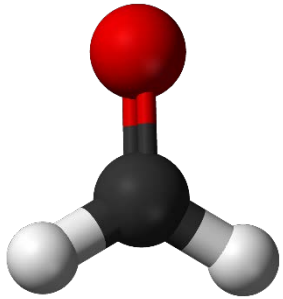
Radio Astronomy and Spectroscopy: Bell Labs to ALMA

Anthony Remijan – Assistant Director, Science Support and Research @ NRAO

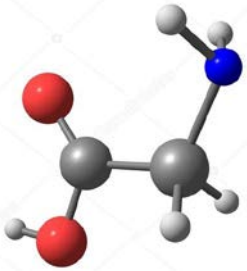
Outline



Let's start at the beginning…detection of Formaldehyde

The hunt for more complex molecules

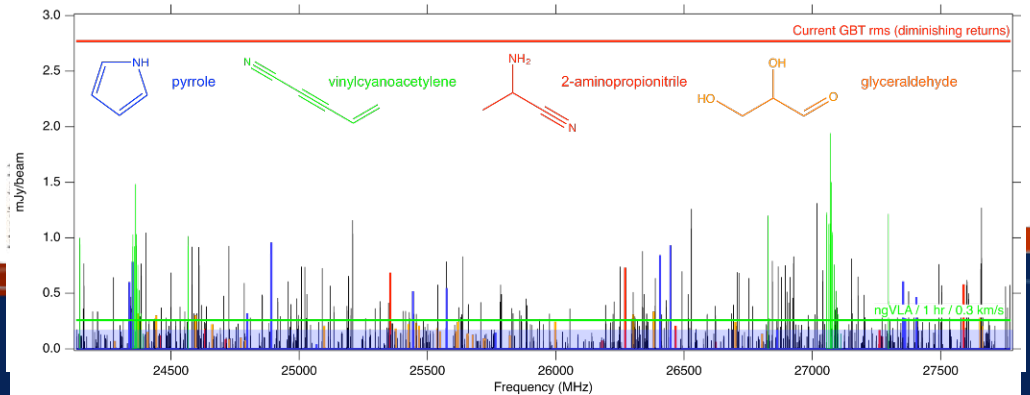
- Glycine
- Dihydroxyacetone
- Urea



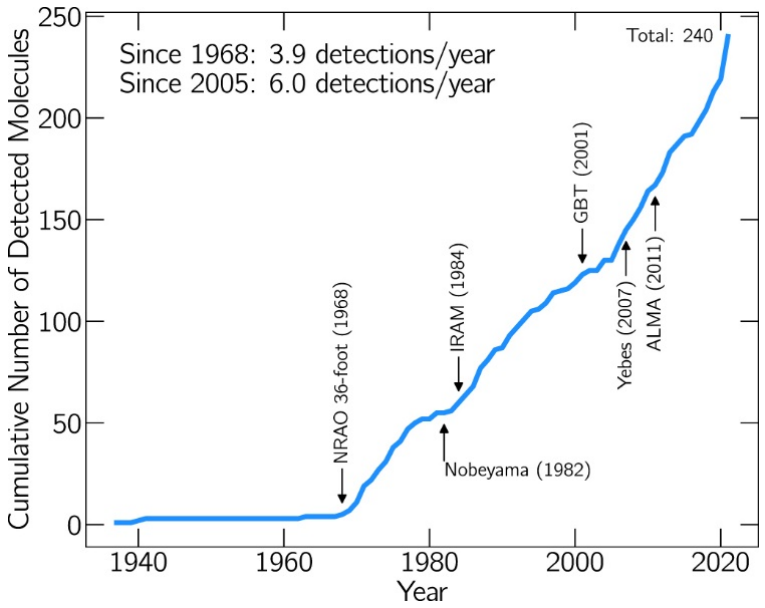
Interstellar mapping campaigns

- Acetic acid
- Acetone
- Formic acid/methyl formate
- $C_2H_4O_2$ isomers

What are the limits to molecular complexity?



Astrochemistry Research – Where are we now?



Total number of molecular detections per year since 1968. Reproduced from McGuire et al. 2022 – and its still growing

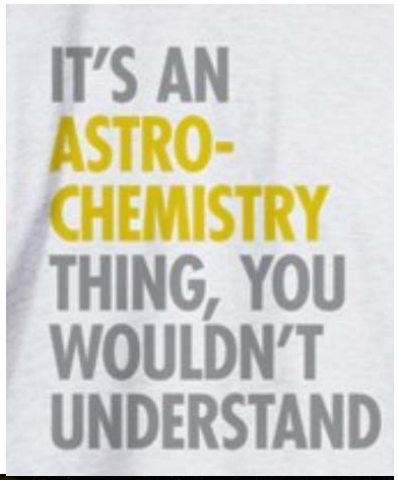
From the simplest, to the most complex, the modern field of radio astrochemistry is uncovering a molecular complexity previously unheard of just 50 years ago.

Happy Birthday to:

- Ammonia – 54 y/o
- Formaldehyde – 53 y/o
- Carbon Monoxide/"X-ogen"
- Methanol – 52 y/o
- Methyl Amine/Dimethyl ether/Remij
- Acetone – 35 y/o
- Acetic Acid/Ethylene Oxide – 2
- Glycolaldehyde – 22 y/o
- Ethylene Glycol – 20 y/o
- Acetamide/C_6H^- – 16 y/o
- C_{60}/C_{70} – 12 y/o
  - C_{60}^+ - 9 y/o
- Benzonitrile – 4 y/o
- Urea – 3 y/o (or 8?)
- 1/2 – cyanonaphthalene – 1 y/o
  - 40 molecules turn 1 this yea molecule detection a week f
  - To get to 40 detected molec 40 years (1937-1975)

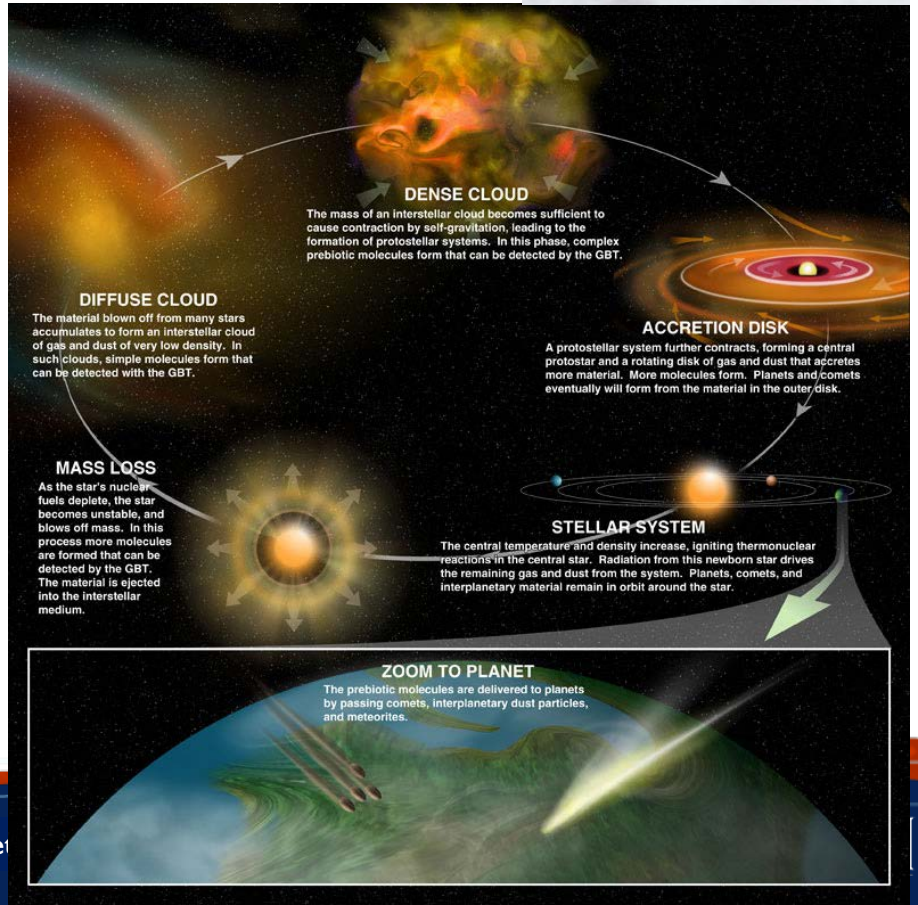
Goals

- Have a little fun, reminisce and pay respect to Lew Snyder



- Even though astrochemistry has been around for more than 50 years, we still don't have a very good understanding of interstellar chemical processes

- Using a combination of chemical mapping and high resolution spectroscopy, we can start answering the question of how large molecules form in space



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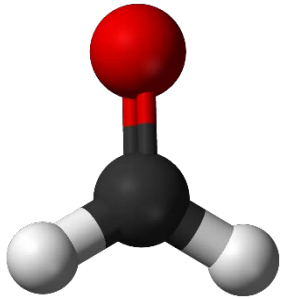

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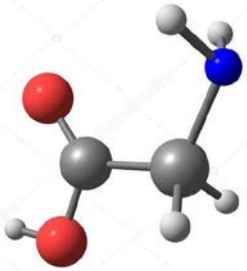

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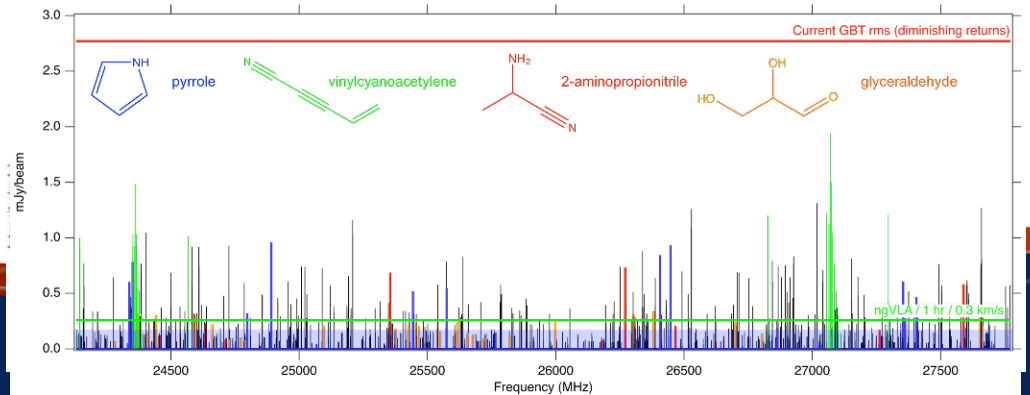


Let's start at the beginning…detection of Formaldehyde

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.

Let's start at the beginning…detection of Formaldehyde

At that time, only CH, CH^+, and CN were identified in optical spectra by Swings and Rosenfeld (1937), McKellar (1940), and Douglas and Herzberg (1941), respectively.

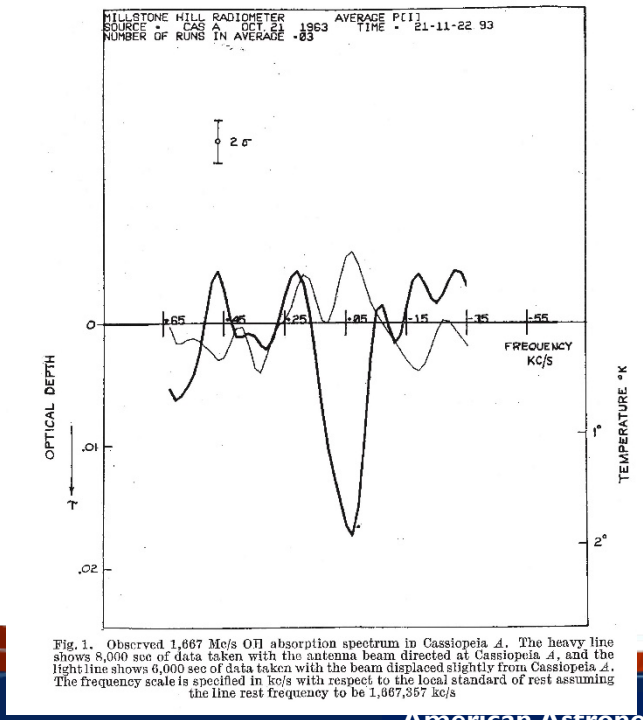


Fig. 1. Observed 1,667 Mc/s OH absorption spectrum in Cassiopeia *A*. The heavy line shows 8,000 sec of data taken with the antenna beam directed at Cassiopeia *A*, and the light line shows 6,000 sec of data taken with the beam displaced slightly from Cassiopeia *A*. The frequency scale is specified in kc/s with respect to the local standard of rest assuming the line rest frequency to be 1,667,357 kc/s

NOTE ON THE INTERPRETATION OF UNIDENTIFIED INTERSTELLAR LINES

ABSTRACT

Spectroscopic objections to recent assignments of Merrill's unidentified stationary lines to molecular absorption bands are outlined.

Since the suggestion of the possible molecular origin[1] of Merrill's four interstellar lines,[2] attempts to correlate them with absorption bands of known molecules have been made.[3,4] The resulting identifications are, unfortunately, open to purely spectroscopic criticism, and indeed it seems highly improbable that these lines can be interpreted as molecular bands.

Many years later, OH was found in absorption against Cas A by Weinreb et al. (1963).

Thus for a 30 year span, only diatomic molecules were found in space: CH, CH^+, CN, and OH.

Let's start at the beginning…detection of Formaldehyde

Lew Snyder arrived at NRAO in 1967 for what was to be a 2 year assignment to search for molecules in space… Along with Dave Buhl, an electrical engineer and fellow molecule hunter, they discussed the possibility of finding H_2O in space.

