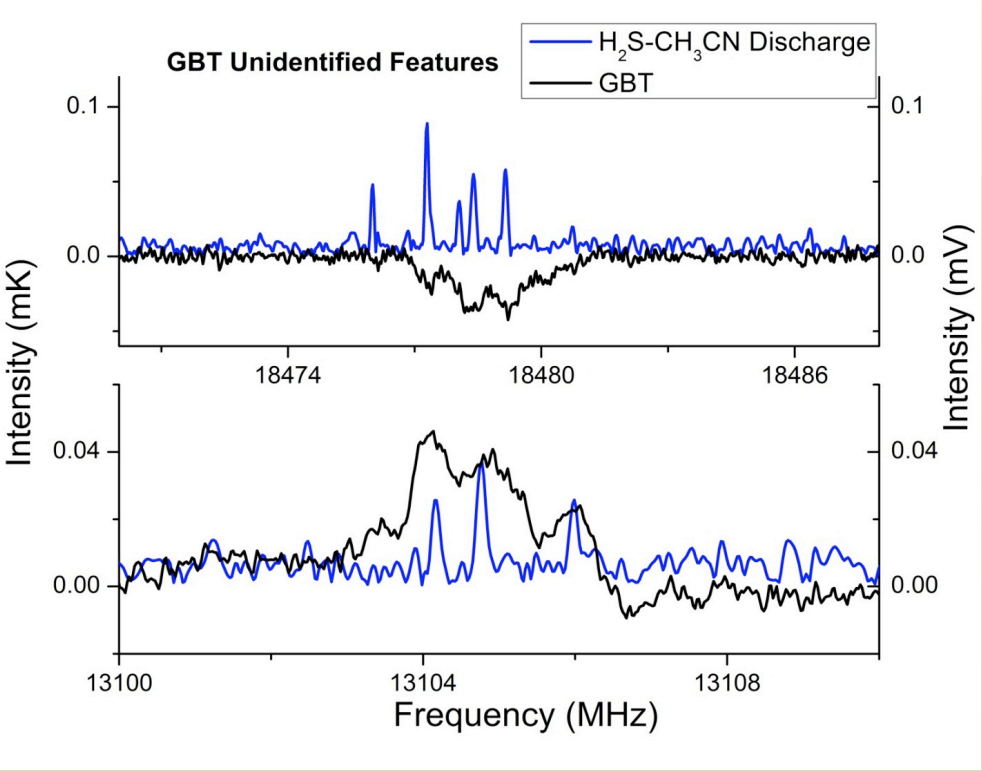
Look for overlapping spectra that flag molecules of special interest because they are "unidentified" in both lab and space

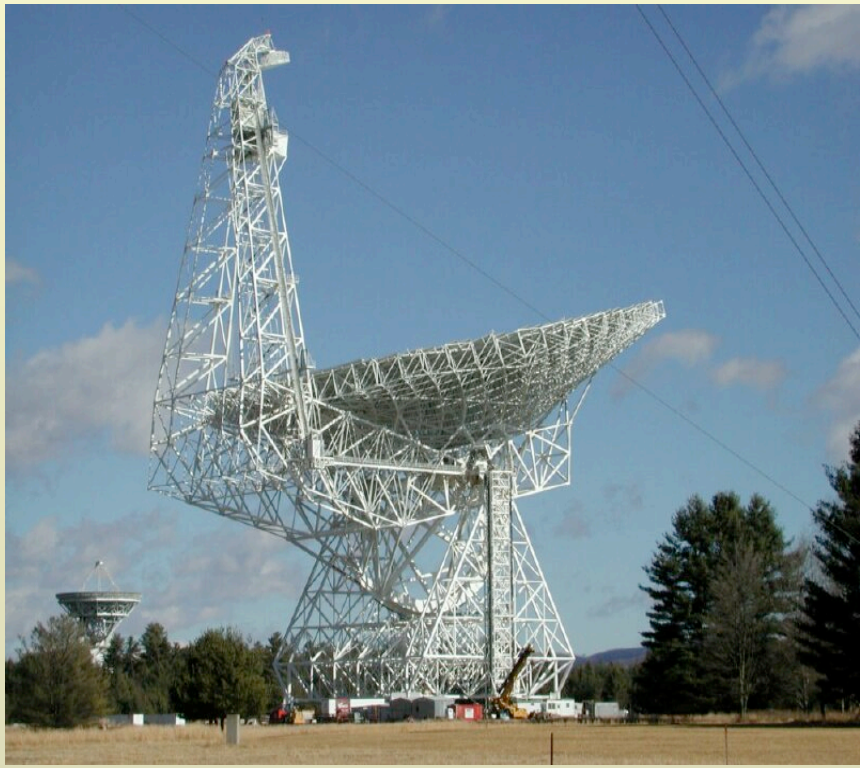
Data Enabled Science approaches that make use of the explosion in data rates for broadband molecular rotational spectroscopy

ALMA – 1 TB/Day
Laboratory (March 2012) – 1 TB/hr

Value of the laboratory data is in the unassigned spectral features!

Reaction Product Screening Against Interstellar Broadband Rotational Spectra – "W-lines"



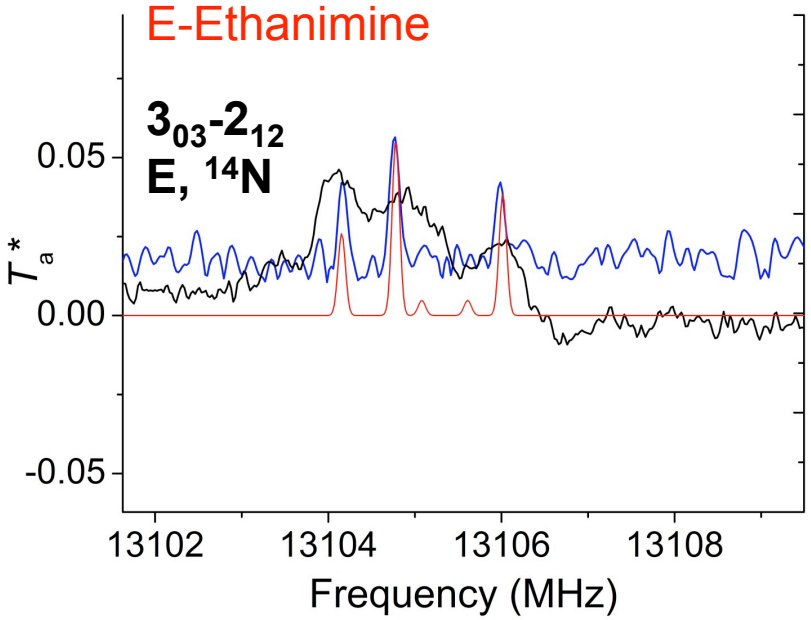


Laboratory Spectrum (Blue): H_2S + CH_3CN
GBT Spectrum (Black): SgrB2(N)

