Molecular Spectroscopy

Anthony Remijan

NRAO NSF Associated Universities, Inc.

Molecule hunting returns to centimeter wavelengths with the Green Bank Telescope

The history of spectral line observations/molecular spectroscopy in Green Bank is long and storied with a wide range of successes – Can't possibly cover everything!

WARNING – this is going to be a very biased presentation – lot of mention of new molecule detections and line surveys.
The GBT does SO MUCH MORE than that to advance molecular spectroscopy!

You can make the argument that modern radio astrochemistry started with the 140ft in Green Bank.

Interstellar Formaldehyde – Where it all began…

A detection in 1969 forever changed the way that astronomers and chemists viewed the universe

MICROWAVE DETECTION OF INTERSTELLAR FORMALDEHYDE

Lewis E. Snyder and David Buhl
National Radio Astronomy Observatory,* Green Bank, West Virginia 22901

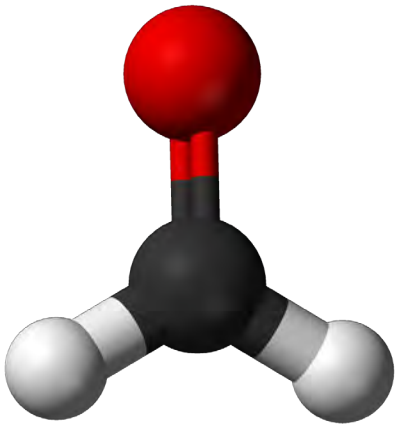
and

B. Zuckerman
University of Maryland, College Park, Maryland 20742

and

Patrick Palmer
University of Chicago, Chicago, Illinois 60680
(Received 17 March 1969)

Interstellar formaldehyde (H_2CO) has been detected in absorption against numerous galactic and extragalactic radio sources by means of the 1_{11}-1_{10} ground-state rotational transition at 4830 MHz. The absorbing regions often correspond in velocity with 18-cm OH features. H_2CO is the first organic polyatomic molecule ever detected in the interstellar medium and its widespread distribution indicates that processes of interstellar chemical evolution may be much more complex than previously assumed.



Interstellar Formaldehyde – Where it all began…

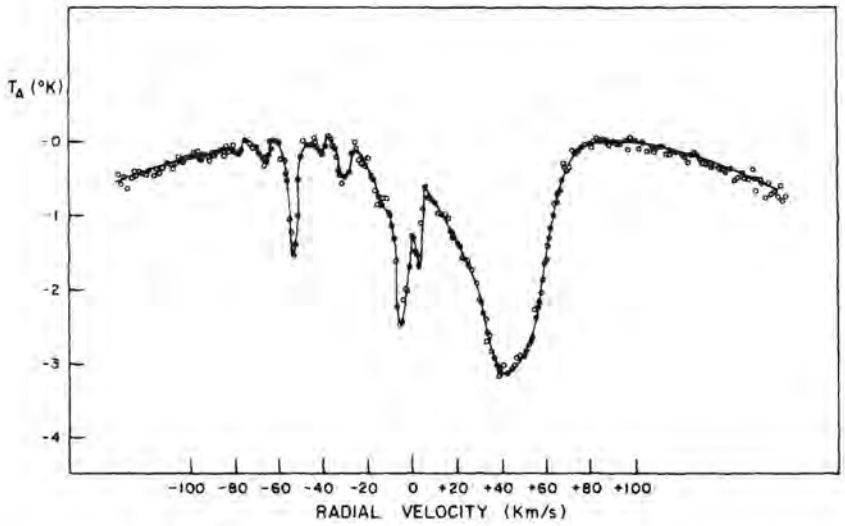
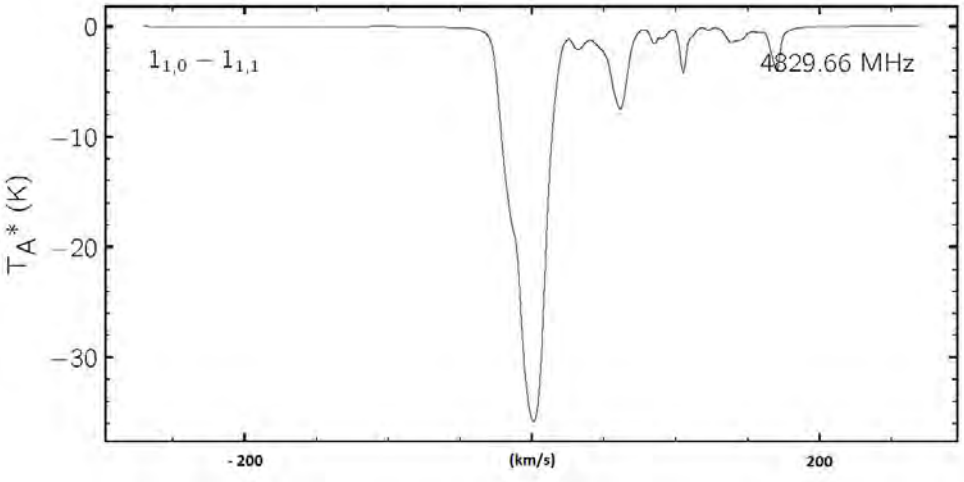


FIG. 1. Formaldehyde absorption against the galactic center (Sgr *A*). The ordinate is antenna temperature and the abscissa is radial velocity with respect to the local standard of rest. This spectrum closely resembles the OH absorption spectrum in the same direction. The effective resolution is ~1 km/sec.



Formaldehyde absorption taken towards SgrB2(N-LMH) with the GBT as part of the GBT PRIMOS Large molecule survey. Velocities are relative to the 64 km/s systemic source velocity.

This line was detected in absorption against numerous continuum sources and eventually the $H^{13}CO$ line was detected.

There was a rush to detect new, especially large organic molecules and it seemed that cm wave observations was NOT the place to be.

Interstellar Glycine Searches…

- Very early searches for interstellar glycine started in the late 70s in the cm – no lines were detected.
- As the search intensifies into the late 80s and 90s, the spectroscopy gets better and better in the lab and searches are conducted on the NRAO 12-m and IRAM 30-m telescopes…

THE ASTROPHYSICAL JOURNAL 241:1001–1006, 1980 November 1

A SEARCH FOR THE LOWEST-ENERGY CONFORMER OF INTERSTELLAR GLYCINE

J. M. HOLLIS
Laboratory for Astronomy and Solar Physics NASA Goddard
L. E. SNYDER
University of Illinois, Urbana
AND
R. D. SUENRAM AND F. J. LOVAS
National Bureau of Standards
Received 1980 February 25; accepted 1980 April 29

THE ASTROPHYSICAL JOURNAL, 268:123–128, 1983 May 1

AN EXTENSIVE GALACTIC SEARCH FOR CONFORMER II GLYCINE

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J. M. HOLLIS
Laboratory for Astronomy and Solar Physics, NASA Goddard Space Flight Center
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National Bureau of Standards
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Laboratory for Extraterrestrial Physics, NASA Goddard Space Flight Center
Received 1982 September 20; accepted 1982 October 26

Interstellar Glycine Searches…

- Results are always the same… lot of blank spectra or worse yet, lots of blended lines…
- This lead to a paper in 1997 on using mm-arrays to search for large molecules..