These efforts were presented at the AAS meeting in Austin in Nov. 1968 by Snyder. But before the presentation could start, Charles Townes announced that his group had discovered ammonia (NH_3) in space with the Hat Creek Millimeter Wave Antenna a few weeks earlier.

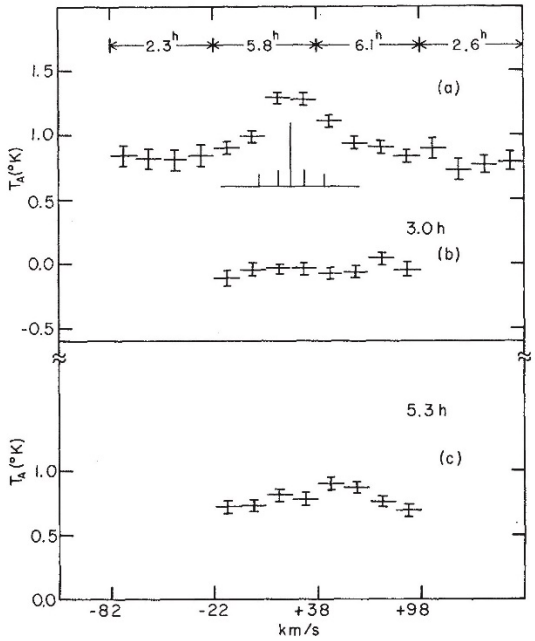


FIG. 2. Observed NH_3 spectra and continuum from the galactic center. (a) $J=1, K=1$ inversion of NH_3 with the expected hyperfine splitting superimposed, (b) baseline from empty sky, and (c) $J=2, K=2$ inversion line of NH_3. The continuum temperature should be scaled down by a factor of 2 because superheterodyne detection accepts both sidebands of continuum radiation.

Let's start at the beginning…detection of Formaldehyde

The detection of NH_3 was soon followed by the detection of water – which turned out to be a source of maser emission.

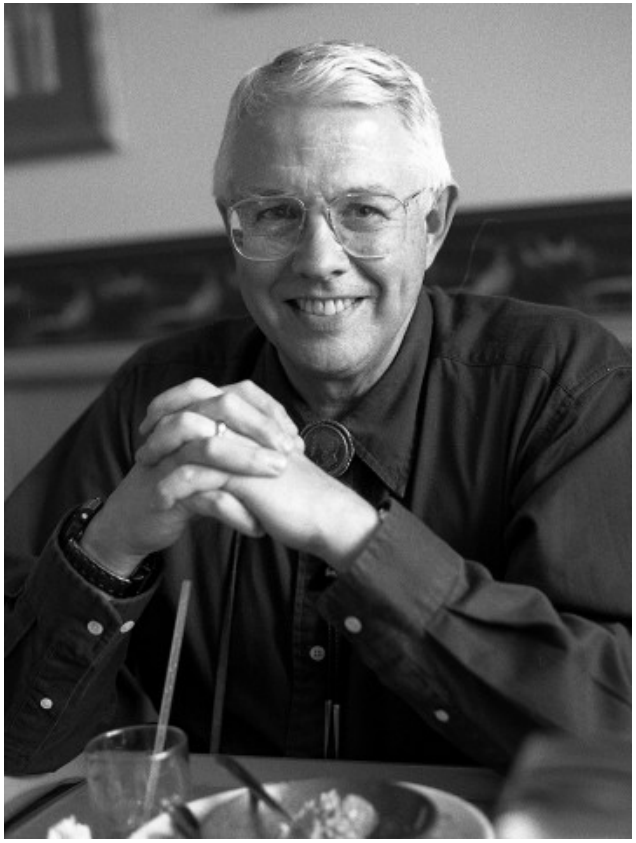
It was time to get serious about searching for larger molecules in astronomical environments and NRAO facilities were well "positioned" to lead these searches.

Rick Suenram "positioning" the 140-ft telescope in Green Bank, WV

Let's start at the beginning…detection of Formaldehyde

Prompted by the Assistant to the Director of NRAO, W.E. (Bill) Howard III, Howard suggested that they write a proposal for all the molecules they wanted to find and submit them to D. S. Heeschen, the NRAO director at the time.

However… NRAO management was not very "enthusiastic" about scheduling months of observations on the 140-ft and nearly a year of observing on the 36-ft.



William E. Howard, III (1932 - 2016) at the 30th anniversary of the 140-ft telescope.

Let's start at the beginning…detection of Formaldehyde

As instructed, Snyder and Buhl submitted their proposal which triggered an explosion by then director David Heeschen.

Paraphrasing the proposal review, it said something to the effect of:
"how irresponsibly the PIs had requested months of 140-ft time for source searches and almost a year of 36-ft time. What were we trying to do?"

In response… Buhl said that "we were trying to interest people in molecules in space."

Heeschen responded, "you have failed to interest me!"

Snyder replied with …something more colorful.

Let's start at the beginning…detection of Formaldehyde

With the pressure mounting with the new detections taking place in Hat Creek, Heeschen instructed Howard to allocate time for "molecule searches" amongst other observing programs… which caught the team by surprise.

Howard negotiated a deal with B. Zuckerman and P. Palmer, who had 140-ft time mixed with the molecule searches. In return for using their OH sources and Berkeley Doppler shift program, Snyder and Buhl let them share in the search for H_2CO.

And in the spring of 1969, they found the H_2CO 4830-MHz line in absorption with the 140-ft of the NRAO – the rest is history!

Let's start at the beginning…detection of Formaldehyde

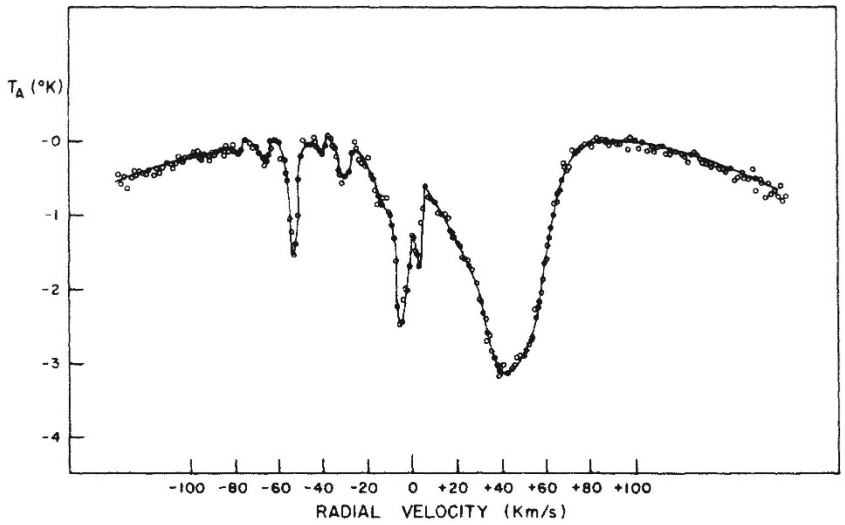
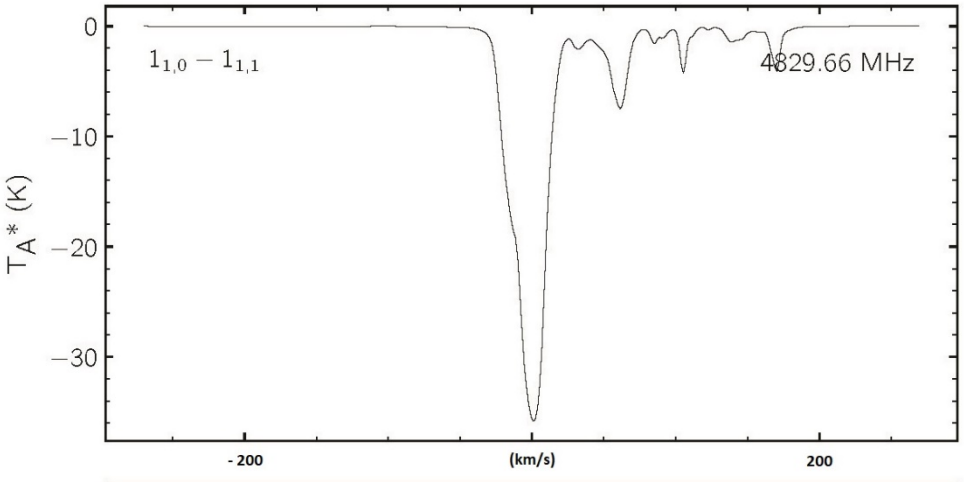


FIG. 1. Formaldehyde absorption against the galactic center (Sgr *A*). The ordinate is antenna temperature and the abscissa is radial velocity with respect to the local standard of rest. This spectrum closely resembles the OH absorption spectrum in the same direction. The effective resolution is ~1 km/sec.

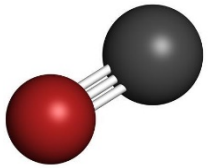


Formaldehyde absorption taken towards SgrB2(N-LMH) with the GBT as part of the GBT PRIMOS Large molecule survey. Velocities are relative to the 64 km/s systemic source velocity.

This line was detected in absorption against the continuum sources M17, W3, W3(OH), W49, NGC2024, Dr21, W43, W44, W51, SgrA, SgrB2, NGC6334, CasA, and 3C123. (Zuckerman, B., Buhl, D., Palmer, P., and Snyder, L.E., Ap, Vol. 160, May 1970.)

During these early observations, $H_2C^{13}O$, an isomer was discovered (Zuckerman, B., Palmer P., Snyder, L.E., and Buhl, D. 1969, Ap.J. (Letters), 157, L167.)

From those humble beginnings, a revolution started…



- The detection of CO in 1970 started a revolution that would change the way astronomers would study the universe:

THE ASTROPHYSICAL JOURNAL, 161:L43–L44, July 1970

CARBON MONOXIDE IN THE ORION NEBULA

R. W. WILSON, K. B. JEFFERTS, AND A. A. PENZIAS
Bell Telephone Laboratories, Inc., Holmdel, New Jersey, and
Crawford Hill Laboratory, Murray Hill, New Jersey
Received 1970 June 5

ABSTRACT

We have found intense 2.6-mm line radiation from nine galactic sources which we attribute to carbon monoxide.

This work was done with a specially constructed line receiver mounted on the NRAO 36′ paraboloid. Schottky barrier diodes developed by C. A. Burrus of Bell Laboratories were used in Sharpless wafer units both in the signal mixer and in a harmonic mixer used to control the frequency of the local oscillator klystron. Calibration noise was provided

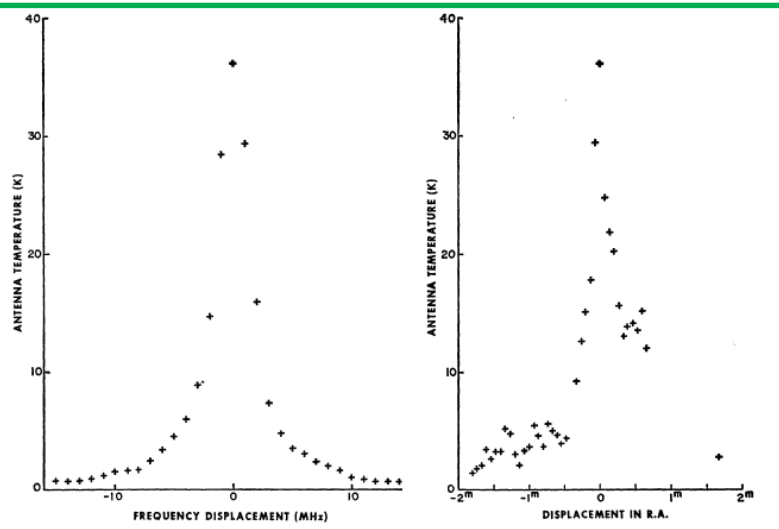
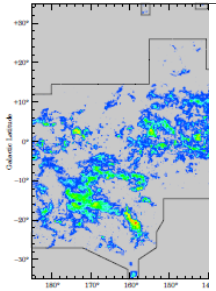


FIG. 1 FIG. 2

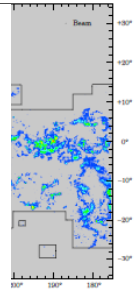
FIG. 1.—Spectrum of CO radiation in the Orion Nebula made with the NRAO forty-channel line receiver. The center frequency is 115, 267.2 MHz.

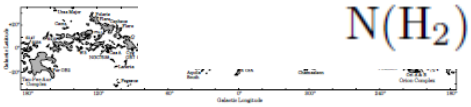
FIG. 2.—Distribution in right ascension of the peak antenna temperature of CO radiation at a declination of −5°24′21″.