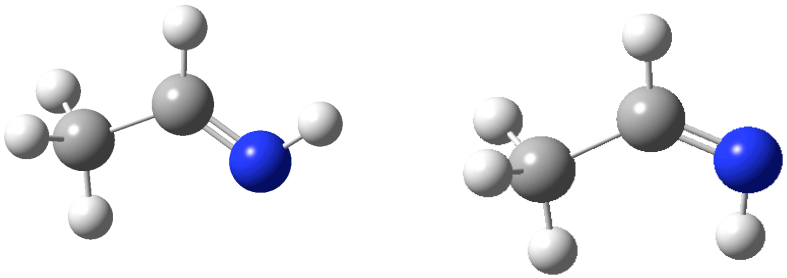
Green Bank Telescope
National Radio Astronomy Observatory

PRIMOS Survey: http://www.cv.nrao.edu/~aremijan/PRIMOS/

Interstellar Detection of Ethanimine Isomers

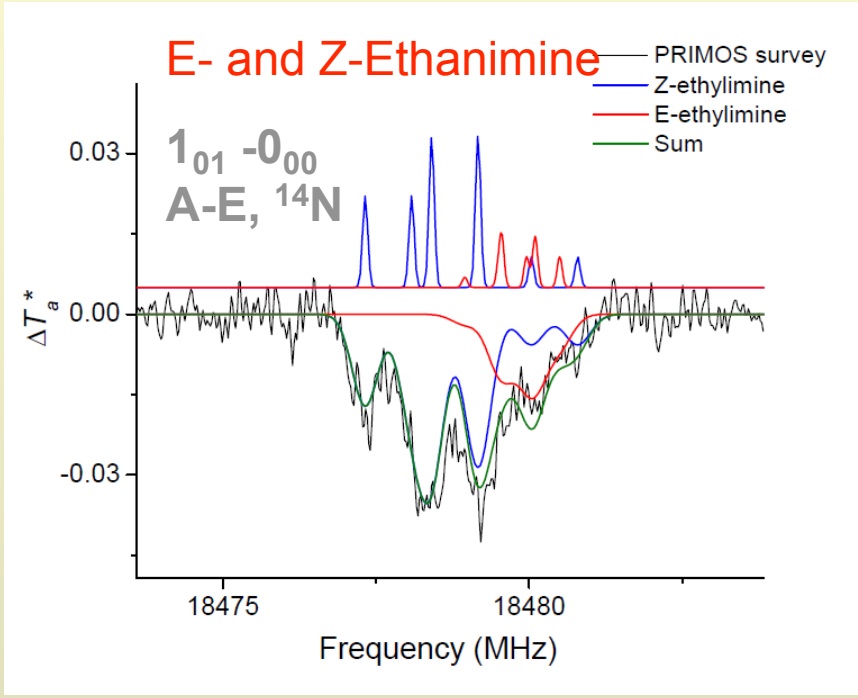


E = 0 cm^{-1} E = 355 cm^{-1}



E-ethanimine Z-ethanimine

MP2/6-311++G(d,p)



Sequential H-atom Addition in Interstellar Ices

$CH_3CN + H \rightarrow CH_3CH=N$

$CH_3CH=N + H \rightarrow CH_3CH=NH$

P. Svejda and D. H. Volman. J. Phys. Chem., (1970), 74, 1872-1875.

How do we identify molecules in a complex mixture?

- Search all space and laboratory spectra for a candidate molecule – *Library Free Chemical Detection*

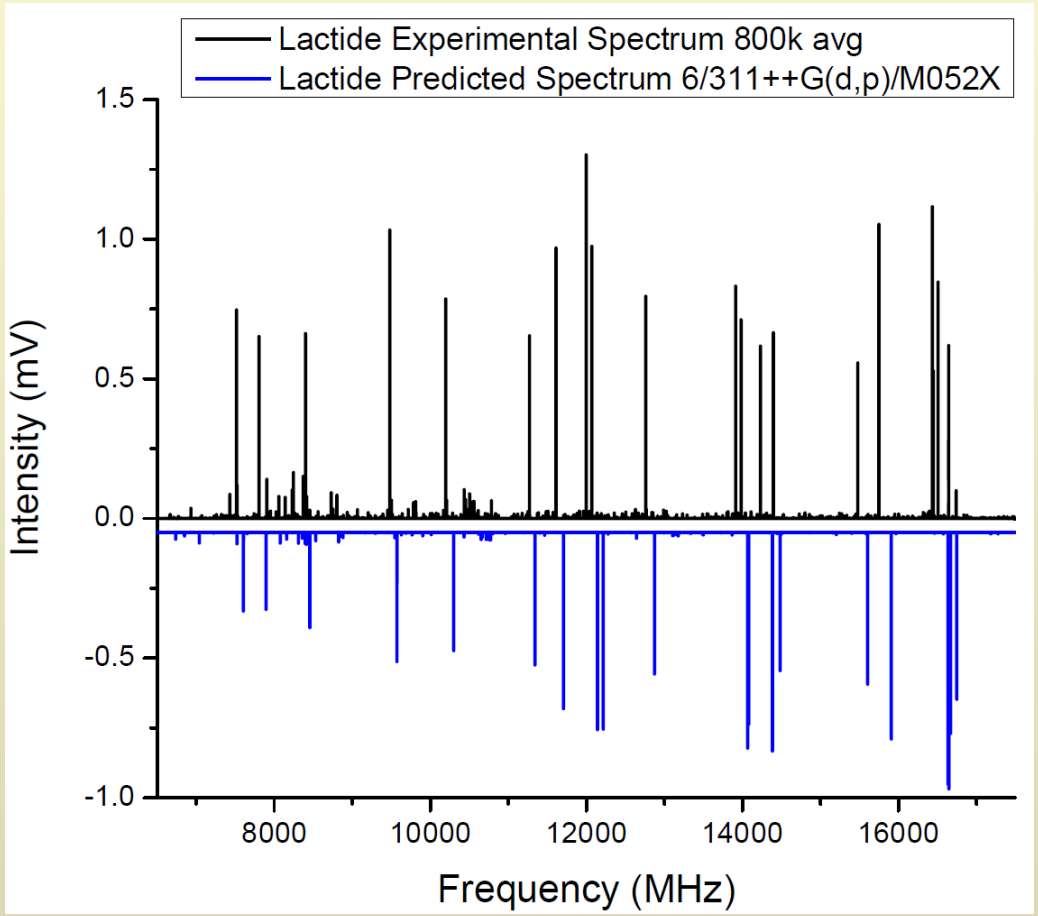
How do you identify a molecule whose spectral signature has never been measured in the laboratory?