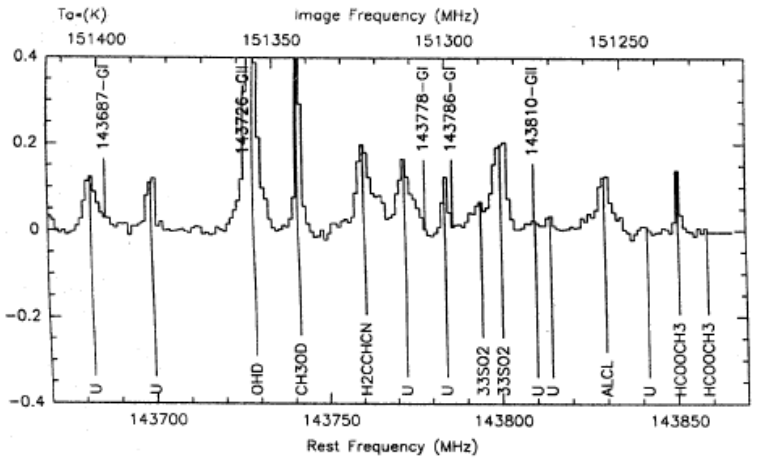


Fig. 1b. Same as 1a, around 143 GHz, the theoretical noise level is 5mK.

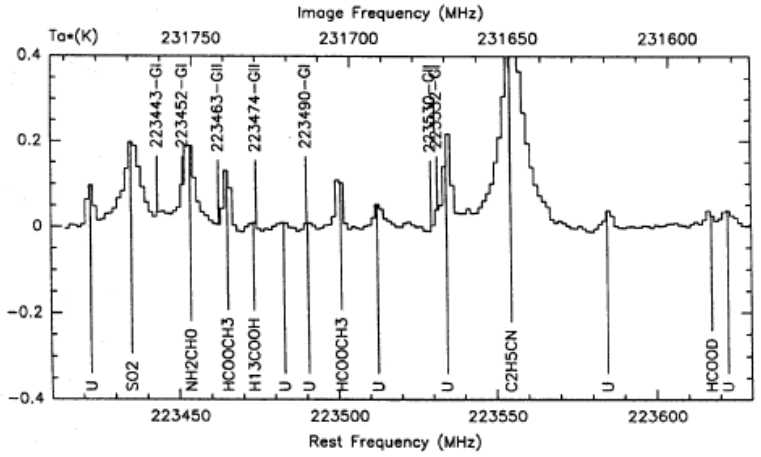


Fig. 1c. Same as 1a, around 223 GHz, the theoretical noise level is 6mK.

Interstellar Glycine Searches…

- It was believed that the reason we were not detecting glycine (or other amino acids) was that their emission was being ***beam diluted***.
- If we were able to use higher resolution and look into the hot cores, these lines would start to come out from the weeds…
- And if it wasn't ugly before, it got ugly soon after…

Detection of large interstellar molecules with radio interferometers

Show affiliations

Snyder, Lewis E.

More than 112 interstellar molecular species have been reported to date. Small interstellar molecules and large interstellar molecules with a low degree of saturation (low hydrogen count) can be formed in quiescent gas clouds or in shock fronts by gas-phase chemical reactions, such as ion- molecule reactions and neutral-neutral reactions. Because these gas-phase species are found in spatially extended clouds, they have dominated most of the past single-element telescope studies of extended interstellar molecular clouds. Now, with the advent of radio interferometric arrays that operate at millimeter wavelengths with high spatial resolution, the study of a rich dust-phase chemistry around small hot molecular cloud cores has become possible. These small cloud cores, less than 0.1 parsec in diameter, form the type of dusty environment that contains presolar nebulae contracting under gravity before the onset of fusion; they contain large, complex, interstellar molecules with a high degree of saturation that are also of some biological interest: acetone, ethyl cyanide, ethanol, acetic acid, and probably the smallest amino acid, glycine. These molecules cannot be formed easily by gas-phase reactions alone; consequently, theories of solid state chemical reactions on grain surface ice mantles are often invoked to form these large molecules and evaporation is proposed as the mechanism that drives them into the gas phase. Hence, high resolution millimeter-wavelength arrays can spectroscopically sample the composition of evaporated presolar material--the material that eventually may form the basis for a type of prebiotic organic chemistry similar to that found on the early Earth.

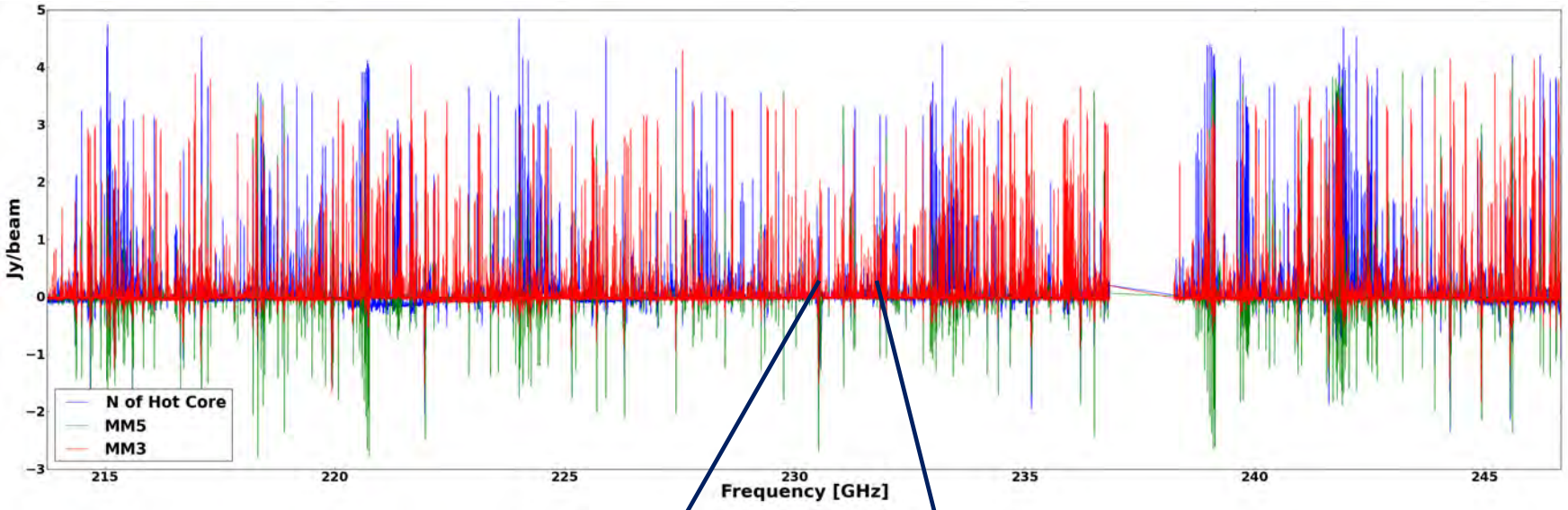
Publication: Proc. SPIE Vol. 3111, p. 296-304, Instruments, Methods, and Missions for the Investigation of Extraterrestrial Microorganisms, Richard B. Hoover; Ed.