As a consequence, astronomers frequently employ CO emission to measure molecular gas masses. The standard methodology posits a simple relationship between the observed CO intensity and the column density of molecular gas, such that

$$\mathrm{N(H_2)} = X_{\mathrm{CO}}\,\mathrm{W}(^{12}\mathrm{C}^{16}\mathrm{O}\,J = 1 \rightarrow 0), \qquad (1)$$





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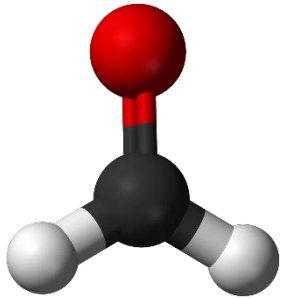
Outline



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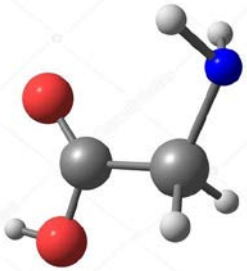

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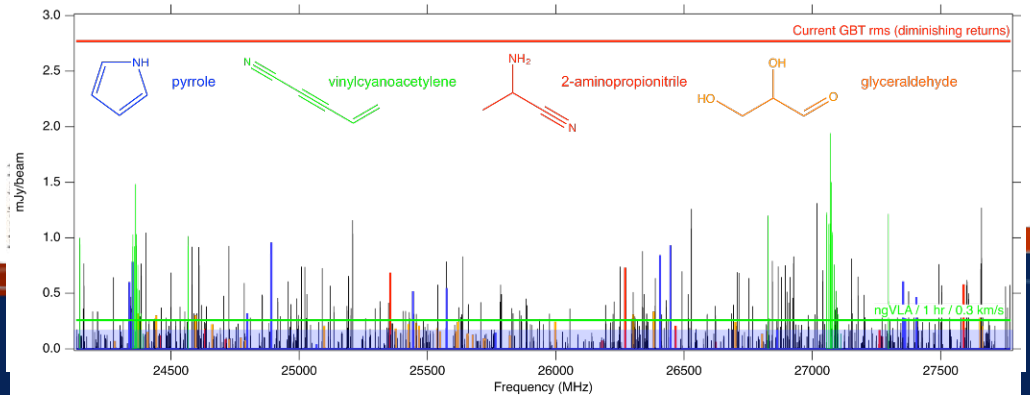


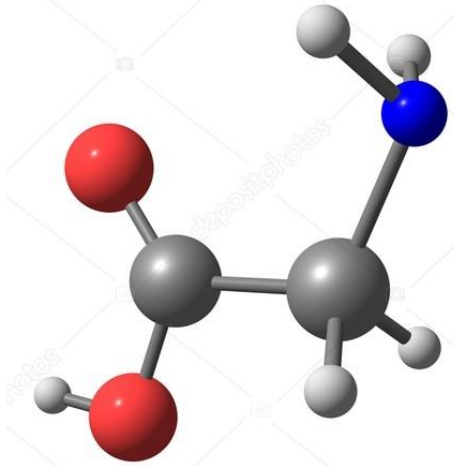
The Search for Larger Molecules - Interstellar Glycine

- Since the spectrum was first characterized in the late 1978s by Suenram and Lovas the hunt was on…

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

L. E. SNYDER
University of Illinois, Urbana
J. M. HOLLIS
Laboratory for Astronomy and Solar Physics, NASA Goddard Space Flight Center
R. D. SUENRAM AND F. J. LOVAS
National Bureau of Standards
AND
L. W. BROWN AND D. BUHL
Laboratory for Extraterrestrial Physics, NASA Goddard Space Flight Center
Received 1982 September 20; accepted 1982 October 26

The Search for Larger Molecules - Interstellar Glycine

- However… nothing was found
  - Well … not quite. During these initial searches, there were a lot of serendipitous detections of molecules like formic acid, methyl formate, dimethyl ether and the large cyanides.

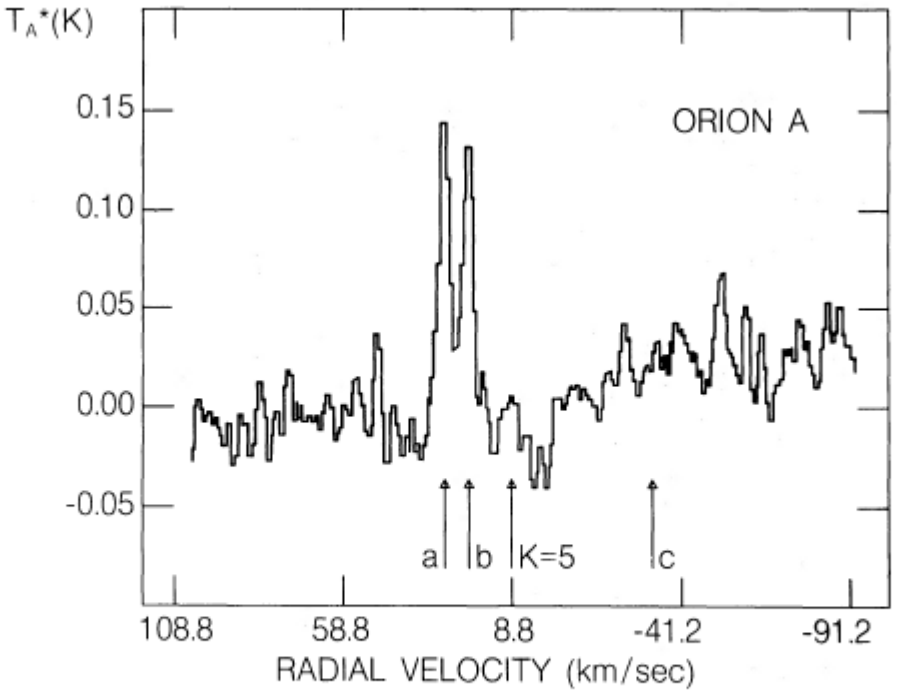


FIG. 5.—The emission spectra for (*a*) the 8_{08}–7_{07} E and (*b*) A resolved transitions of methyl formate in Orion are shown. Fiducial marks for glycine and acetic acid positions are delineated the same as Fig. 2. *Ordinate*, antenna temperature T_A^*, corrected for atmospheric and antenna losses; *abscissa*, radial velocity with respect to the LSR calculated for an upper sideband rest frequency of 90,233.78 MHz. The data were taken with 250 kHz width and spacing, and a three-point boxcar smoothing function has been applied.

Interstellar Glycine Searches…

- 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…
- Results are always the same… lot of blank spectra or worse yet, lots of blended lines…
- And, blank spectra and/or blended(contaminated) transitions can lead to erroneous detections

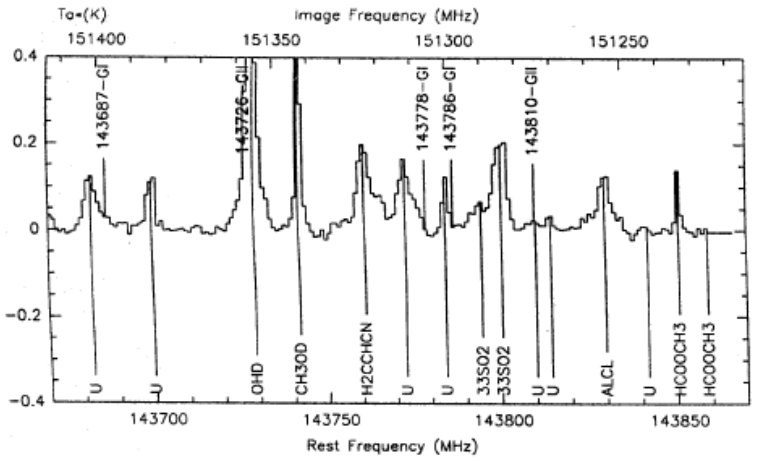


Fig. 1b. Same as 1a, around 143 GHz, the theoretical noise level is 5mK.

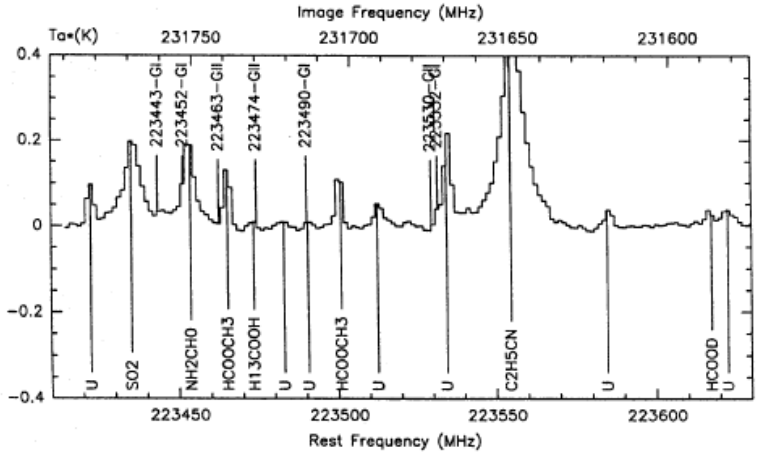


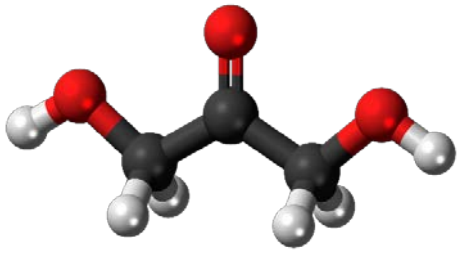
Fig. 1c. Same as 1a, around 223 GHz, the theoretical noise level is 6mK.

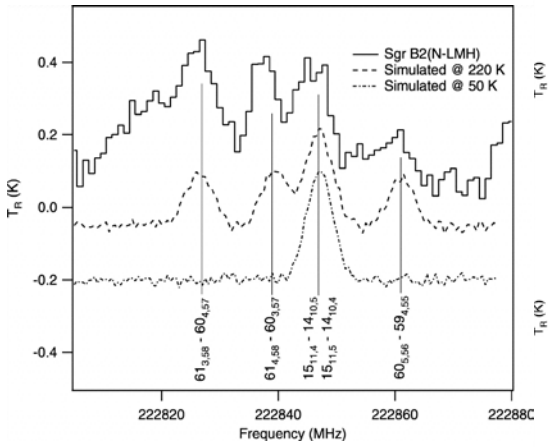
Dihydroxyacetone

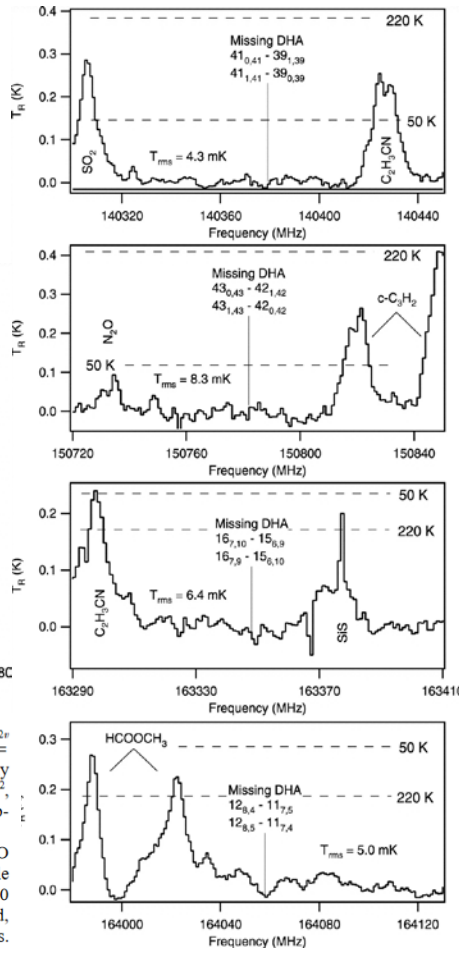
The Astrophysical Journal, 643:L29–L32, 2006 May 20

INVESTIGATING THE LIMITS OF CHEMICAL COMPLEXITY IN SAGITTARIUS B2(N): A RIGOROUS ATTEMPT TO CONFIRM 1,3-DIHYDROXYACETONE

A. J. Apponi, D. T. Halfen, and L. M. Ziurys
Departments of Chemistry and Astronomy, University of Arizona, 933 North Cherry Avenue, Tucson, AZ 85721; aapponi@as.arizona.edu





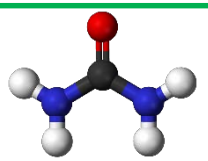


DHA is a near-prolate asymmetric top. Owing to its C_{2v} symmetry, its only dipole moment lies along the *b*-axis (μ_b = 1.765 D), which results in a complex spectrum of many closely spaced transitions. With $T_{rot} \sim 220$ K and $N_{tot} = 1.5 \times 10^{16}$ cm^{-2}, as proposed by WB05, hundreds of DHA lines should be observable throughout the millimeter region.

Sixty-one transitions of DHA were covered at the ARO 12 m and two lines at the GBT toward Sgr B2(N). Plausible spectral lines were detected at only two frequencies; for 20 transitions, typical upper limits of $T_R < 10$–30 mK were found, and the remaining lines were contaminated by other molecules.