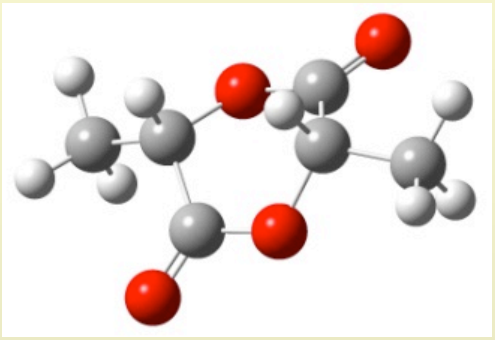
Unique Features of Molecular Rotational Spectroscopy

Molecular Hamiltonian is Known (Angular Momentum)
Spectrum Has High Redundancy (No. lines >> No. parameters)
Quantum Chemistry Can Estimate the Parameters to High Accuracy
Frequency accuracy of measurements is exceptional (reusability)

Library-Free Chemical Analysis: Chemical Identification by Quantum Theory

Molecule Identification using Theoretical Spectral Libraries





(S,S)-Lactide

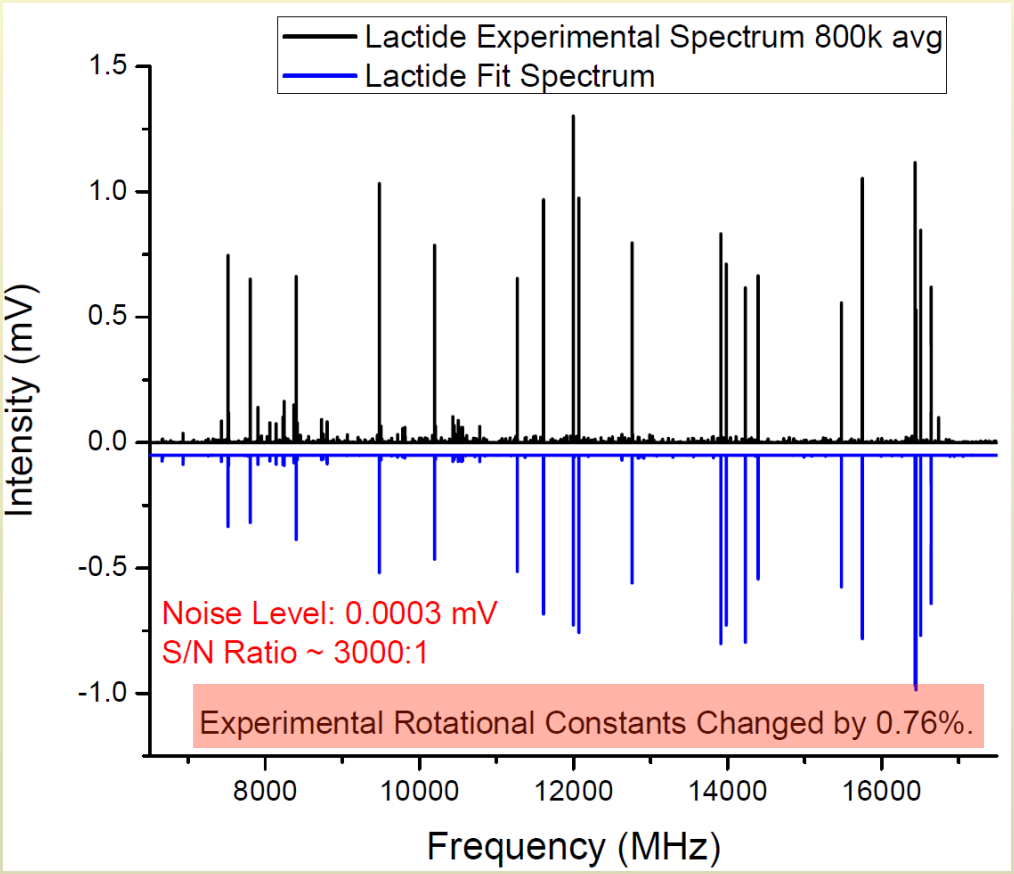
Simple rules, not simple patterns

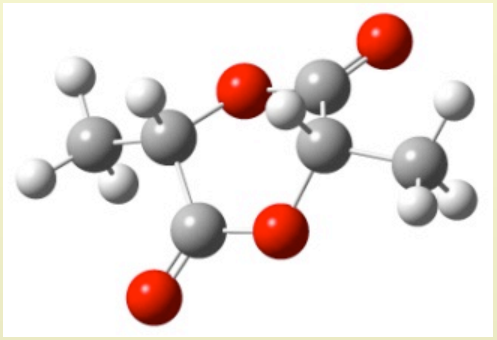
Ab initio input:
Rotational Constants (A, B, C)
Dipole Components (μ_a, μ_b, μ_c)

Pulsed-jet Chirped-Pulse Fourier Transform Spectroscopy
Dan Zaleski and Zbigniew Kisiel (Jan. 2011)