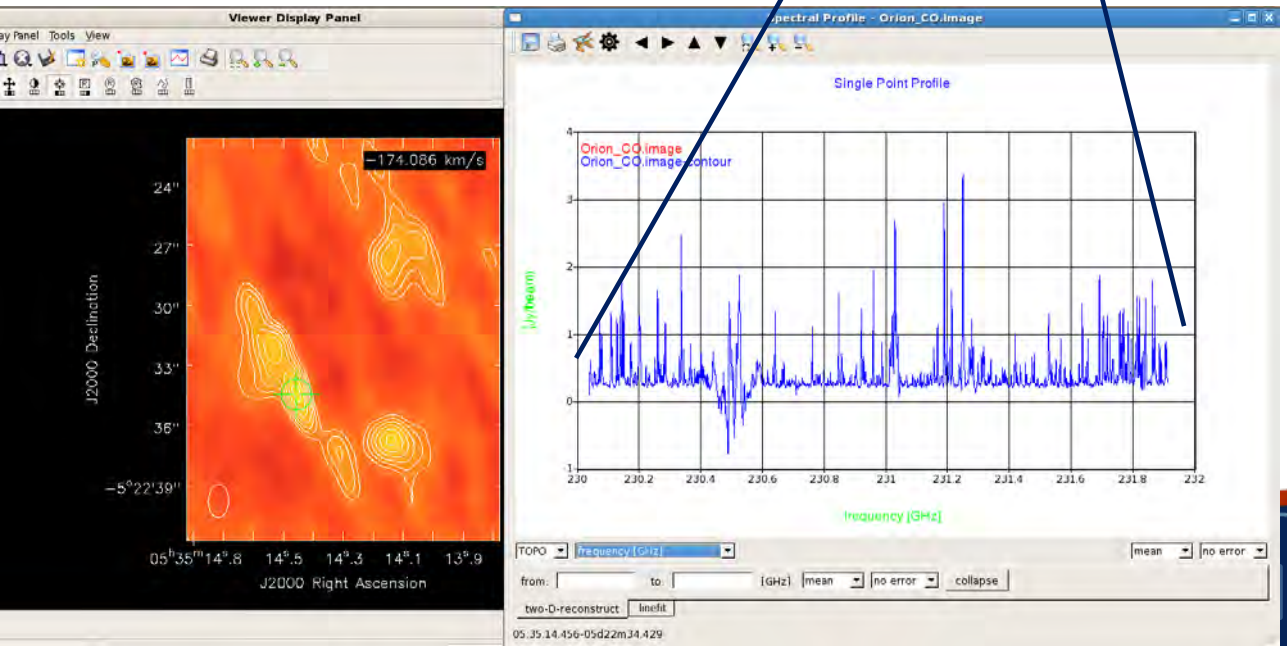
Pub Date: July 1997

DOI: 10.1117/12.278783

Bibcode: 1997SPIE.3111..296S

ALMA was born! And this is what we got…





Orion Band 6 (214 – 246 GHz) – Publically available off www.almascience.org

There is signal in nearly every channel and it is very hard to find "clean" transitions of well known molecules.

Molecule Discoveries Stall using ALMA

- ALMA did not give the watershed of new molecule detections that were anticipated.

- This is/was largely due to the tremendous amount of line confusion and the fact that the rotational energy of large molecules was spread over a wide range of frequencies.

- Very wisely, looking at the proposal for the Green Bank Telescope…

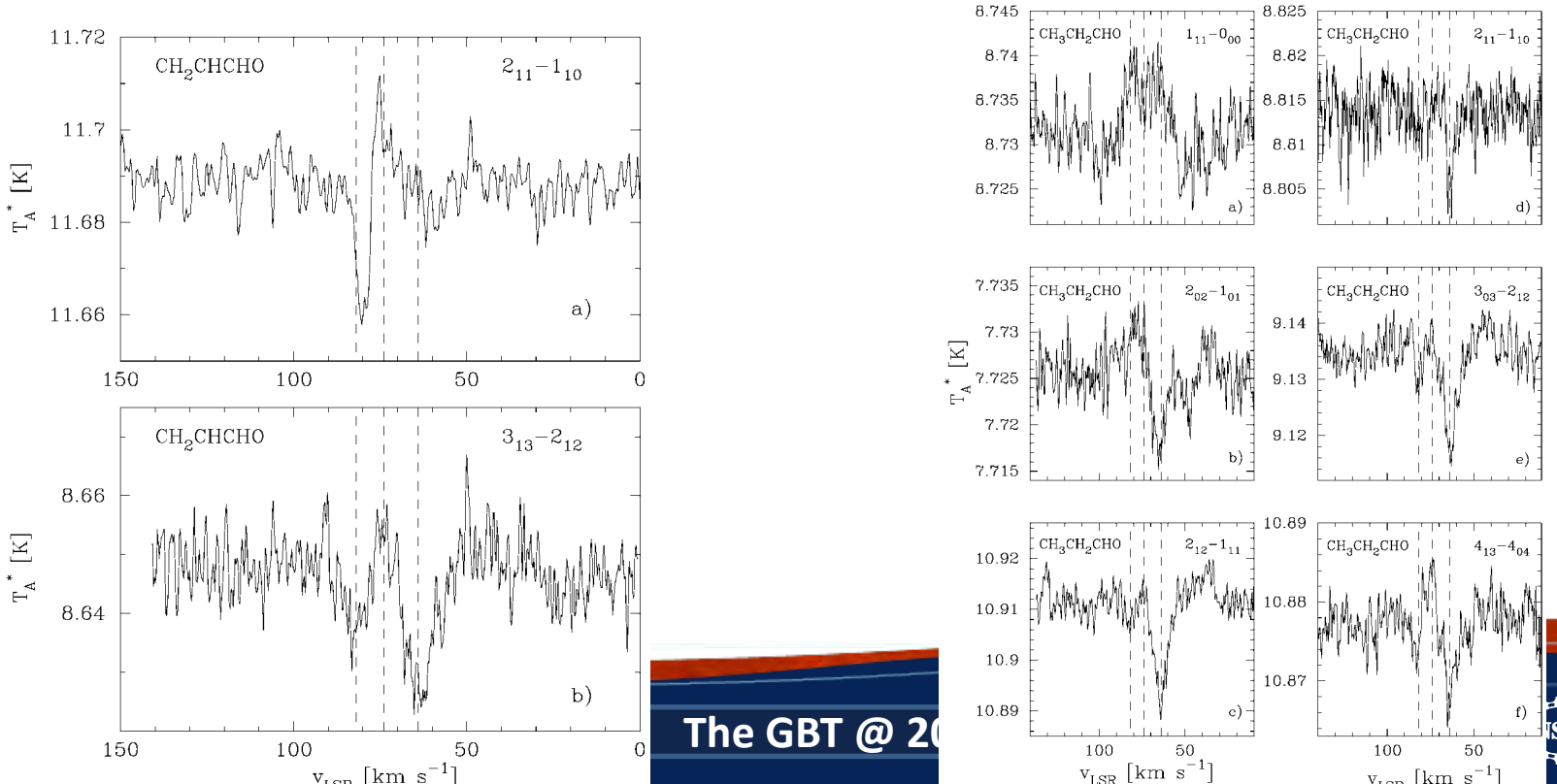
> The strong spectral features of larger molecules will be in the centimeter range, whereas those of smaller molecules will be in the millimeter or even the submillimeter range. *Thus, the centimeter spectral region, in addition to playing an important role in the astrophysics of molecular clouds, is now being recognized as highly important in clarifying the astrochemistry as well, a role previously emphasized more for the millimeter and submillimeter spectral regions.*

The Green Bank Telescope provides the sensitivity and resolution needed to continue the search for molecule material in the ISM.