Urea

A&A 628, A10 (2019)
https://doi.org/10.1051/0004-6361/201935428



Astronomy & Astrophysics

Re-exploring Molecular Complexity with ALMA (ReMoCA): interstellar detection of urea

A. Belloche[1], R. T. Garrod[2], H. S. P. Müller[3], K. M. Menten[1], I. Medvedev[4], J. Thomas[4], and Z. Kisiel[5]

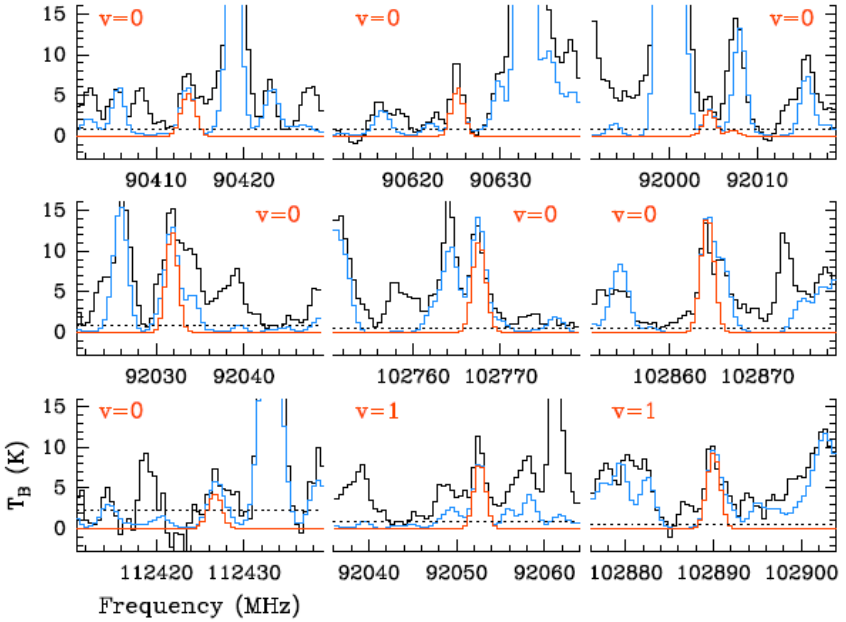
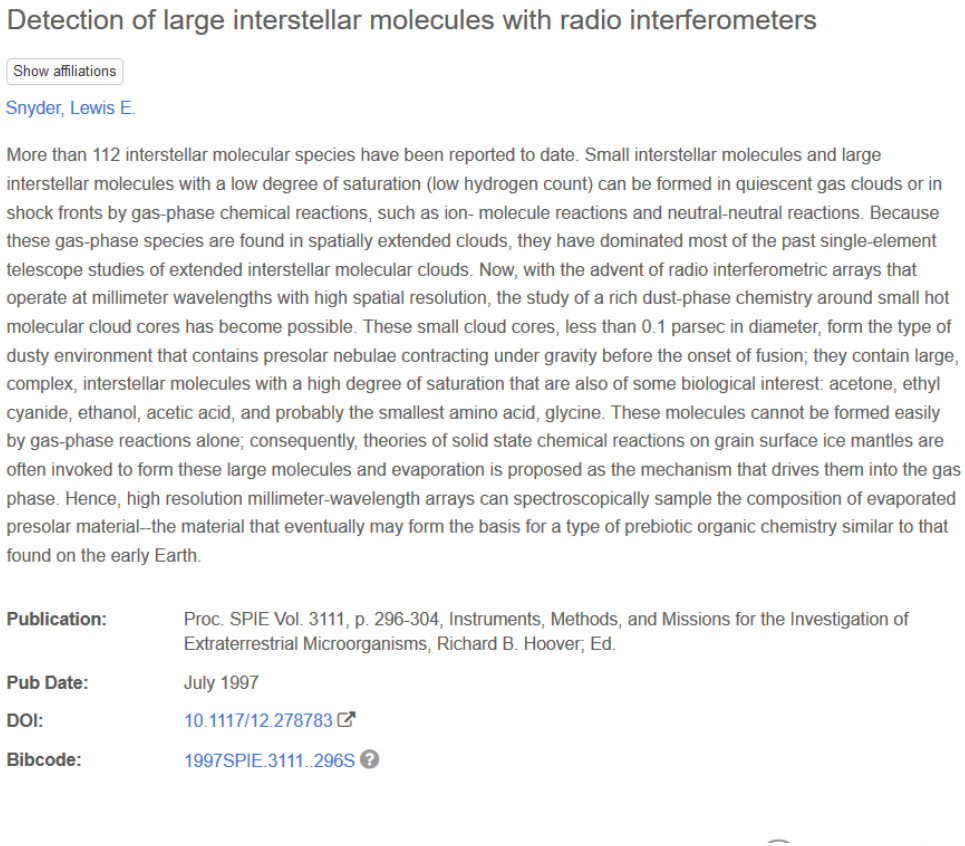


Fig. 4. Transitions of $NH_2C(O)NH_2$ in its vibrational ground state or first vibrationally excited state detected in the ReMoCA survey toward Sgr B2(N1S). The best-fit LTE synthetic spectrum of $NH_2C(O)NH_2$ is displayed in red and overlaid on the observed spectrum of Sgr B2(N1S) shown in black. The blue synthetic spectrum contains the contributions of all molecules identified in our survey so far, including $NH_2C(O)NH_2$. The dotted line indicates the 3σ noise level.

Additional Large Molecule 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 it seemed as if Lew's argument was correct…



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.

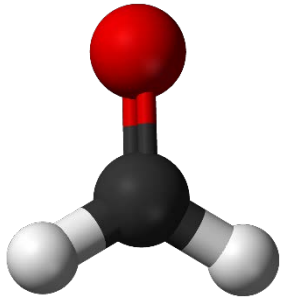
Publication: Proc. SPIE Vol. 3111, p. 296-304, Instruments, Methods, and Missions for the Investigation of Extraterrestrial Microorganisms, Richard B. Hoover; Ed.

Pub Date: July 1997

DOI: 10.1117/12.278783

Bibcode: 1997SPIE.3111..296S

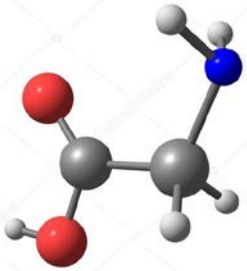
Outline



Let's start at the beginning…detection of Formaldehyde

The hunt for more complex molecules

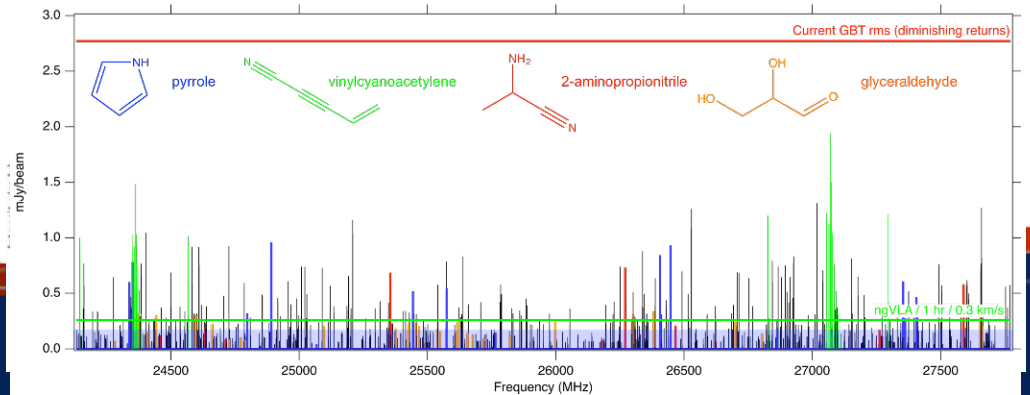
- Glycine
- Dihydroxyacetone
- Urea



Interstellar mapping campaigns

- Acetic acid
- Acetone
- Formic acid/methyl formate
- $C_2H_4O_2$ isomers

What are the limits to molecular complexity?



Interstellar Acetic Acid Searches…

- Acetic acid was the first molecule ever to be detected with an array without having first been detected with a single dish telescope. And I would argue (to this day) there has yet to be a detection of acetic acid with a single dish telescope!

DETECTION AND CONFIRMATION OF INTERSTELLAR ACETIC ACID

DAVID M. MEHRINGER,[1] LEWIS E. SNYDER, AND YANTI MIAO
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dmehring@socrates.caltech.edu, snyder@astro.uiuc.edu, yanti@astro.uiuc.edu

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FRANK J. LOVAS
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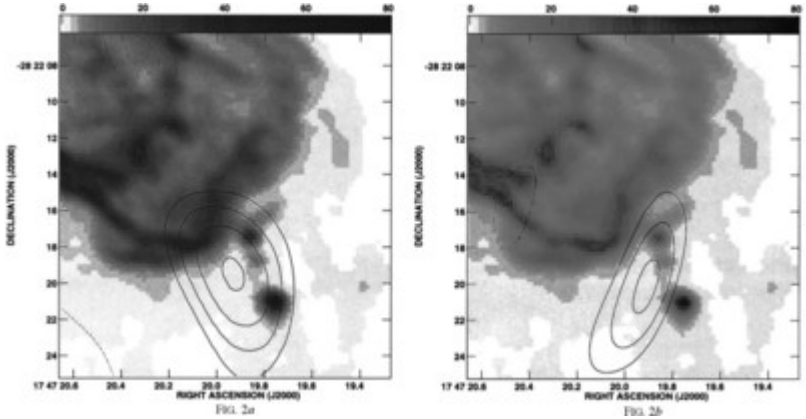
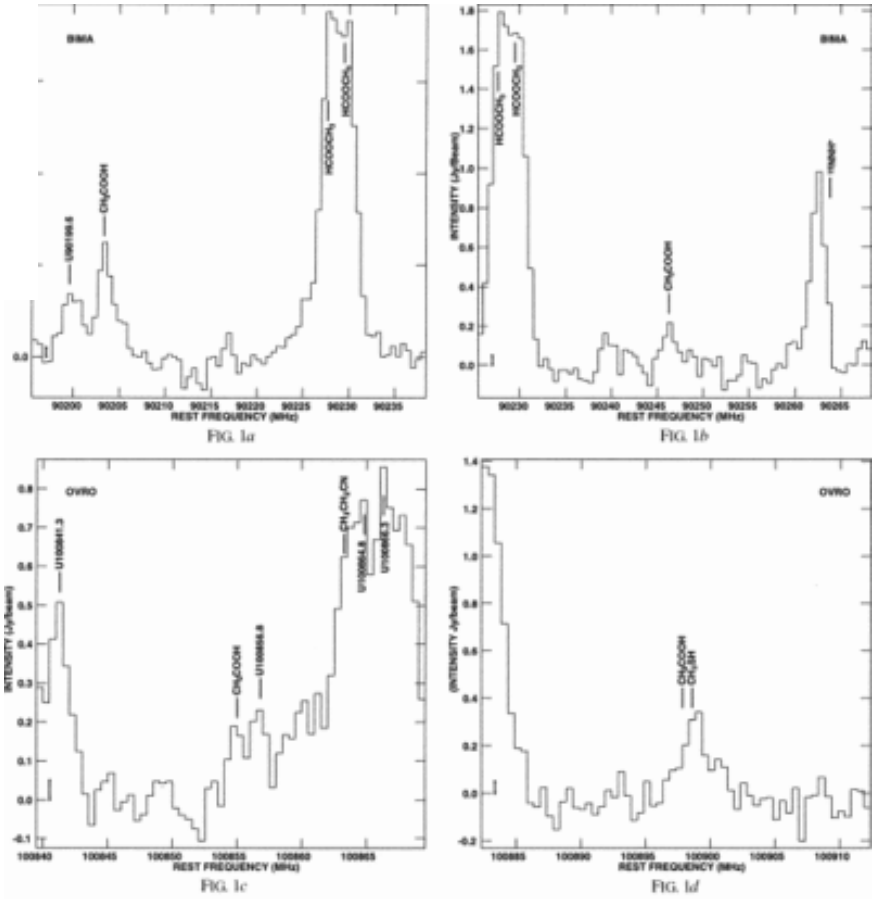
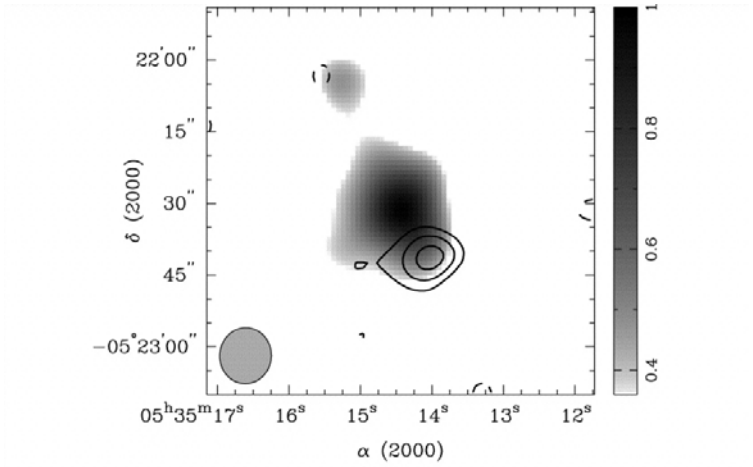
Received 1996 July 17; accepted 1997 February 7

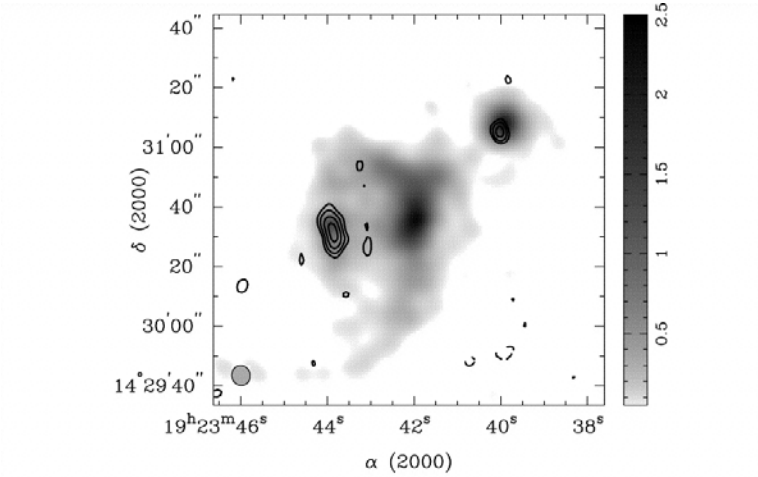


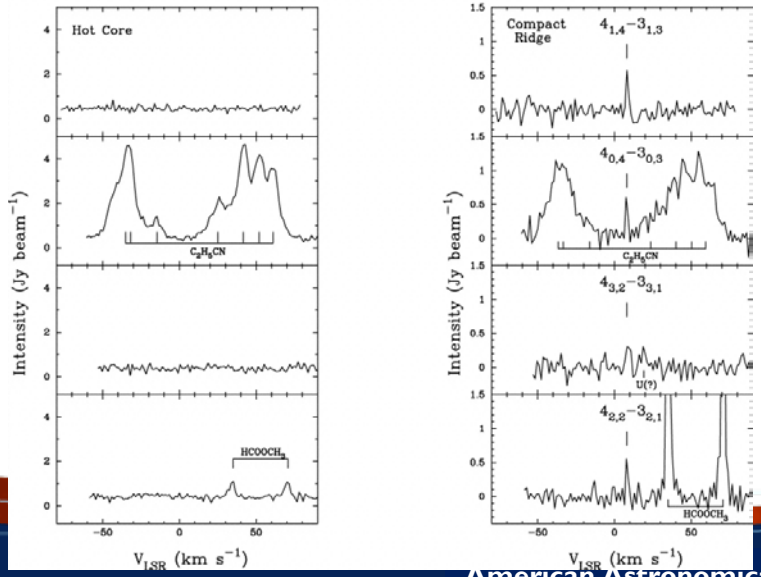


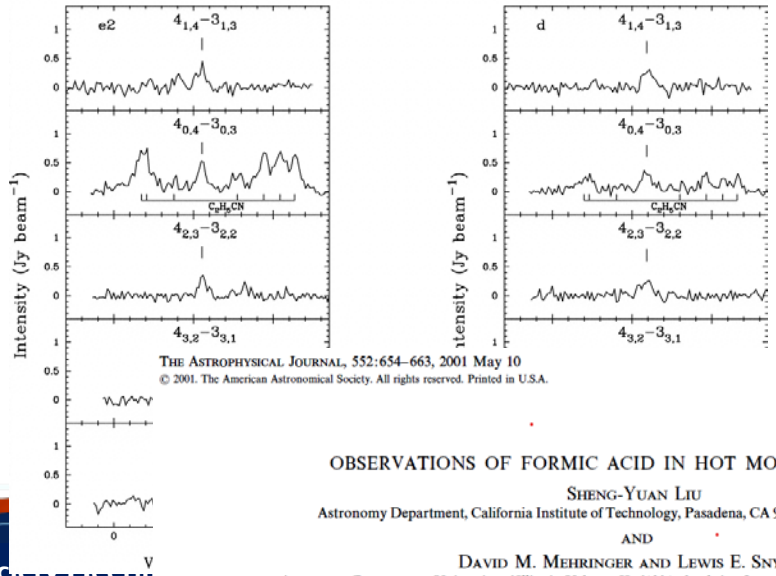
At the same time…

- Shortly after the detection, comparative mapping campaigns started to look at the relative distributions of acetic acid, methyl formate and formic acid.