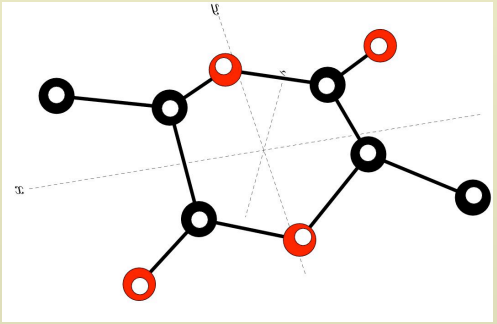
Library-Free Chemical Analysis: Direct Structure Determination from Isotopic Analysis

Sample-in / Structure-out Chemical Analysis





Direct Structure Determination



Comparison of Kraitchman Analysis to Electronic Structure Theory

Tools for Automated Spectrum Analysis and Structure Determination (Plusquellic, Pate, and Kisiel)

Molecular Discovery in the Laboratory Spectrum

Identification of known molecules suggested the dominant reaction chemistry in Discharge source was radical-radical reactions (followed by subsequent energetically feasible chemical transformations).

Known radicals in the sample are HS and CH_2CN

Proposed that two reaction products are: HS – CH_2CN, S=CHCN

HS-CH_2CN	Theory	Expt	S=CHCN	Theory	Expt
A (MHz)	23134	23598		42458	42910.0
B (MHz)	3105.7	3104.83		3151.0	3195.39
C (MHz)	2825.8	2820.80		2933.3	2970.12

Generally 1% Accuracy in Parameter Estimates

Can we completely reverse the molecular discovery paradigm?

Idea for a Candidate Molecule in Space → Suggested Laboratory Synthesis → Laboratory Identification of Rotational Spectrum

Application for Observing Time (Single Dish) → Targeted Search in Frequency Windows

Lab ⟶ Space

Space ⟶ Lab

Can we completely reverse the molecular discover paradigm?

- Reduce the astronomical broadband spectrum to a set of “u-spectra”

  Use the fact that we know the Hamiltonian
  Automated fitting procedures
  Spatial Double-Resonance Spectroscopy

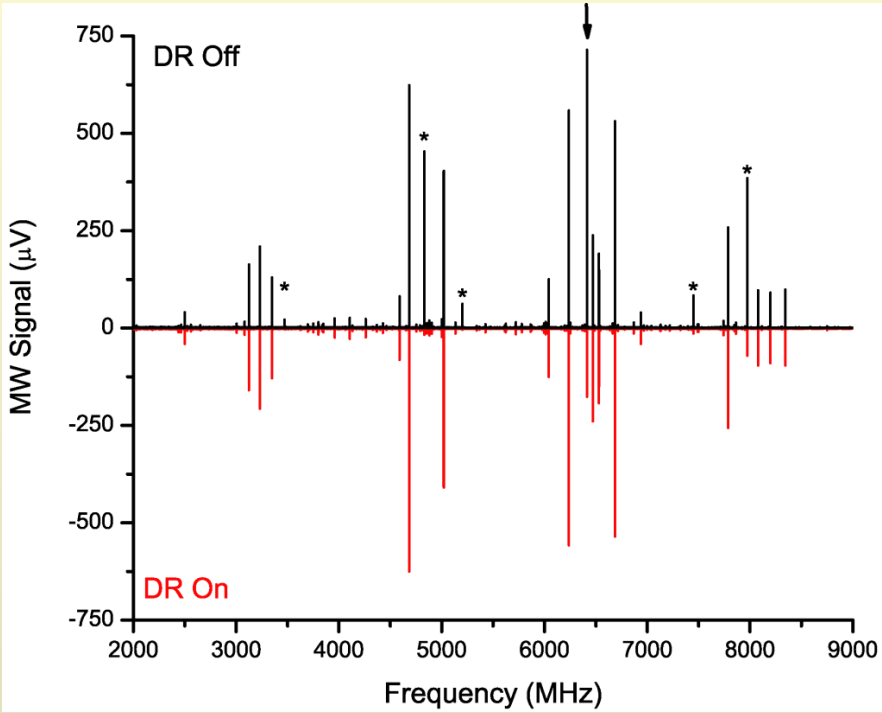
- Compare spectral parameters to theoretical data bases to get candidate molecular structures