Detections came fast and furious starting around 2004…

Green Bank Telescope Observations of New Interstellar Aldehydes: Prepenal and Propanal

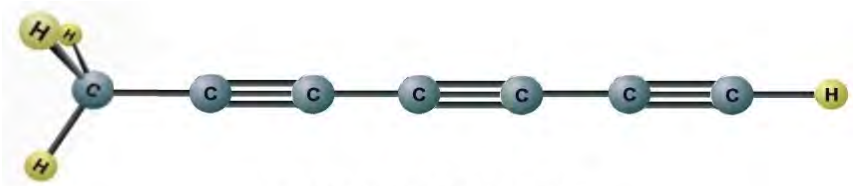
(Hollis et al. 2004, ApJ, 610, L21)



Methyltriacetylene (CH_3C_6H) toward TMC-1: The Largest Detected Symmetric Top

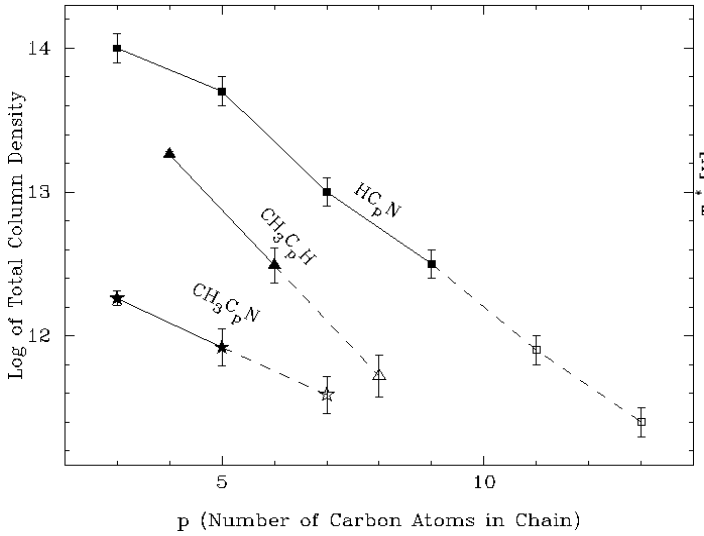
(Remijan et al. 2006, ApJ, 643, L37)

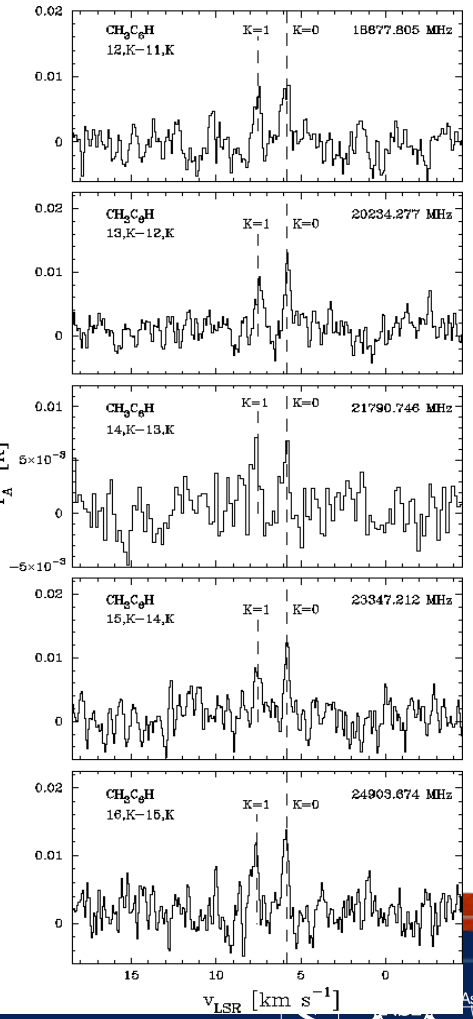
In this work, we identified interstellar methyltriacetylene (CH_3C_6H) using the GBT toward the dark Taurus Molecular Cloud (TMC-1).



METHYLTRIACETYLENE

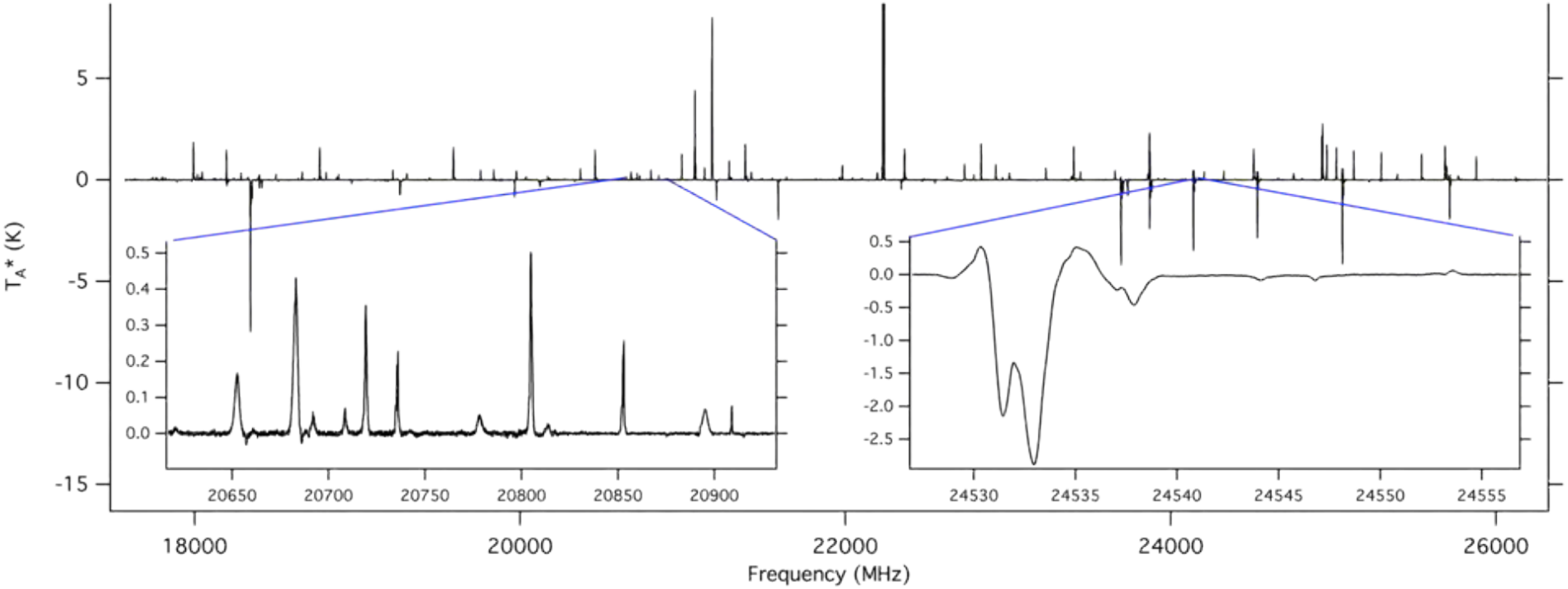
Strong correlations are found among the values of the three different carbon-chain slopes when total column densities of sequence members are plotted against the number of carbon atoms in the carbon chain. This result suggests that the formation chemistry for all these carbon-chain sequences is common.