THE ASTROPHYSICAL JOURNAL, 552:654–663, 2001 May 10

OBSERVATIONS OF FORMIC ACID IN HOT MOLECULAR CORES

SHENG-YUAN LIU
Astronomy Department, California Institute of Technology, Pasadena, CA 91125; syl@astro.caltech.edu
AND
DAVID M. MEHRINGER AND LEWIS E. SNYDER
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Received 2000 September 20; accepted 2001 January 8

Mapping molecular emission

- Even before ALMA came online, CARMA, PdB and the eVLA were very active in mapping the distribution of large molecules toward these regions.

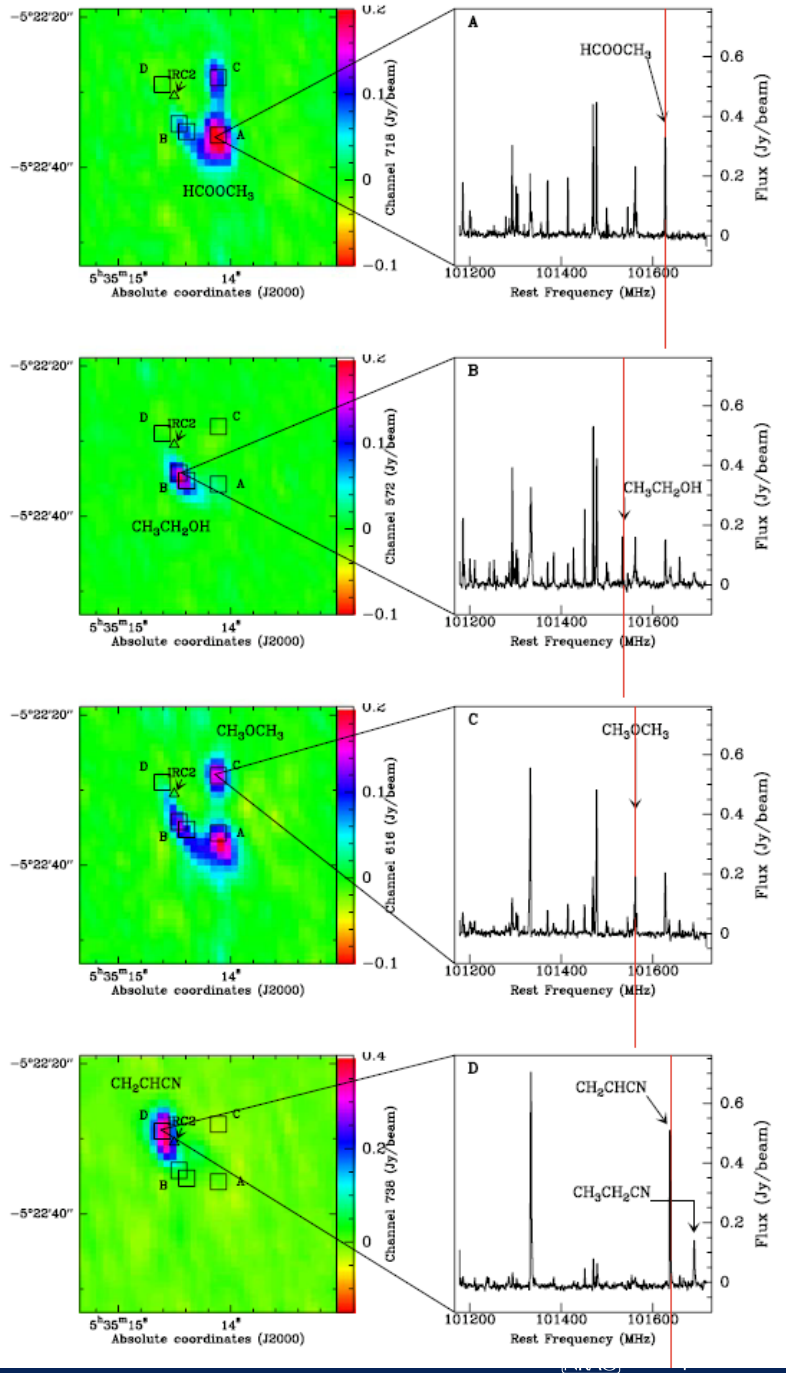
- Molecules were not in the same location nor did they have the same morphology

Astrophys Space Sci (2008) 313: 45–51
DOI 10.1007/s10509-007-9684-4

ORIGINAL ARTICLE

Unveiling the chemistry of hot protostellar cores with ALMA

M. Guélin · N. Brouillet · J. Cernicharo · F. Combes · A. Wooten



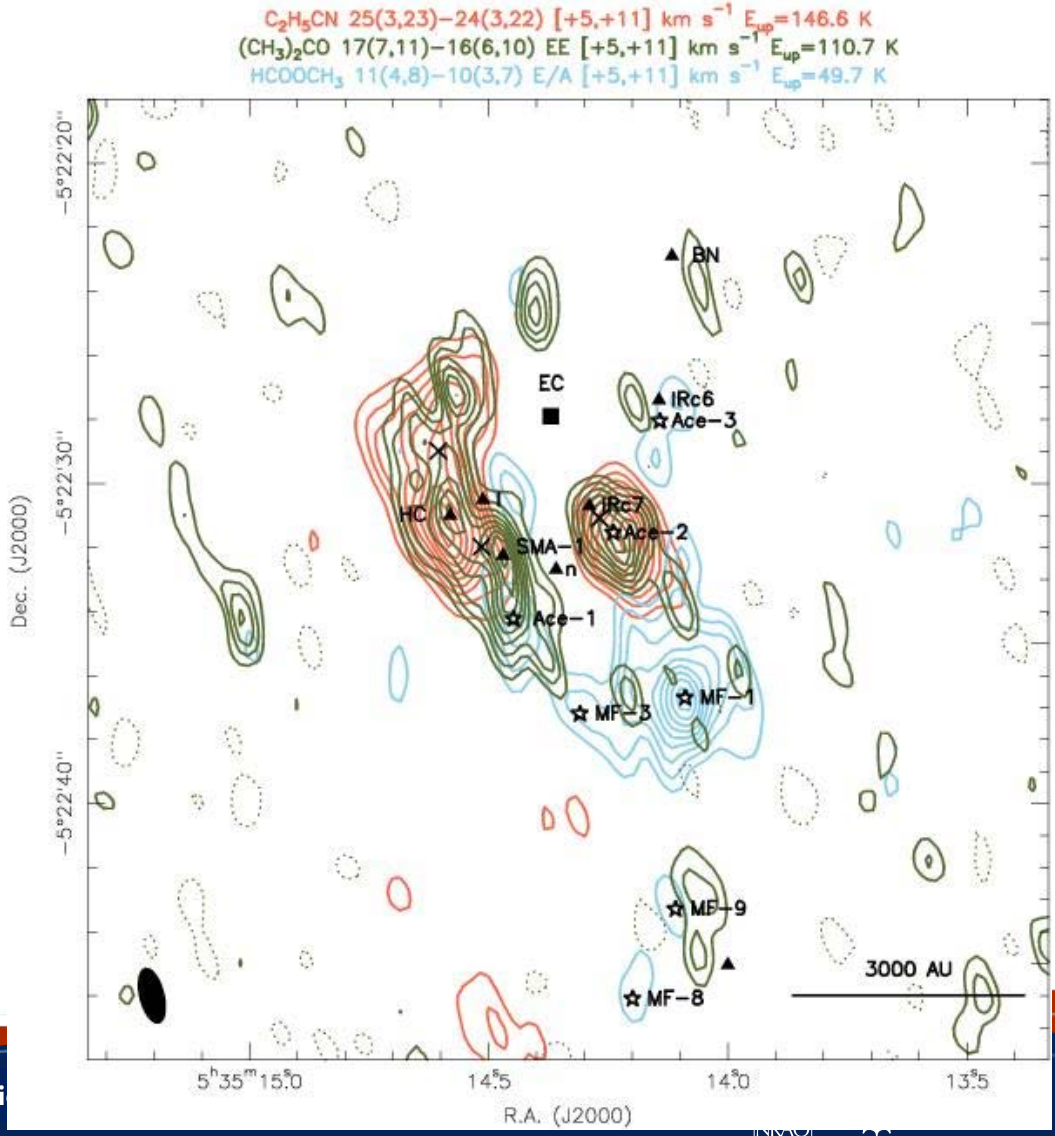
Mapping molecular emission

- Orion was believed to contain distinct "N-rich" and "O-rich" cores. Yet when the detection and mapping of large molecules at high sensitivity started, the distinction was not as apparent and also, molecules like acetone – didn't follow the convention at all.

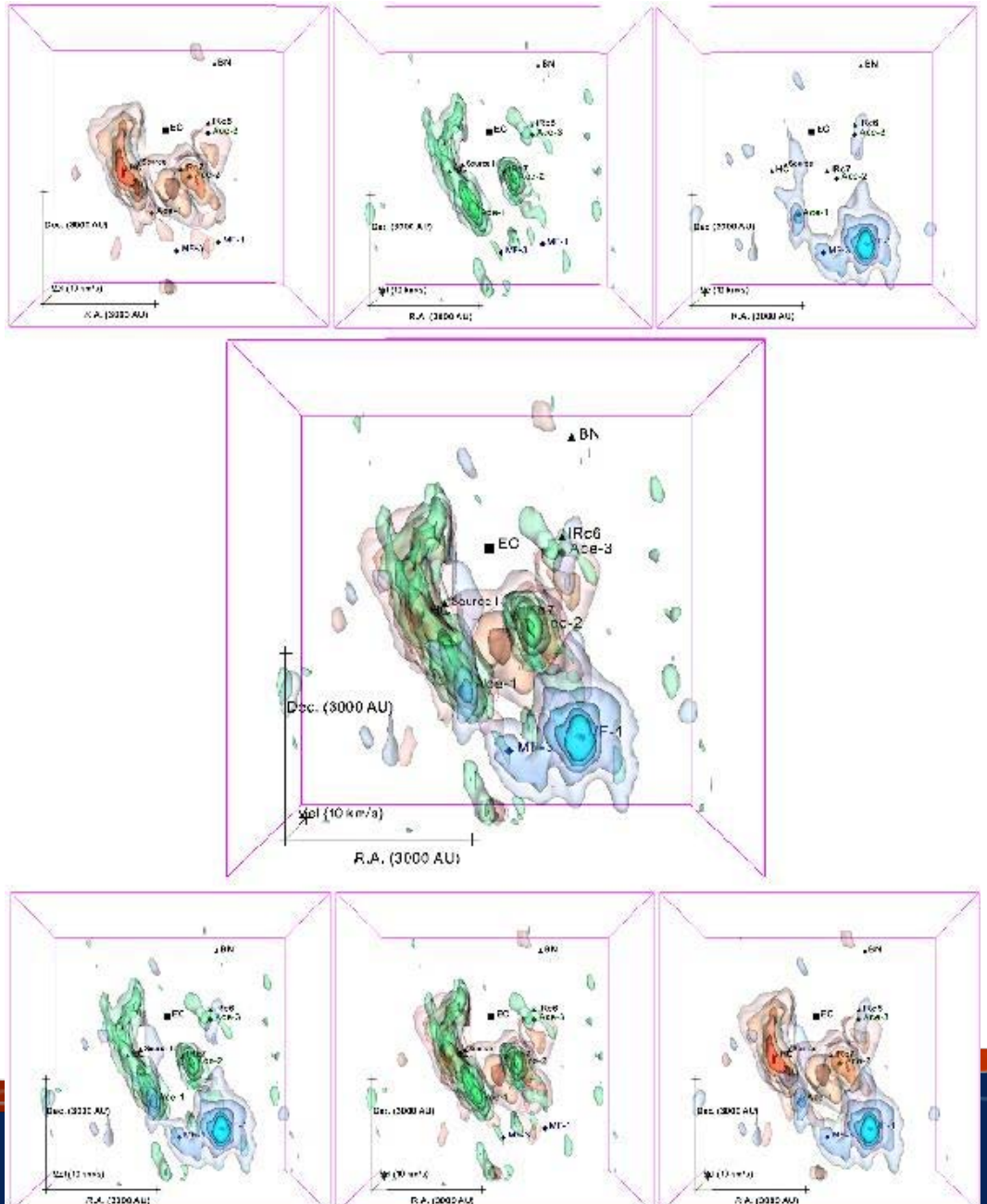
Acetone in Orion BN/KL⋆,⋆⋆

High-resolution maps of a special oxygen-bearing molecule

T.-C. Peng[1,2,3], D. Despois[1,2], N. Brouillet[1,2], A. Baudry[1,2], C. Favre[4], A. Remijan[5], A. Wootten[5], T. L. Wilson[6], F. Combes[7], and G. Wlodarczak[8]