  Heavy dose of quantum chemistry

- Laboratory verification of the candidate structure

  Controlled reaction conditions
  Isotopic checks

Double Resonance or Spectrum Editing



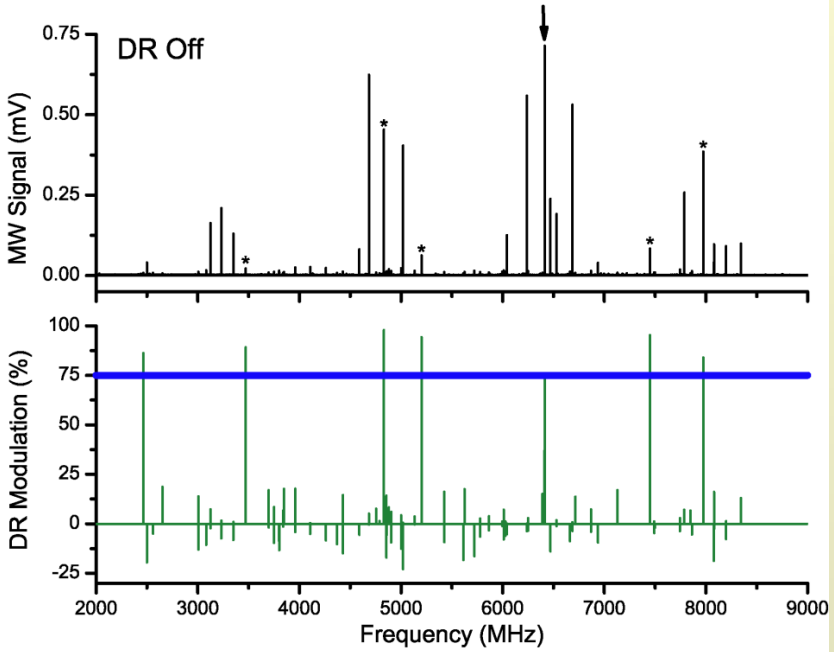
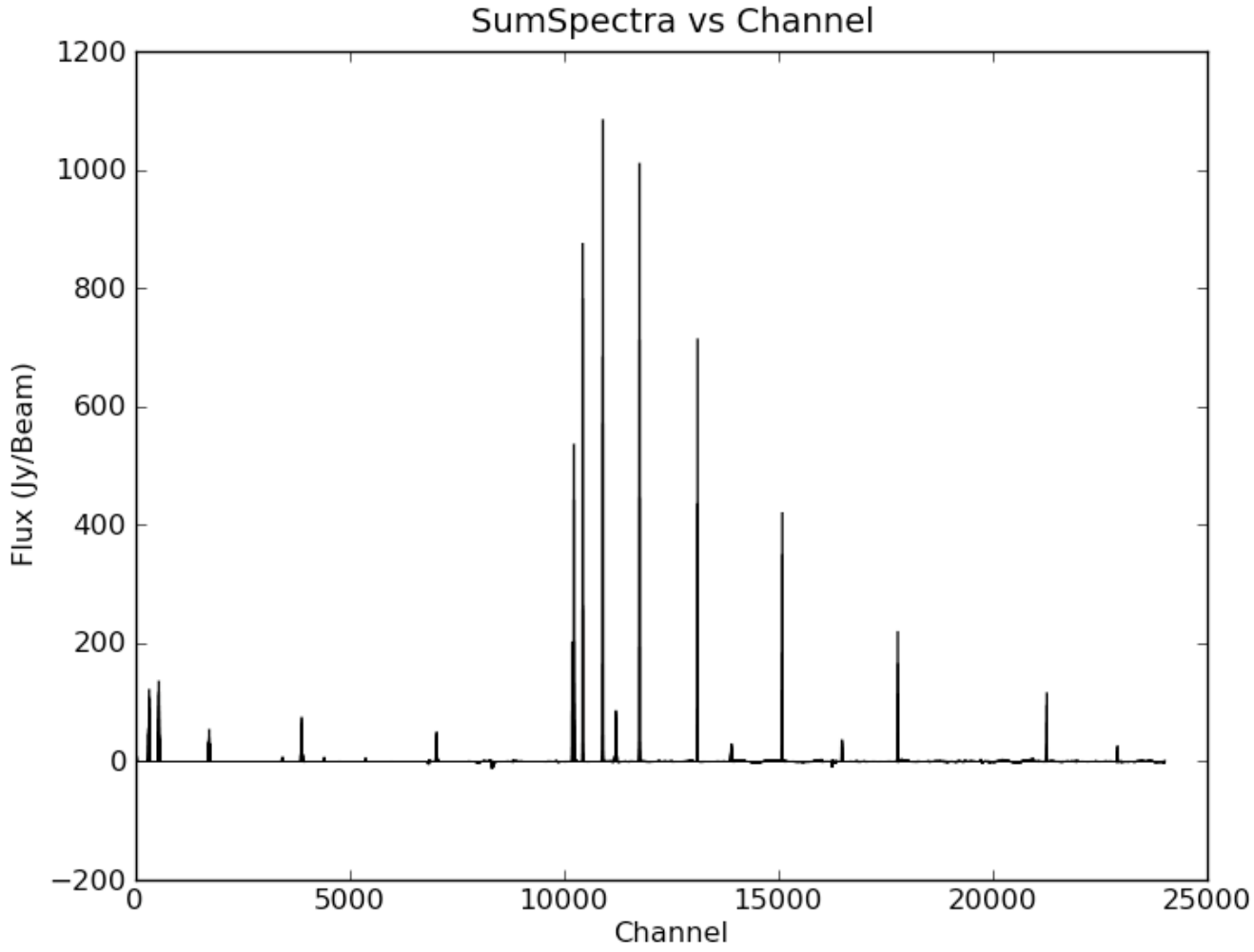


Table 3. Selective-Excitation Double-Resonance Modulation Following Driving of the Suprane 4_{04}-3_{03} Transition

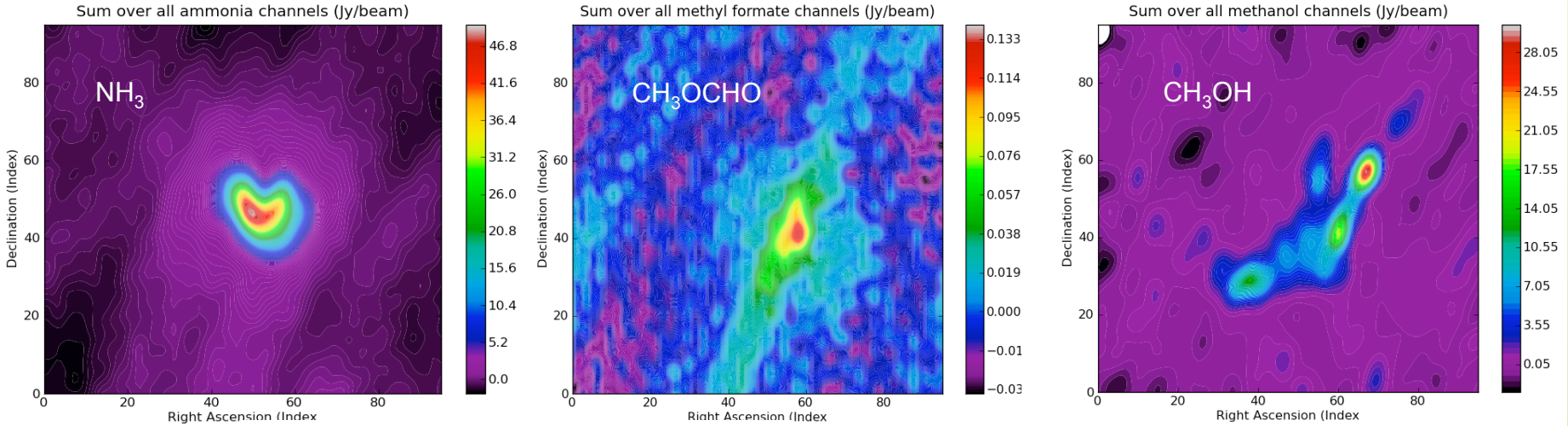
Freq. (MHz)	Transition	Abs. Mod (μV)	Rel. Mod (%)
3472.20	$\mathbf{3_{03}} - 2_{12}$	19.3	89.2
4830.99	$\mathbf{3_{03}} - 2_{02}$	444.3	97.9
5201.90	$\mathbf{4_{04}} - 3_{13}$	58.8	94.4
7449.50	$4_{14} - \mathbf{3_{03}}$	80.2	95.4
7974.10	$5_{05} - \mathbf{4_{04}}$	321.2	83.4