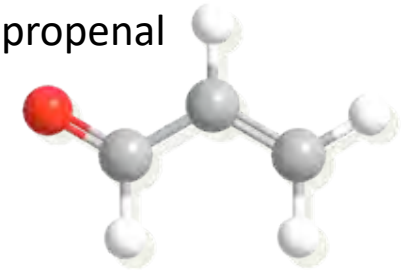
PRebiotic Interstellar MOlecular Survey

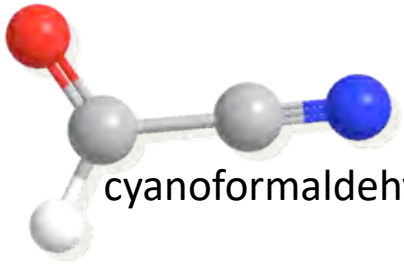
- One of the earliest "Large" programs on the GBT
- Target: Sgr B2(N-LMH)
- Coverage: 40.4 GHz of Bandwidth from 300 MHz - 50 GHz
- Noise level of ~2 mK
- Publicly available with no proprietary period



(Some) New Molecule Detections

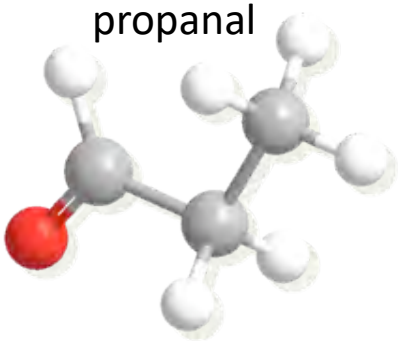
propenal

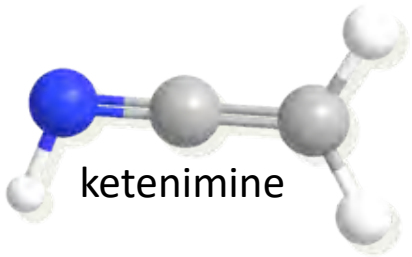




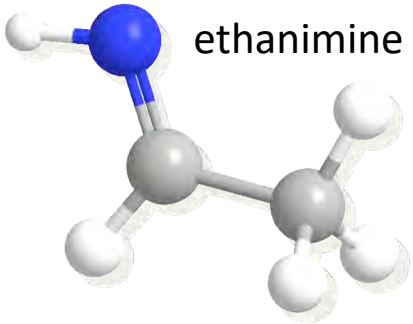
cyanoformaldehyde

propanal

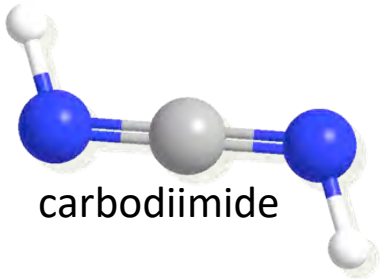




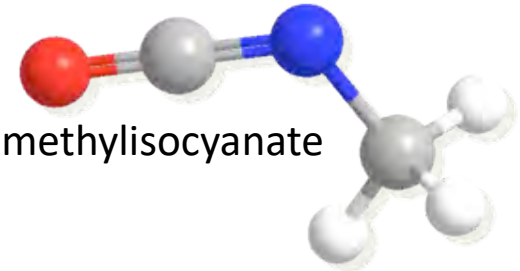
ketenimine



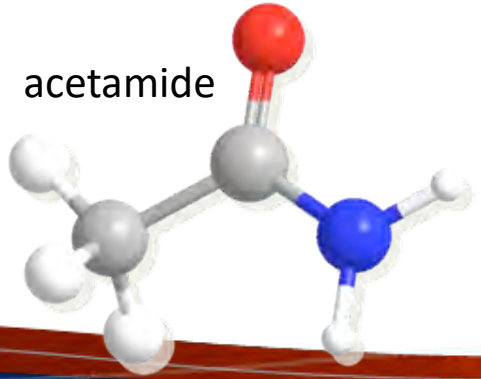
ethanimine



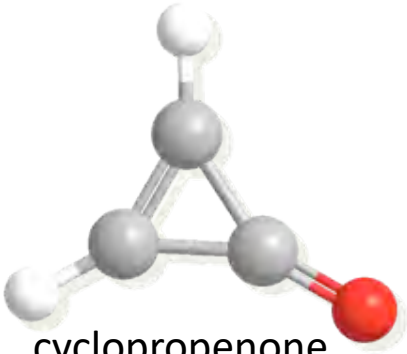
carbodiimide



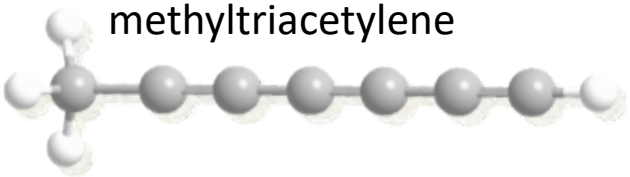
methylisocyanate



acetamide

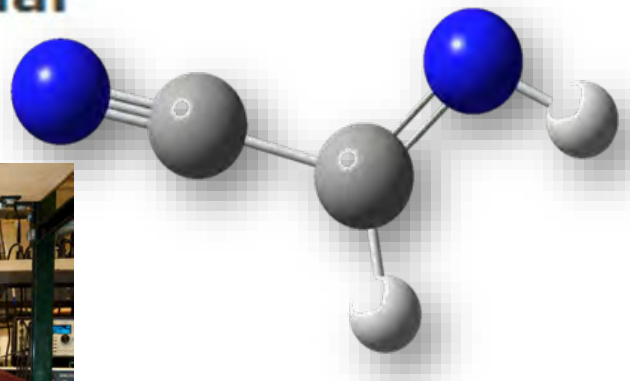


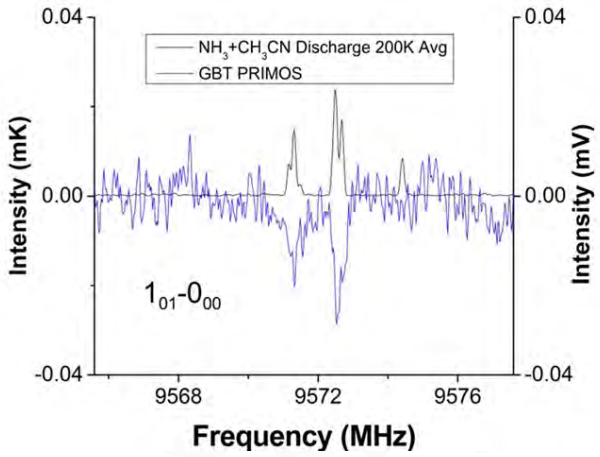
cyclopropenone

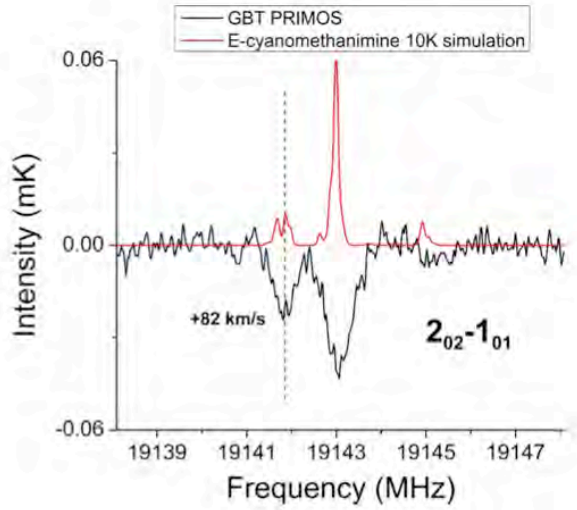


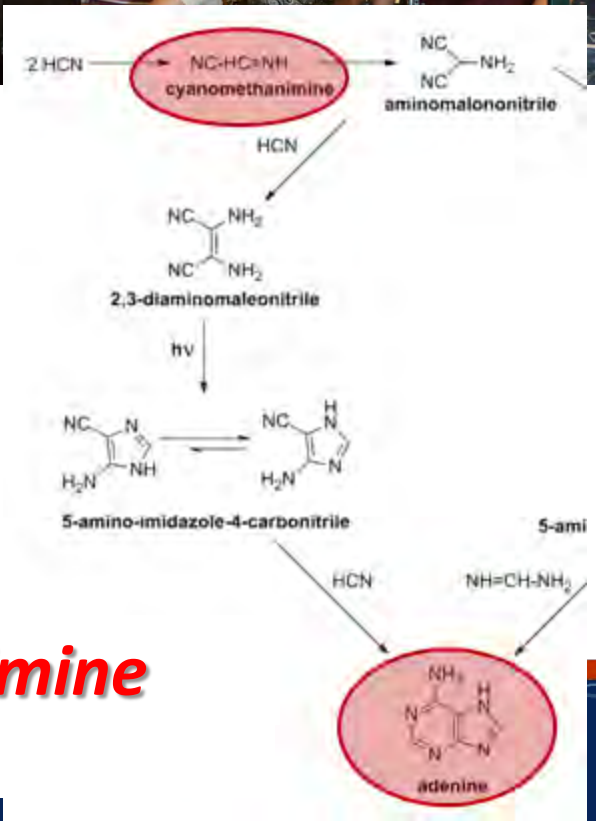
methyltriacetylene

Student Team Discovers New Interstellar Molecule During Summer Program







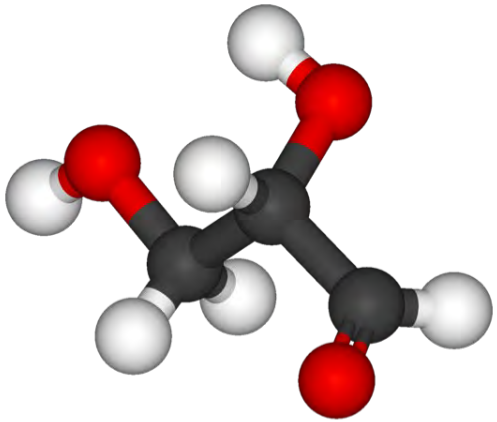


- **Precursor to prebiotic oligomers of HCN**
- **Formation of adenine using only addition of HCN**
  - **Adenine is a nucleobase with a variety of roles in organic chemistry including cellular respiration.**
  - **energy-rich adenosine triphosphate (ATP)**
  - **Protein synthesis, as a chemical component of DNA and RNA**

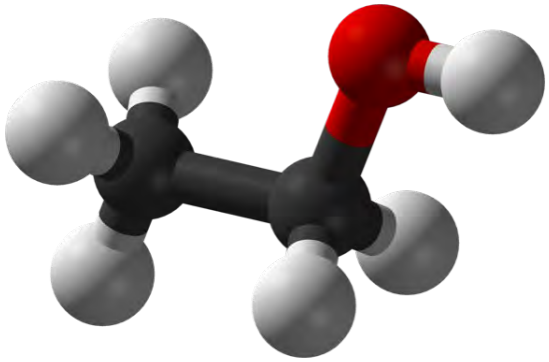
E-Cyanomethanimine

Zaleski et al. 2013 ApJ, 765, L9

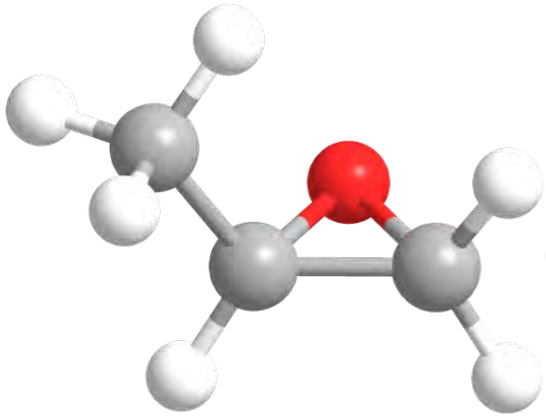
GBT Observations reveal the first signal from a chiral molecule