Here is another really cool way to visualize the acetone distribution



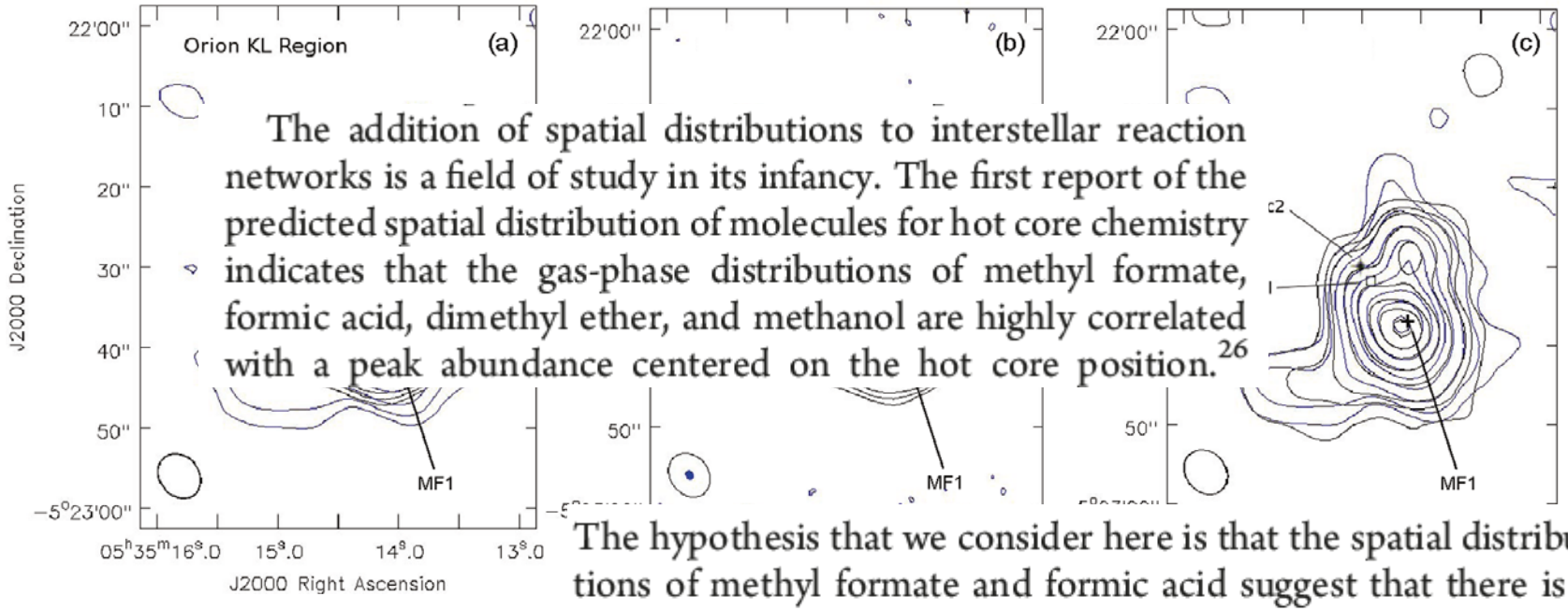
THE JOURNAL OF PHYSICAL CHEMISTRY A

ARTICLE

pubs.acs.org/JPCA

Spatial Distributions and Interstellar Reaction Processes

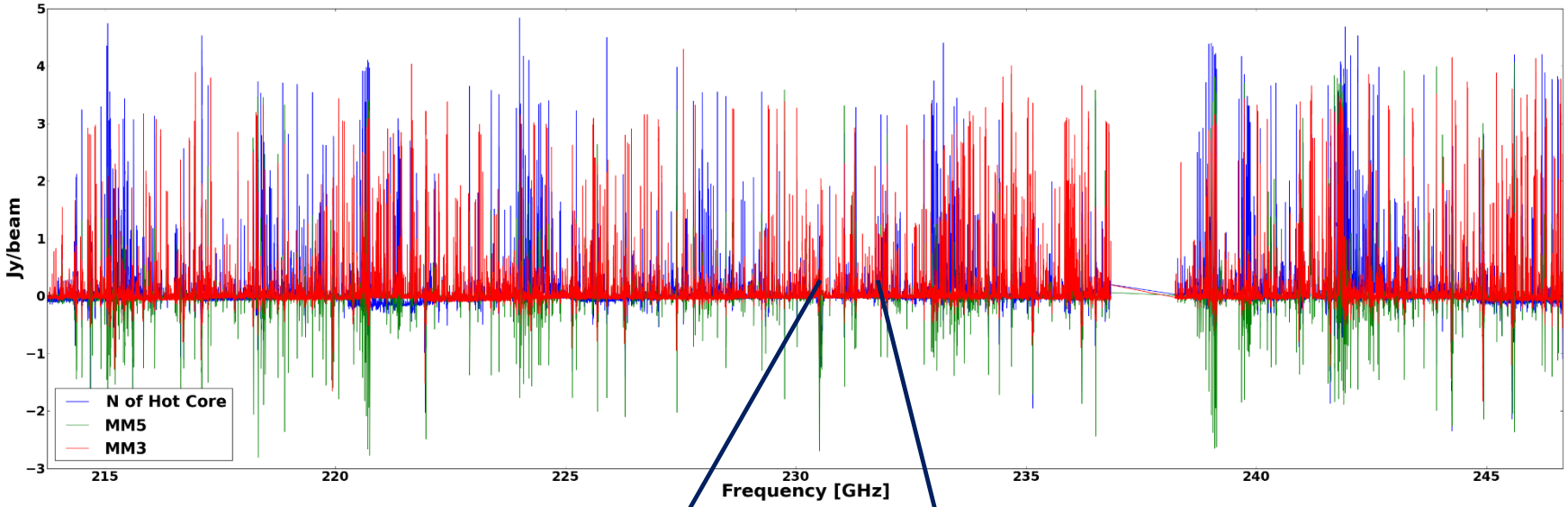
Justin L. Neill,[†] Amanda L. Steber,[†] Matt T. Muckle,[†] Daniel P. Zaleski,[†] Valerio Lattanzi,[‡,§] Silvia Spezzano,[‡,§] Michael C. McCarthy,[‡,§] Anthony J. Remijan,[∥] Douglas N. Friedel,[⊥] Susanna L. Widicus Weaver,[#] and Brooks H. Pate*[,†]

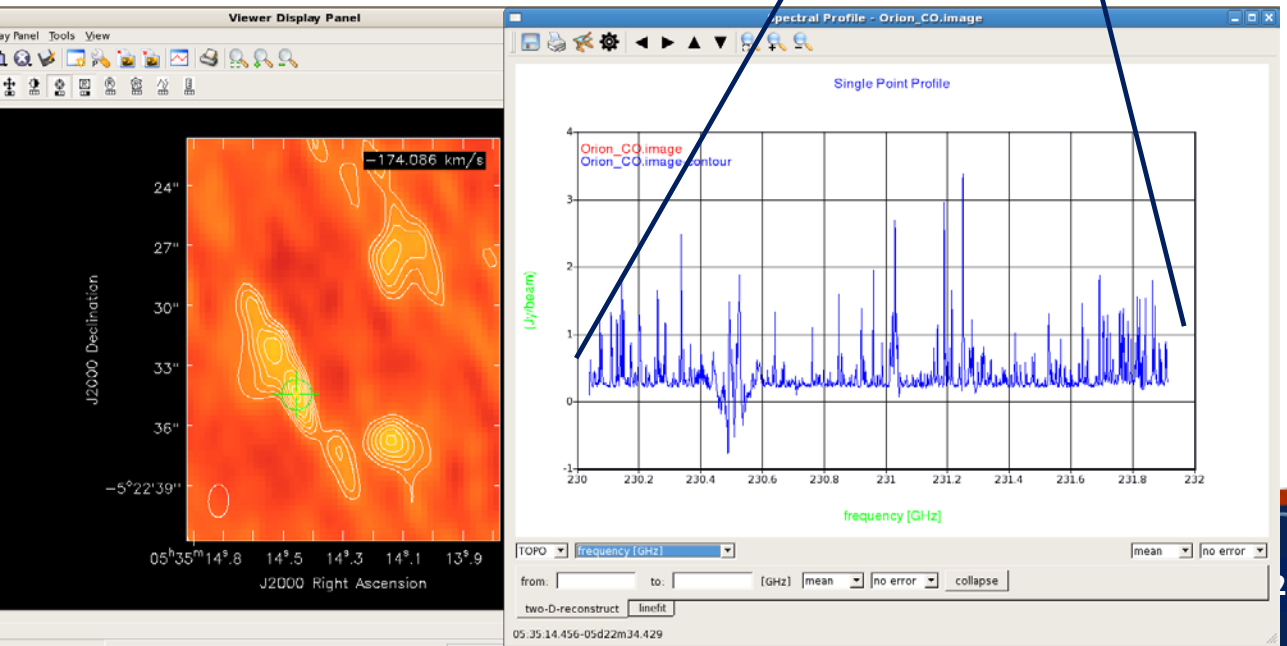


The addition of spatial distributions to interstellar reaction networks is a field of study in its infancy. The first report of the predicted spatial distribution of molecules for hot core chemistry indicates that the gas-phase distributions of methyl formate, formic acid, dimethyl ether, and methanol are highly correlated with a peak abundance centered on the hot core position.[26]

The hypothesis that we consider here is that the spatial distributions of methyl formate and formic acid suggest that there is a gas-phase reaction process that consumes formic acid to produce methyl formate. This idea is suggested by the apparent reduction in formic acid density at the position of peak methyl formate production (MF1). We also note that this same anticorrelation of

ALMA was here! And this is what we got…





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

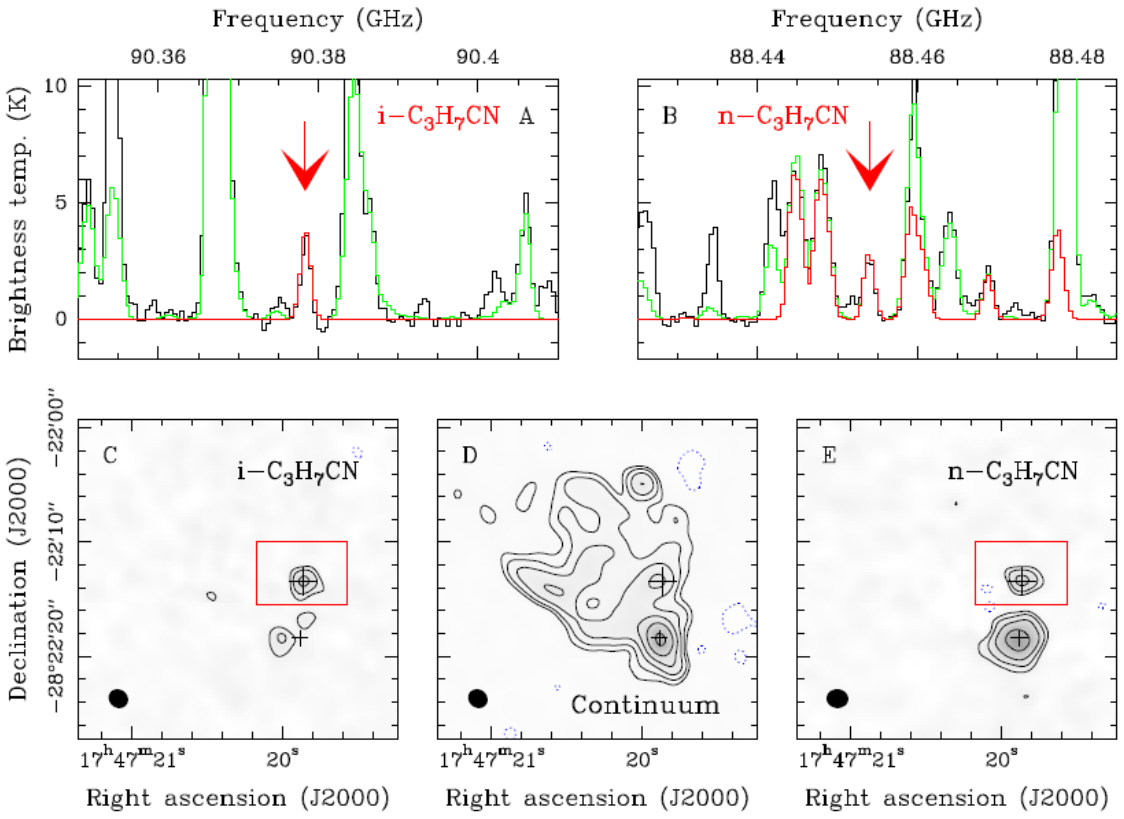
There is signal in nearly every channel and it is very hard to find "clean" transitions of well known molecules.

Mapping molecular emission

- Once ALMA starting mapping large molecules, it was clear that we were given a wealth of information about the distribution of molecules that were never before seen.