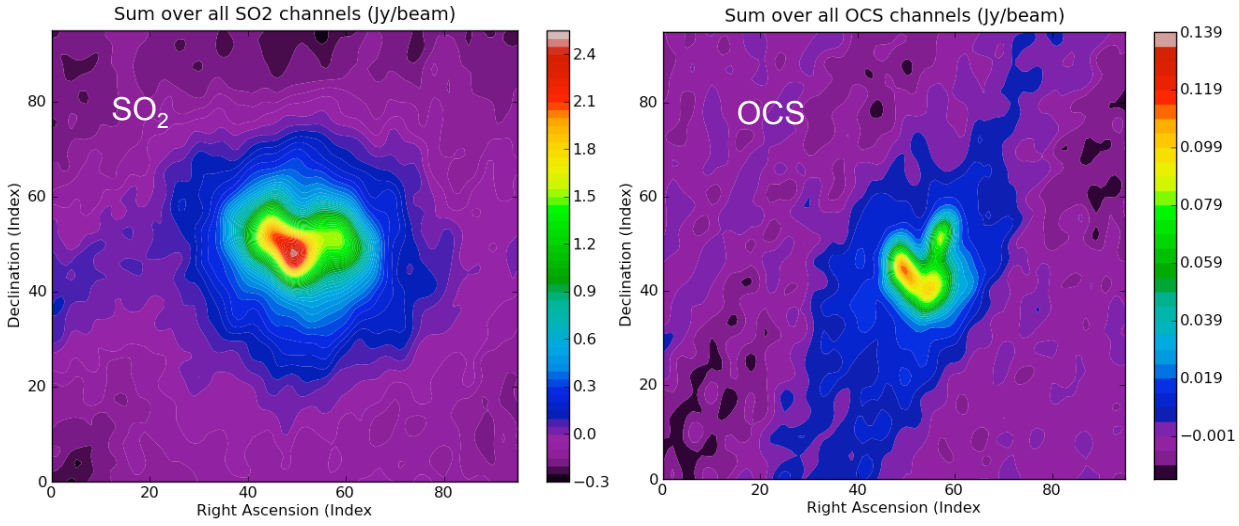
EVLA Demonstration: Spectrum of the Data Cube (3100 MHz)



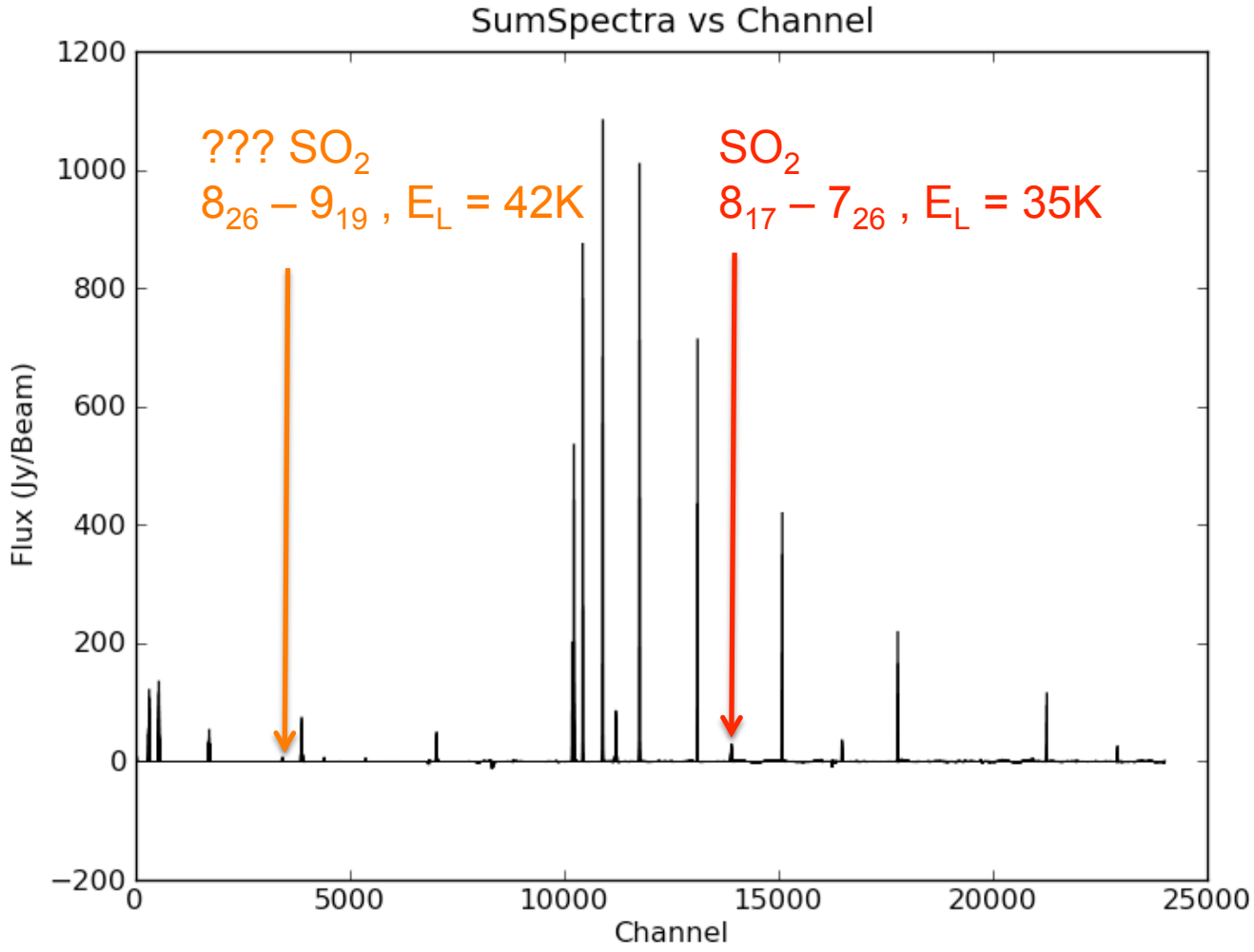
2D Line Assignments

Spatial Distributions for "Double Resonance"