glyceraldehyde



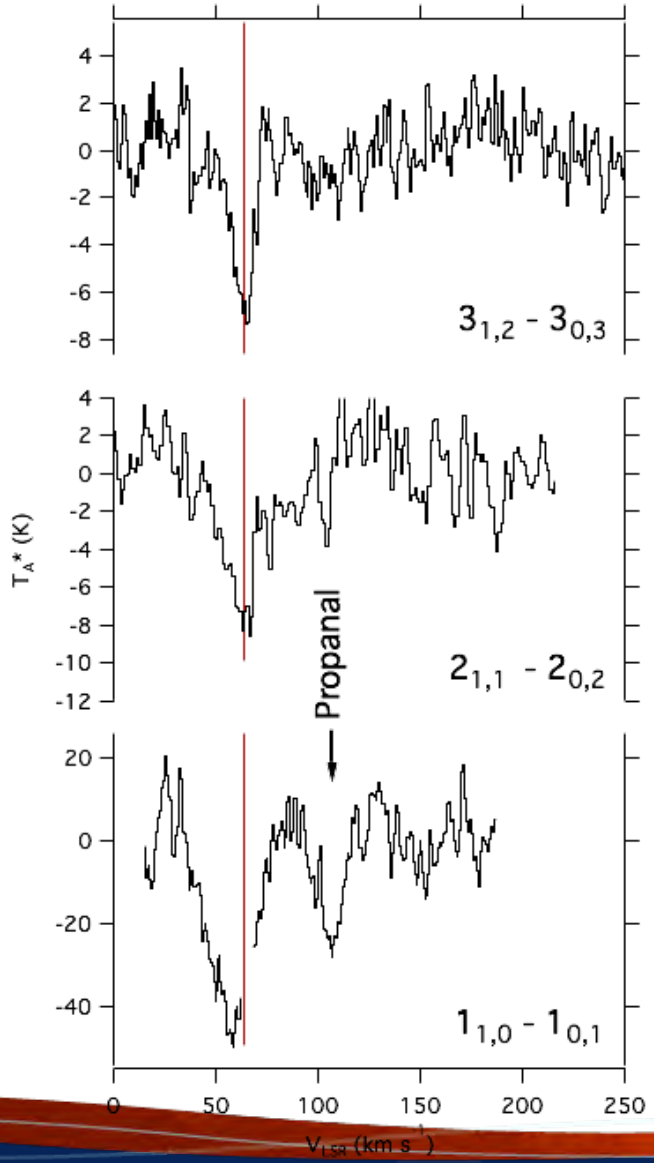
deuterated ethanol



propylene oxide

Joint GBT/Parkes Detection

GBT Observations reveal the first signal from a chiral molecule

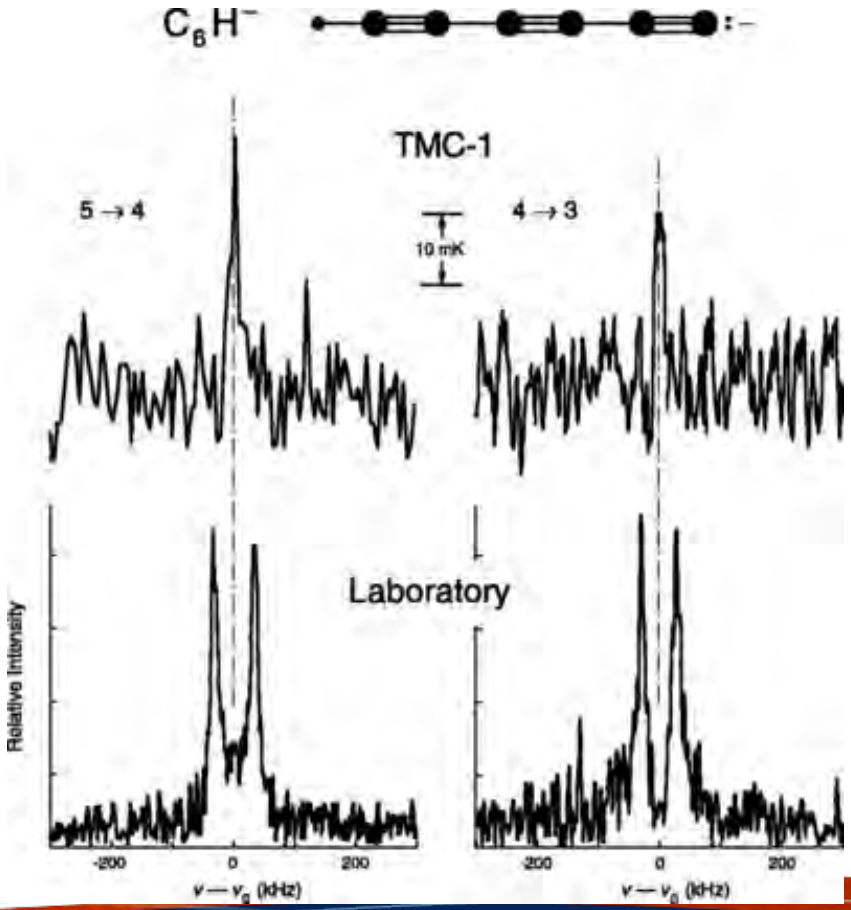


One of the most surprising and unanticipated discoveries was the first detection of interstellar anions toward the dark cloud TMC-1

Laboratory and Astronomical Identification of the Negative Molecular Ion C_6H^-
2006ApJ...652L.141