Increased complexity in interstellar chemistry: detection and chemical modeling of ethyl formate and *n*-propyl cyanide in Sagittarius B2(N)⋆,⋆⋆

A. Belloche[1], R. T. Garrod[2,1], H. S. P. Müller[3,1], K. M. Menten[1], C. Comito[1], and P. Schilke[1]

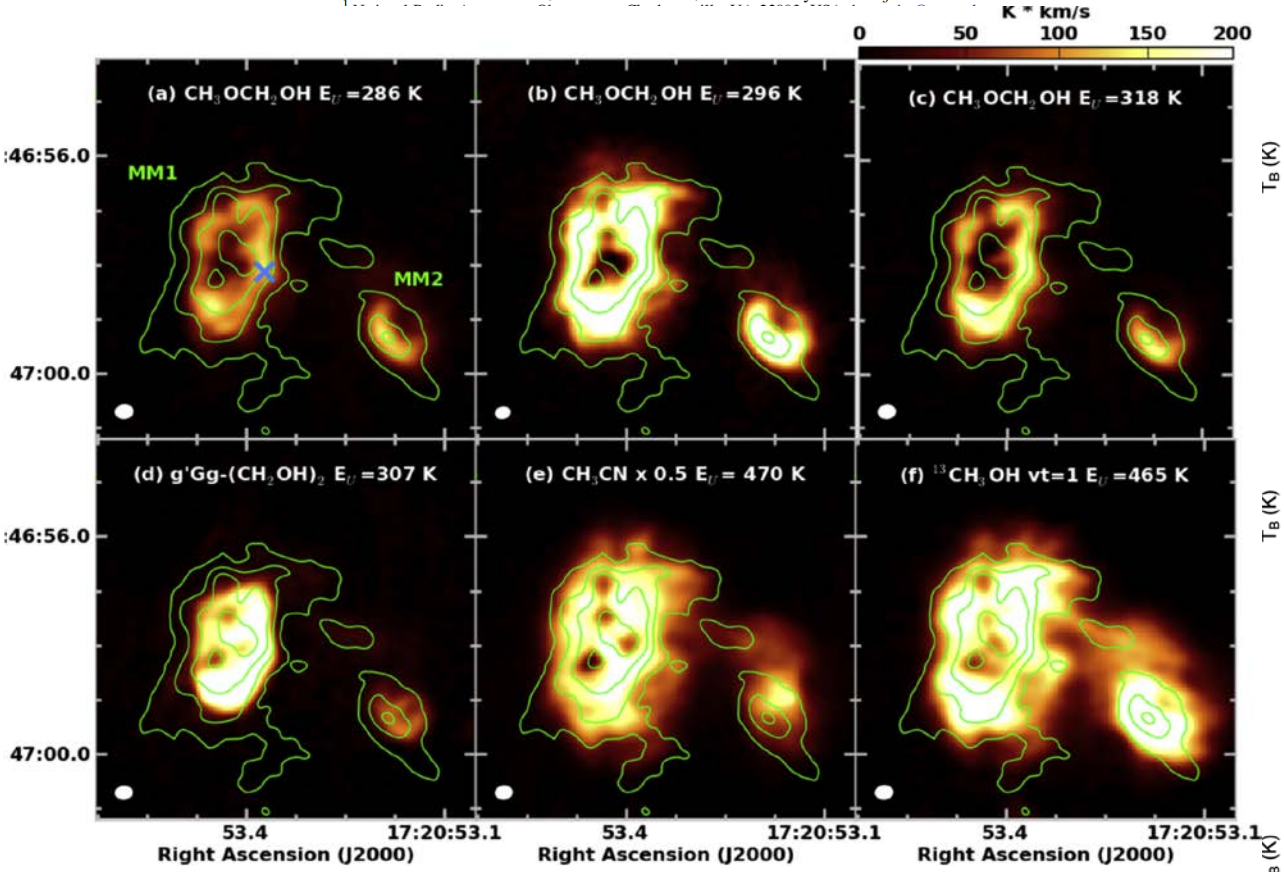


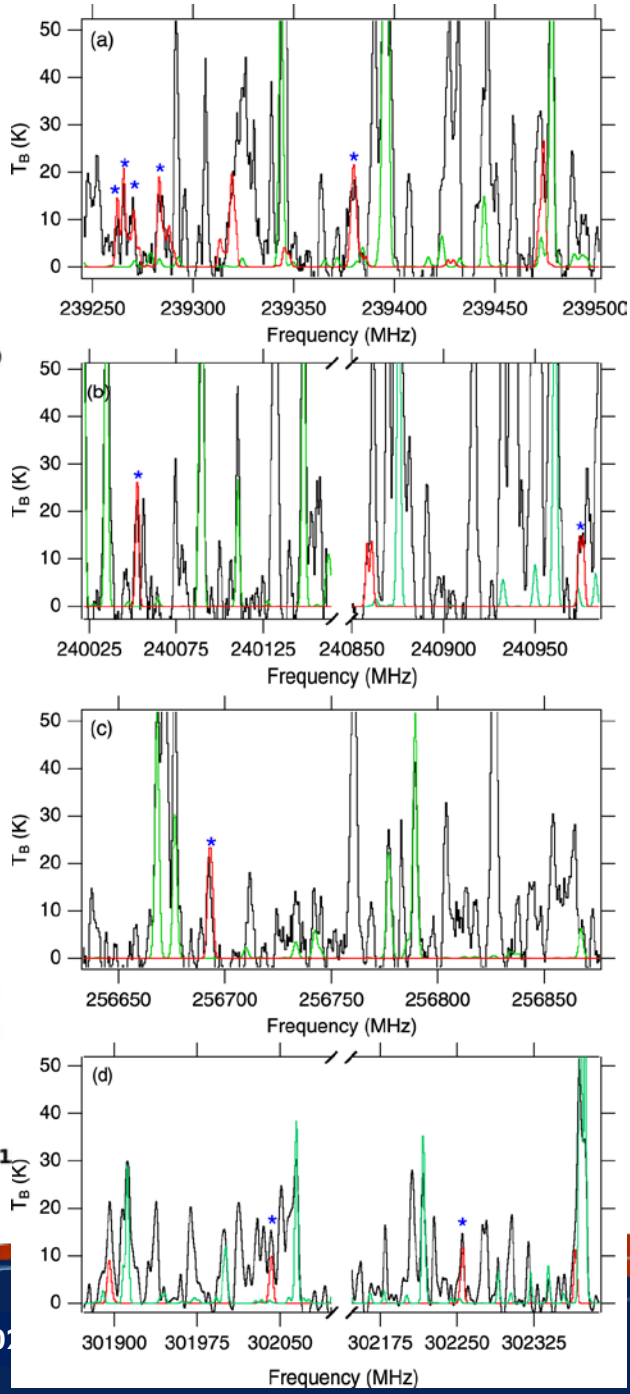
Mapping molecular emission

The Astrophysical Journal Letters, 851:L46 (8pp), 2017 December 20
https://doi.org/10.3847/2041-8213/aaa0c3

ALMA Detection of Interstellar Methoxymethanol (CH_3OCH_2OH)

Brett A. McGuire[1,2,7], Christopher N. Shingledecker[3], Eric R. Willis[3], Andrew M. Burkhardt[4], Samer El-Abd[4], Roman A. Motiyenko[5], Crystal L. Brogan[1], Todd R. Hunter[1], Laurent Margulès[5], Jean-Claude Guillemin[6], Robin T. Garrod[3,4], Eric Herbst[3,4], and Anthony J. Remijan[1]



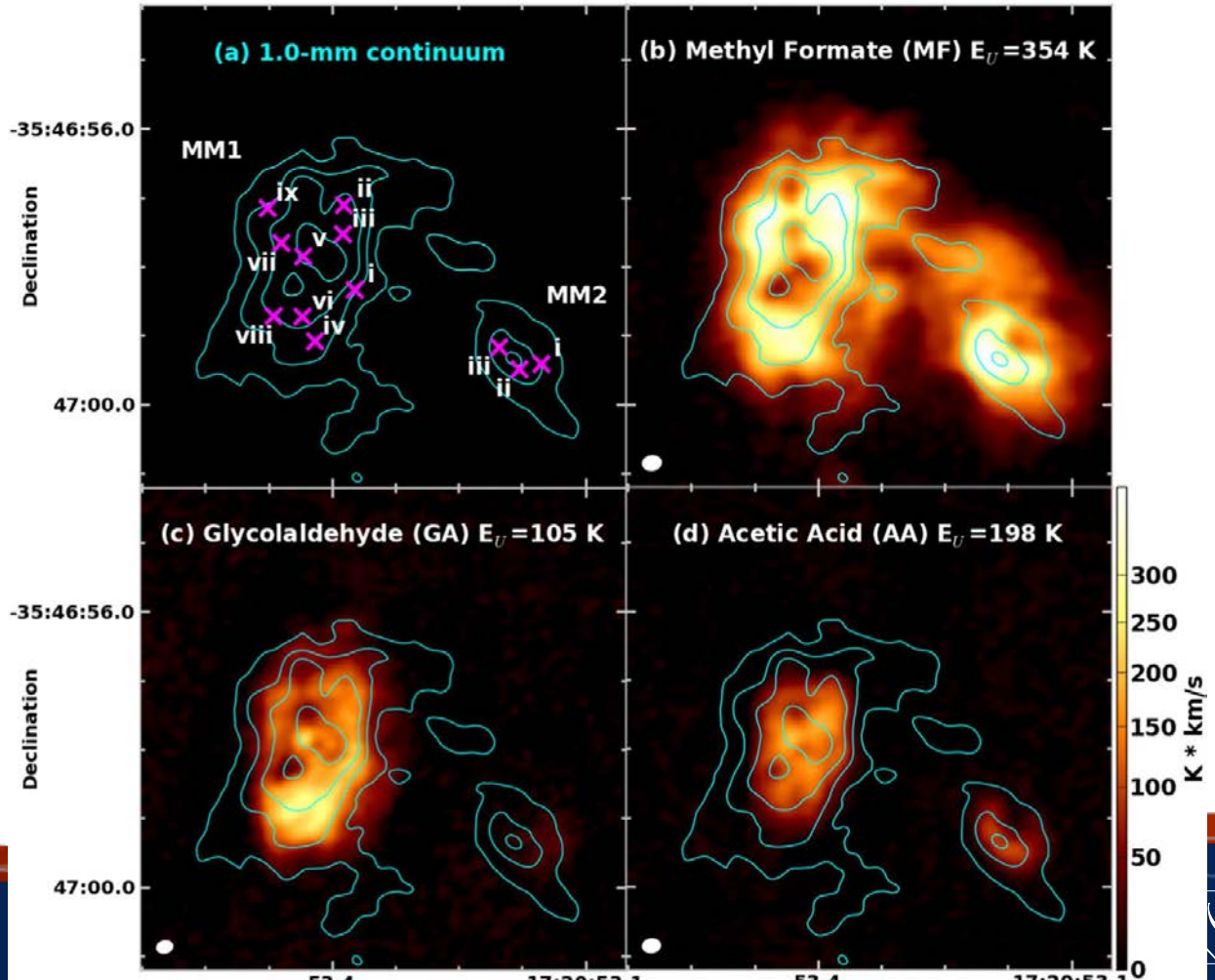


Mapping molecular emission

The Astrophysical Journal, 883:129 (24pp), 2019 October 1 https://doi.org/10.3847/1538-4357/ab3646

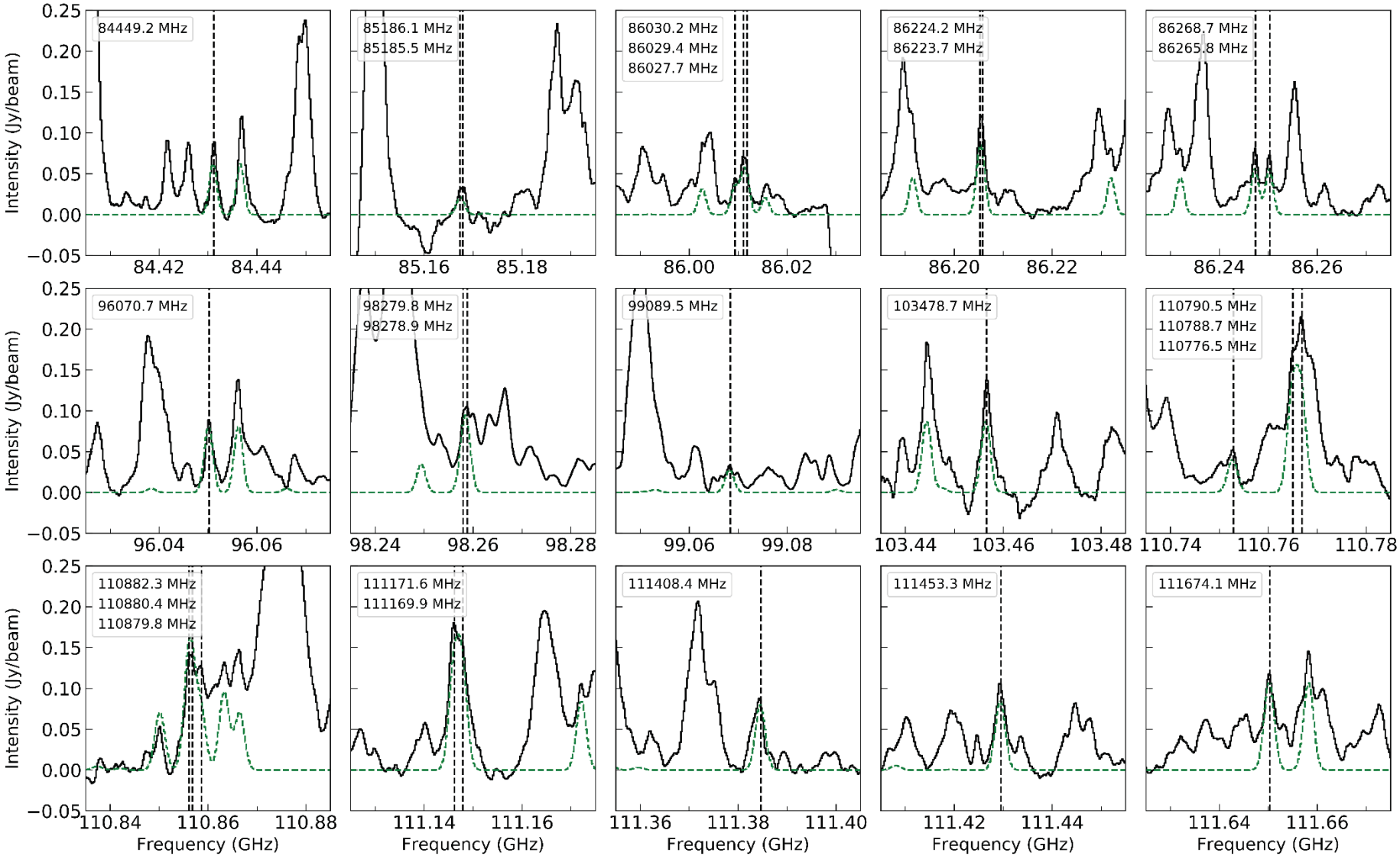
Interstellar Glycolaldehyde, Methyl Formate, and Acetic Acid. I. A Bimodal Abundance Pattern in Star-forming Regions