SO_2 Assignment



SO_2 Assignment

Image Correlation 1D and 2D

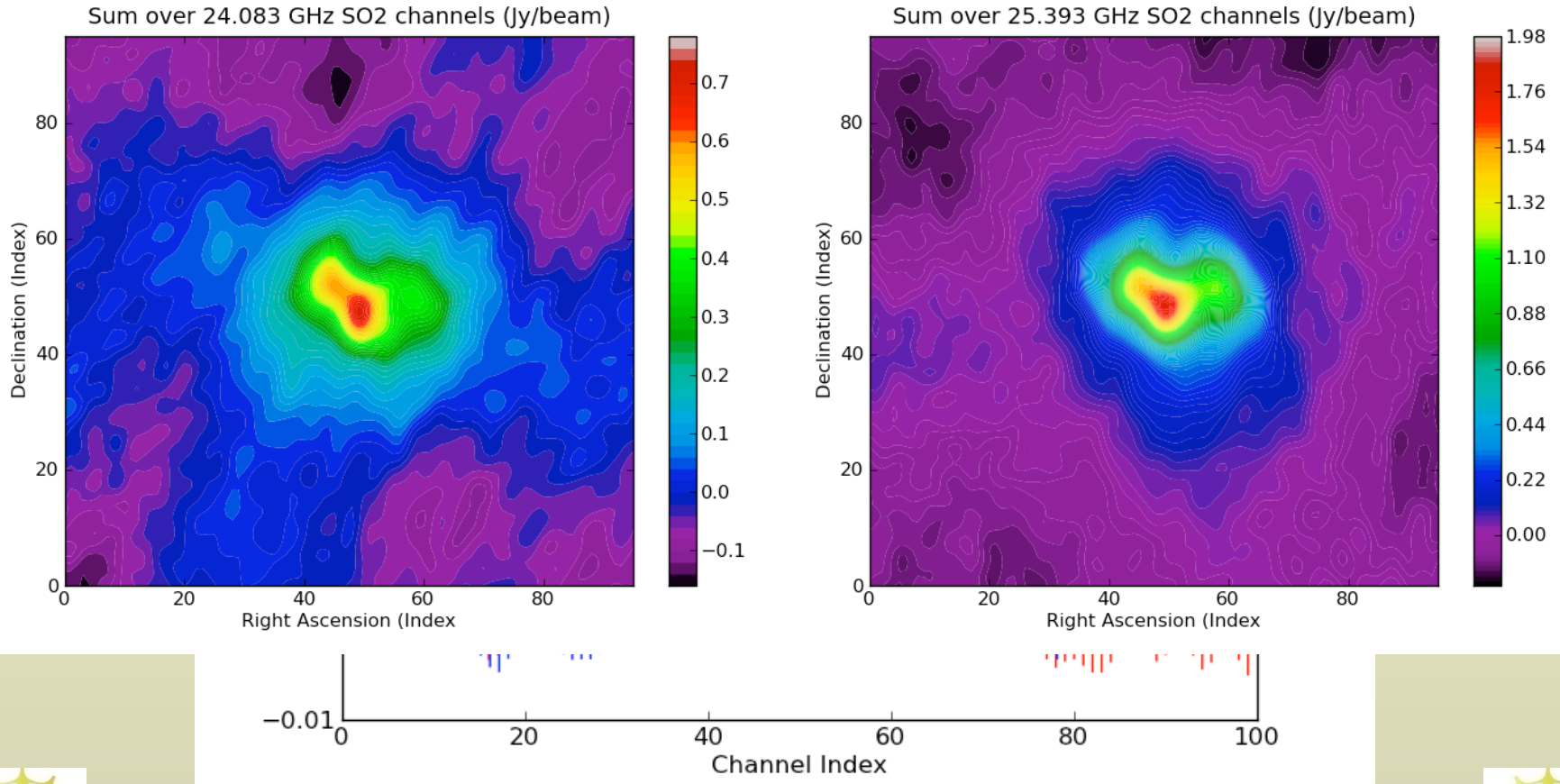
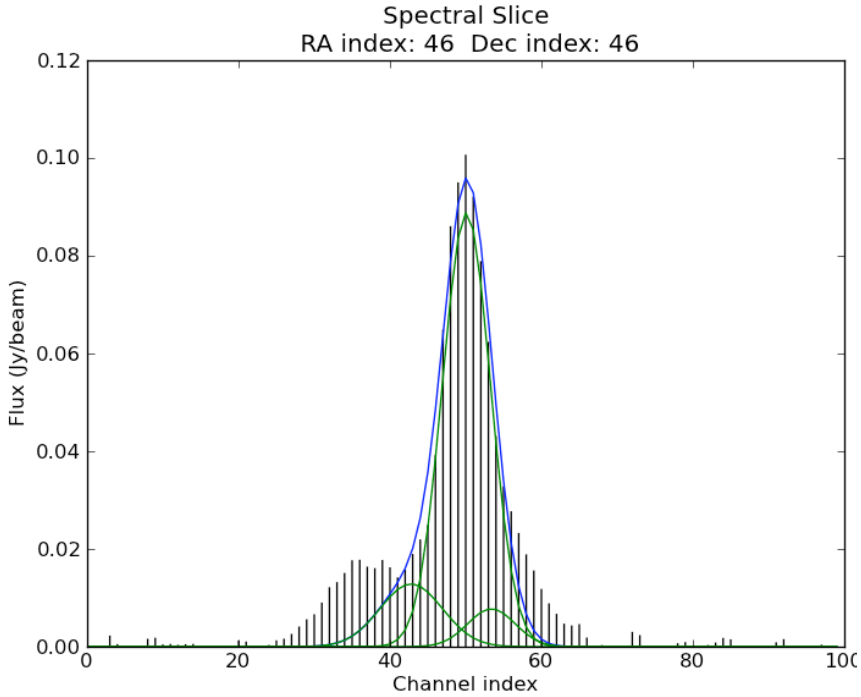
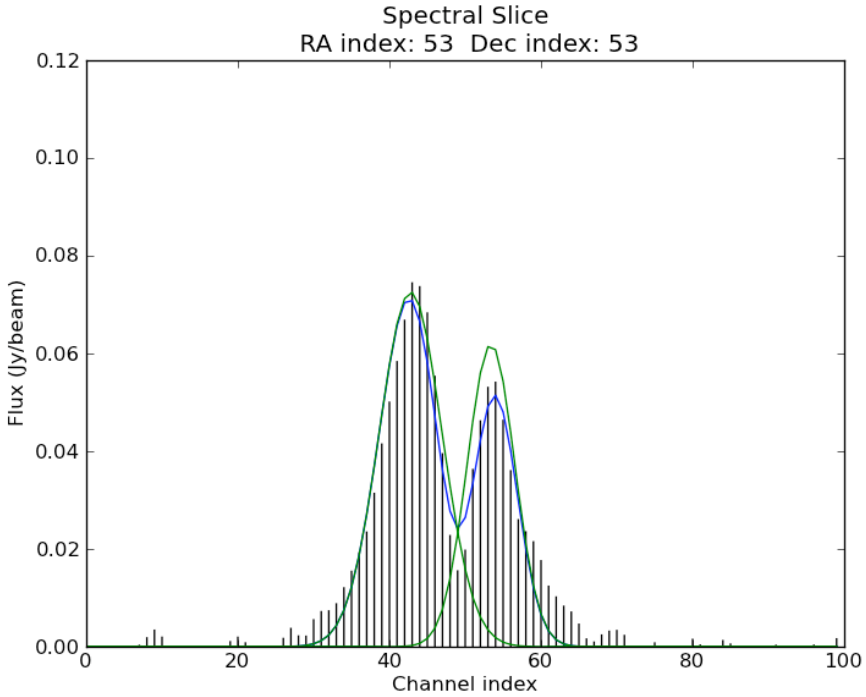