Surprising because it was believed that the smaller anions (e.g. C_2H^-) would be detected before the larger anions.

Turns out the larger molecules had a larger electron affinity which would preferentially favor larger molecules forming anions.

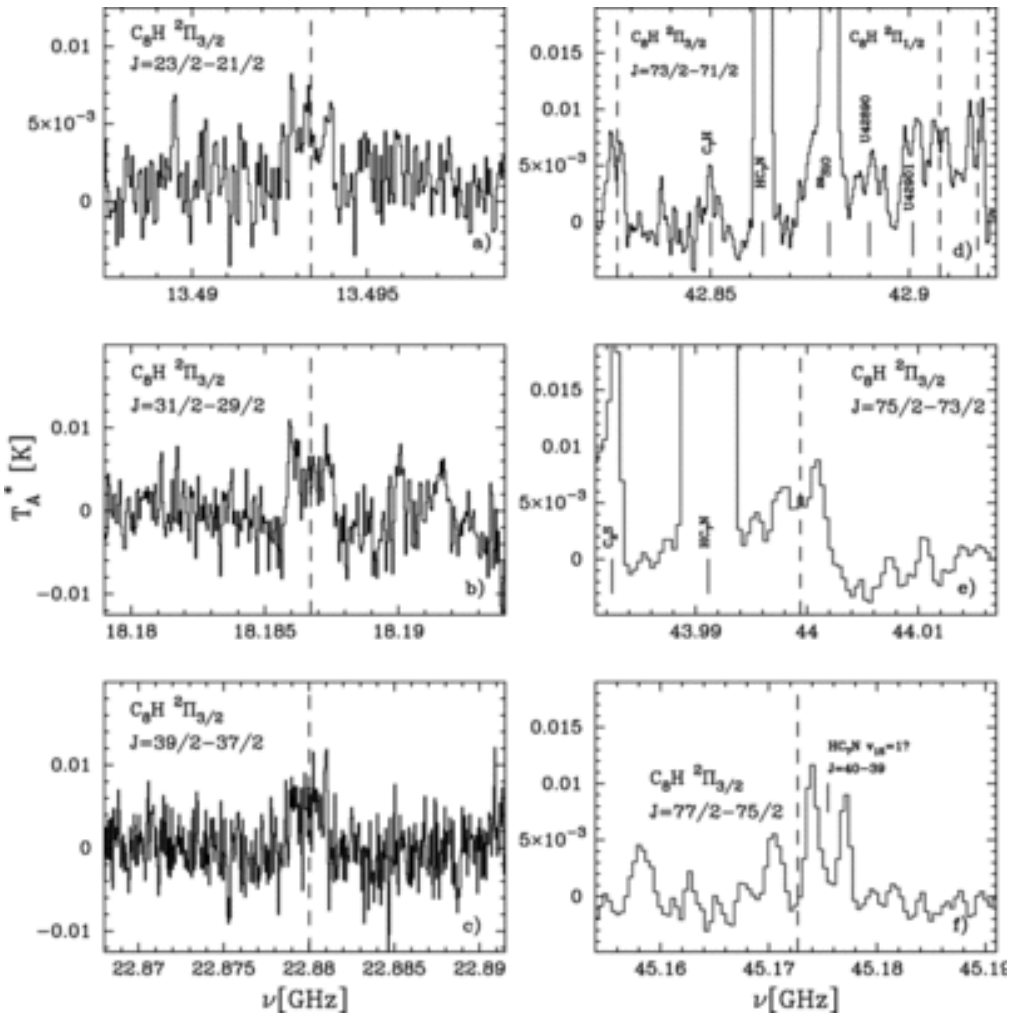


Soon after the discovery of C_6H^-…

Detection of the Carbon Chain Negative Ion C_8H^- in TMC-1
2007ApJ...664L..43B

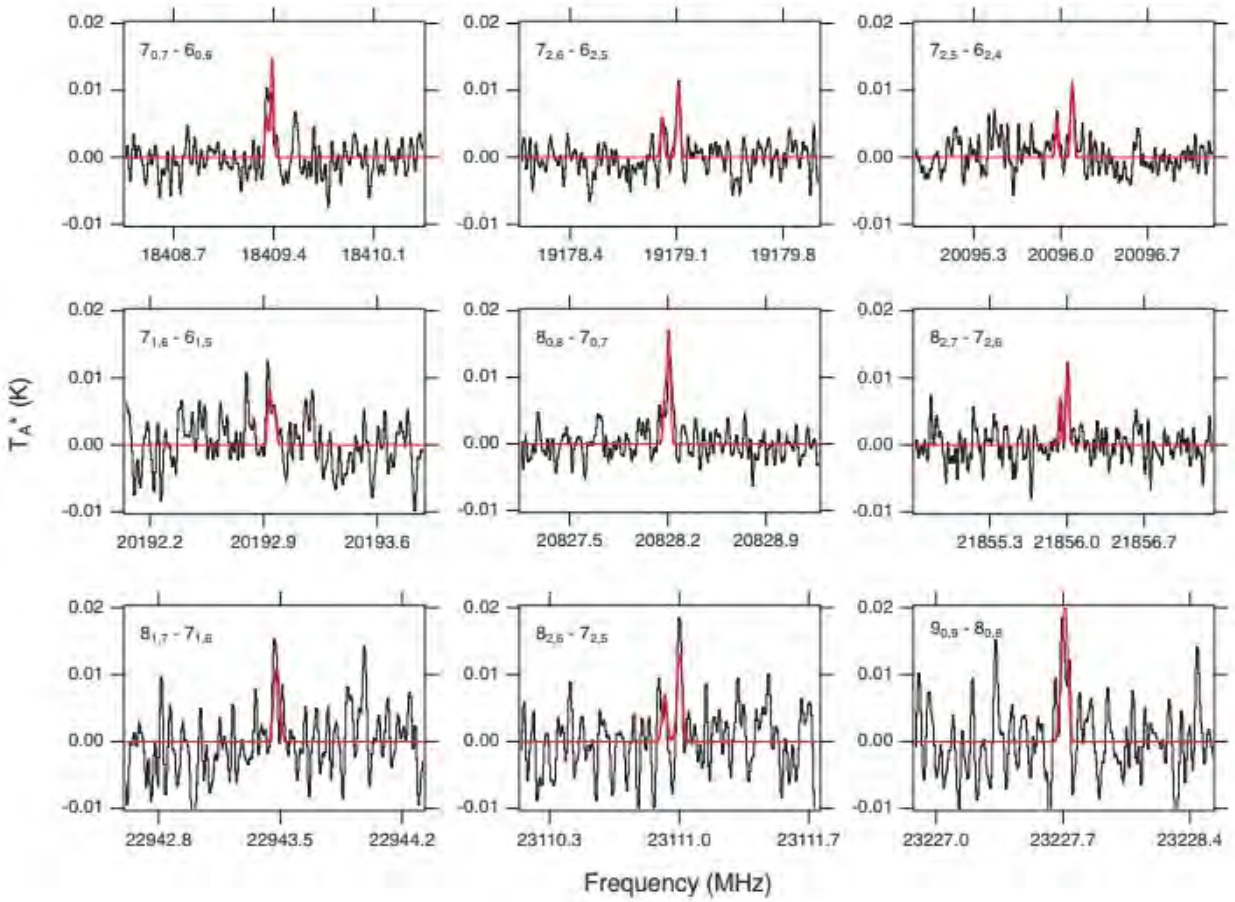
Detection of C_8H^- and Comparison with C_8H toward IRC +10 216
2007ApJ...664L..47R