Image correlation provides further confidence in assignment

SO_2
Deconvolution of line shapes

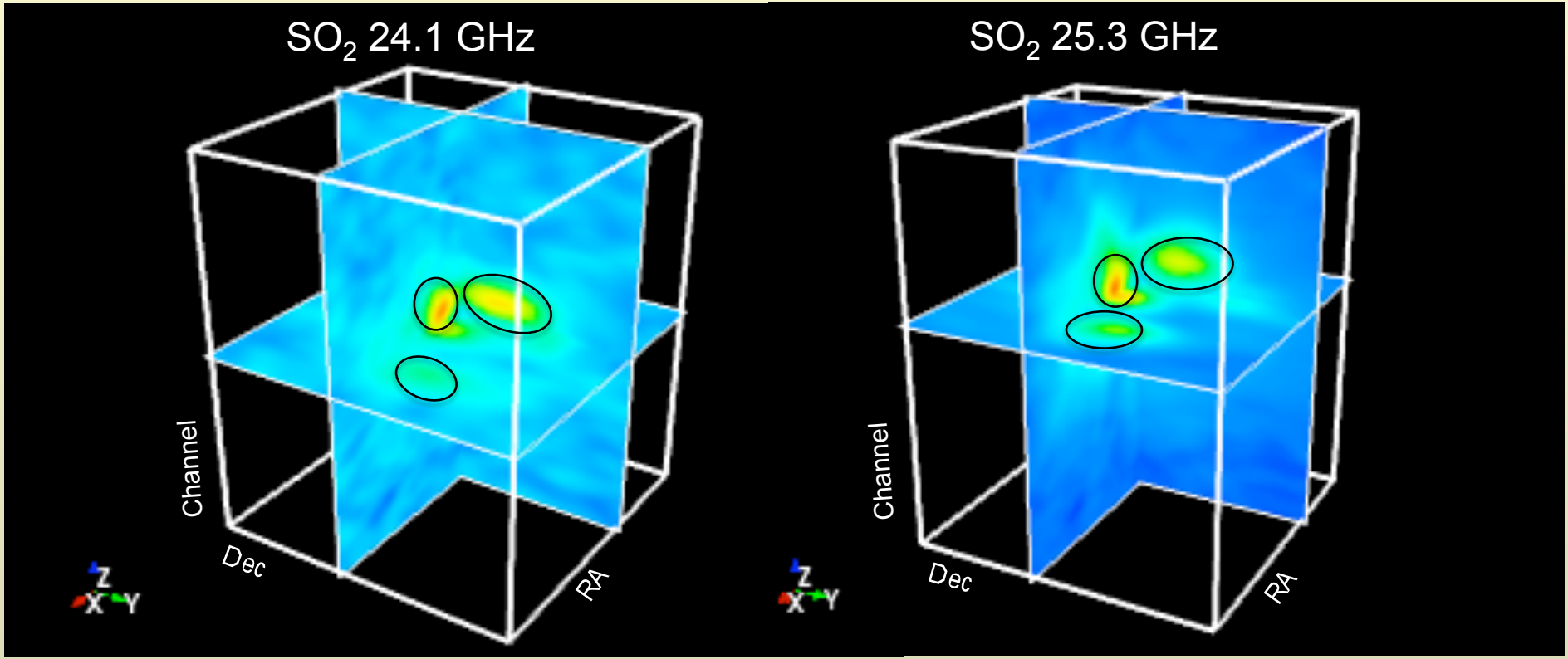




Several velocity components are apparent.

3D imaging

Pattern matching of an isosurface



What is the % correlation between the two surfaces?

ALMA Software for Molecular Discovery and Astrochemistry

Molecular Discovery: Molecule catalogs move from line to spectrum format
New broadband databases that archive lab and space data
Enhance the rate of molecular discovery using data mining and citizen science:

- Molecule Queries: Adopt-a-molecule; Molecule builder and search
- Spectral Reduction: 2D image classification; 3D image classification

Spectrum Analysis: Still research level problem but early results are promising
Very large computing requirements
Significant contribution from quantum chemistry required

Chemical Imaging: Tools to treat the (column) densities of molecules like colors
Challenges for image interpretation based on chemical composition for both chemistry and astronomy