For the better part of 4 years, the search for anions with the GBT continued at a furious pace and expanded to more anions and more sources



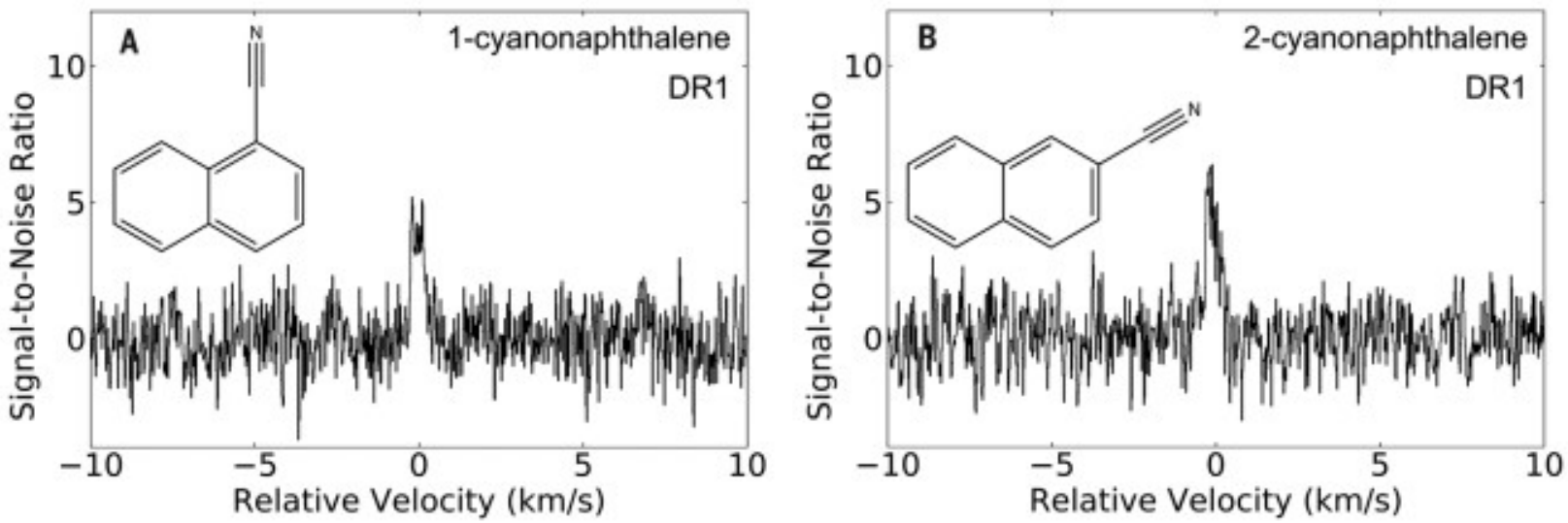
Where we are today?
New molecule detections and a better understanding of the molecular makeup of the Galaxy continues to grow because of GBT Observations.

- The shift has moved to an old (but new again) source, TMC-1, with the detection of the first true ***aromatic*** species in the ISM.
- The detection of benzonitrile in 2018 started the first of many new aromatic species detected towards TMC-1



And the GBT Large Program…

GBT Observations of TMC-1: Hunting Aromatic Molecules (GOTHAM) collaboration has used the tried and true technique of averaging and matched filtering to detect even more complex species, such as 1 and 2-cyanonaphthalene



If you believe that "imitation is the sincerest form of flattery"…

- The Yebes telescope in Spain is now equipped with Q-band receivers and is detecting new, large molecules towards TMC-1… clearly showing the ingenuity of the designers for the GBT that the largest molecules were going to be detected at centimeter wavelengths.

And, there is no doubt that the GBT will continue to detect more complex molecules in astronomical environments.

Haven't even mentioned the GBT's role in understanding star formation and molecular cloud evolution with observations of NH3, and HCN with the new cameras…

And megamasers…

The list goes on!

Finally, one of the best stories of a molecule detection was for HC11N…

There and Back Again

DETECTION OF $HC_{11}N$ IN THE COLD DUST CLOUD TMC-1

M. B. Bell and H. E. Matthews
Herzberg Institute of Astrophysics, National Research Council of Canada
Received 1984 November 19; accepted 1984 December 28

ABSTRACT

We report the detection of the $J = 41 \rightarrow 40$ rotational transition of $HC_{11}N$ in the direction of the Taurus molecular cloud complex. The line strength is in good agreement with predicted values, and the rotational parameters, although determined more accurately with these results, remain unchanged from those obtained previously using observations of IRC +10°216 alone.

Subject heading: interstellar: molecules

There was the first claimed detection of this molecule in 1997 using the 140-ft telescope…

There and Back Again

Non-detection of $HC_{11}N$ towards TMC-1: constraining the chemistry of large carbon-chain molecules

ABSTRACT

Bell et al. reported the first detection of the cyanopolyyne $HC_{11}N$ towards the cold dark cloud TMC-1; no subsequent detections have been reported towards any source. Additional observations of cyanopolyynes and other carbon-chain molecules towards TMC-1 have shown a log-linear trend between molecule size and column density, and in an effort to further explore the underlying chemical processes driving this trend, we have analysed Green Bank Telescope observations of HC_9N and $HC_{11}N$ towards TMC-1. Although we find an HC_9N column density consistent with previous values, $HC_{11}N$ is not detected and we derive an upper limit column density significantly below that reported in Bell et al. Using a state-of-the-art chemical

However, subsequent observations on the GBT 20 years later could not confirm the detection…

Our Precious was LOST!

There and Back Again

An Investigation of Spectral Line Stacking Techniques and Application to the Detection of $HC_{11}N$

probe molecular complexity while still retaining observational specificity. Toward this end, we present a method for detecting and characterizing new molecular species in single-dish observations toward sources with sparse line spectra. We have applied this method to data from the ongoing GOTHAM (GBT Observations of TMC-1: Hunting Aromatic Molecules) Green Bank Telescope (GBT) large program, discovering six new interstellar species. In this paper we highlight the detection of $HC_{11}N$, the largest cyanopolyyne in the interstellar medium.

Only to be found and confirmed in 2020 using the novel techniques from the GOTHAM consortium!

www.nrao.edu
science.nrao.edu

The National Radio Astronomy Observatory is a facility of the National Science Foundation operated under cooperative agreement by Associated Universities, Inc.