Samer J. El-Abd[1,5], Crystal L. Brogan[2], Todd R. Hunter[2], Eric R. Willis[3], Robin T. Garrod[1,3], and Brett A. McGuire[2,4,6]

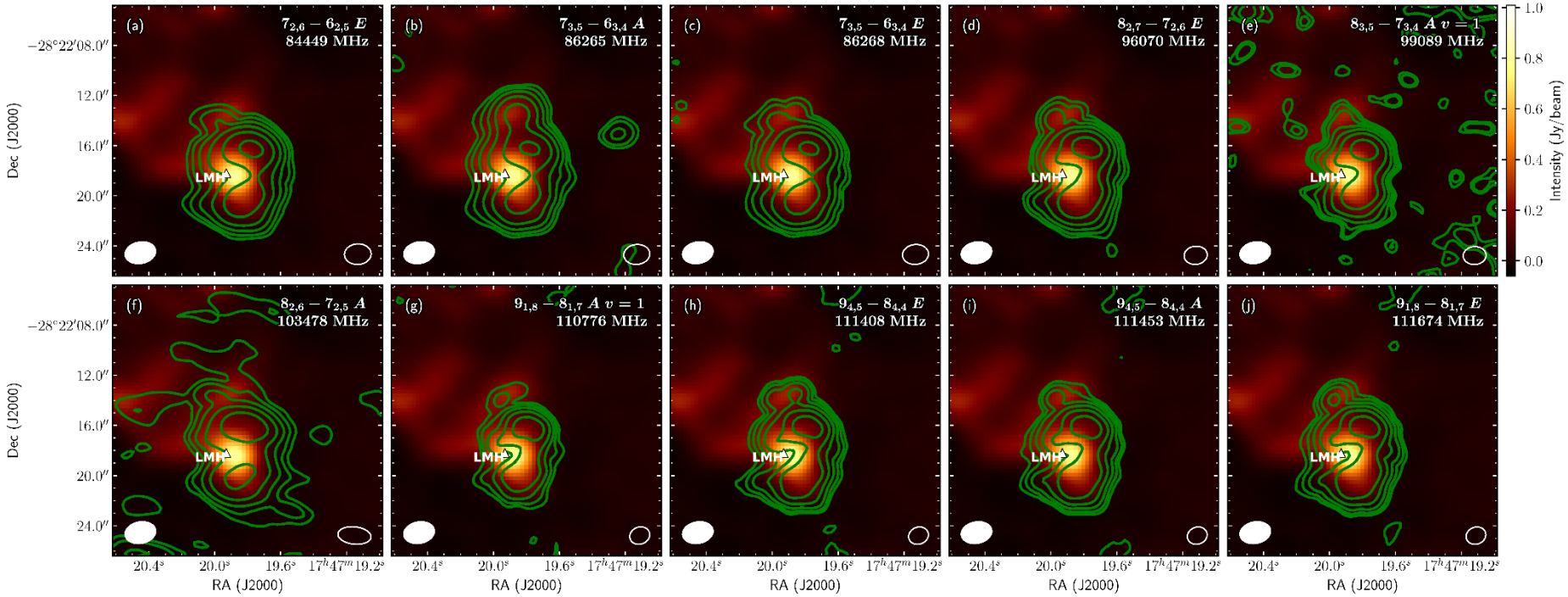


Transition Maps vs. Chemical Maps

Xue et al. 2019, ApJ, 871, 112

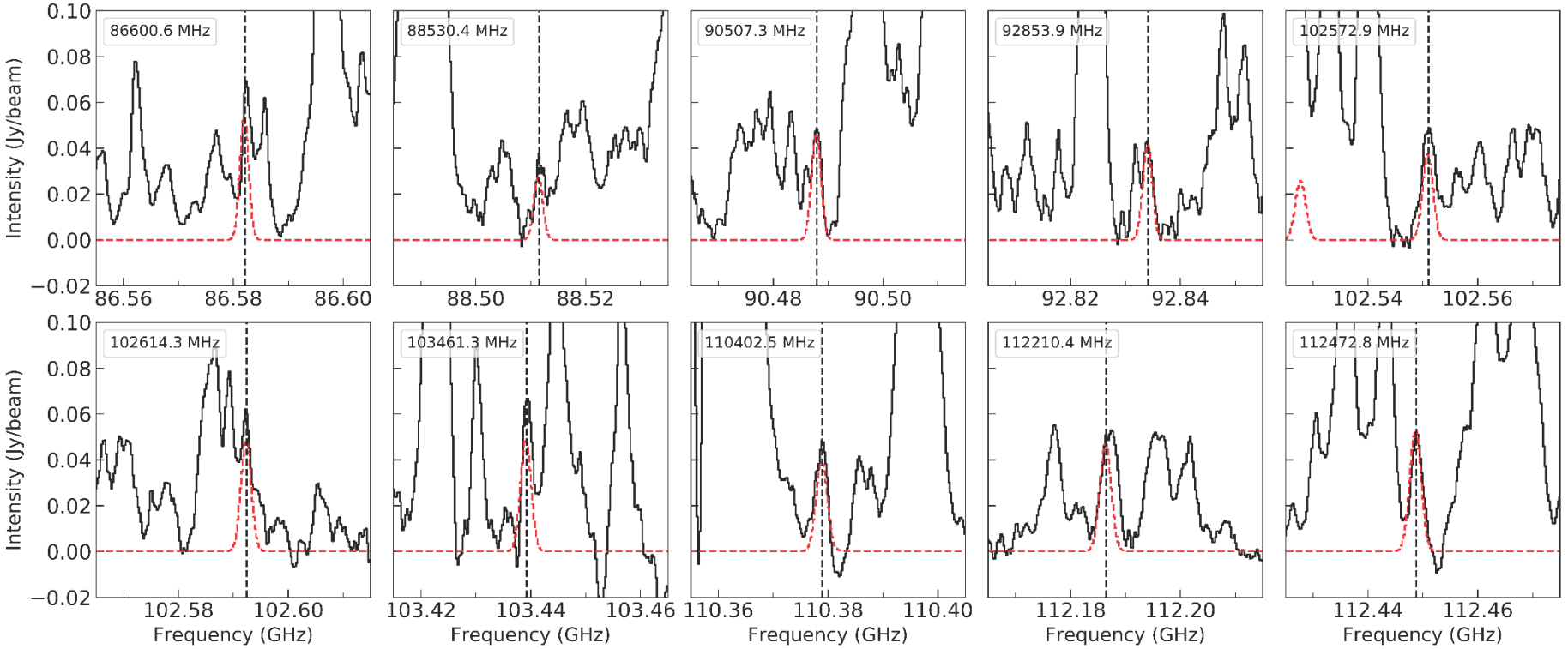


- When mapping the detected transitions, care has to be taken to differentiate between physical and chemical difference and transitions that are "contaminated"…



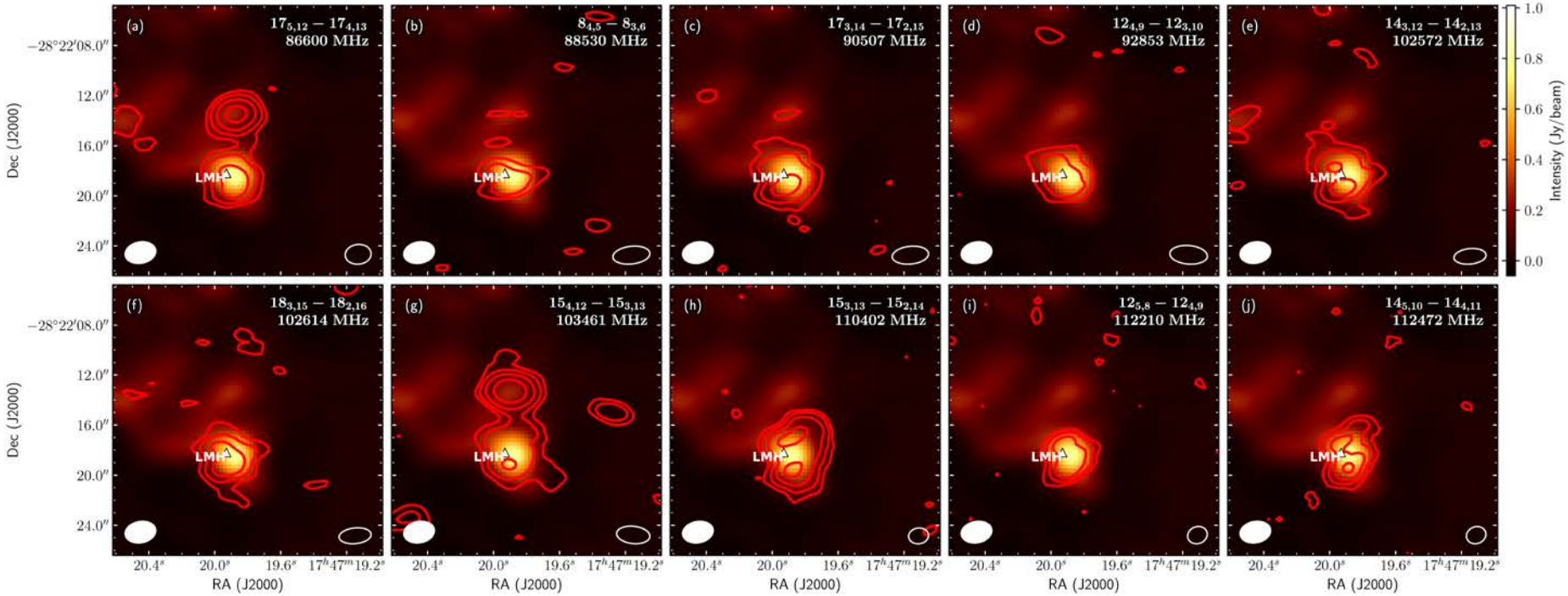
Transition Maps vs. Chemical Maps

Xue et al. 2019, ApJ, 871, 112

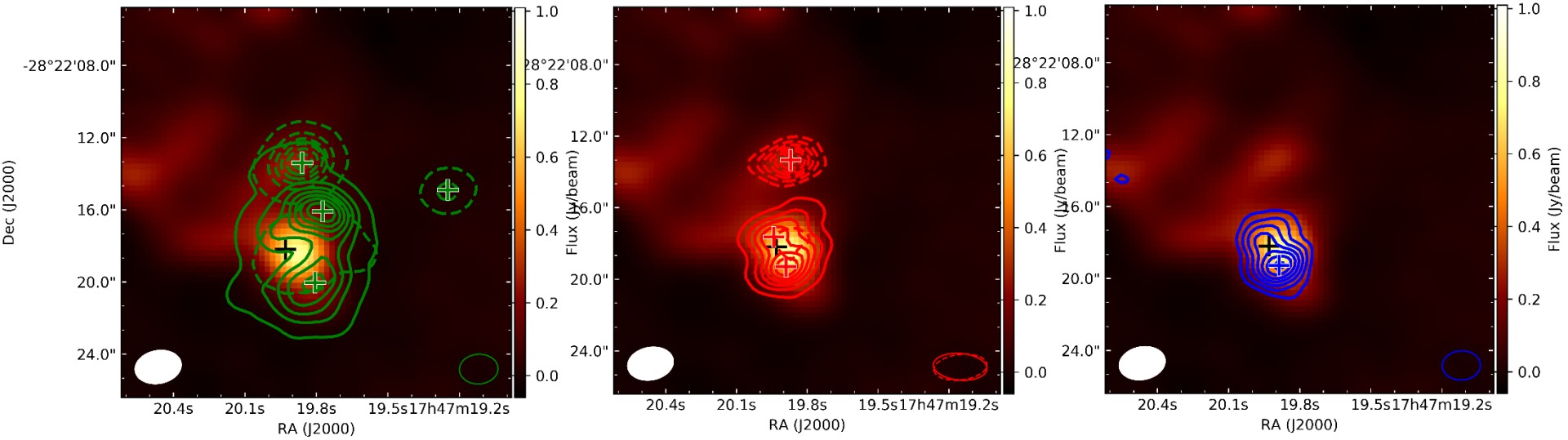


Transition Maps vs. Chemical Maps

Xue et al. 2019, ApJ, 871, 112



A "chemical map" will allow us to truly get a chemical picture of the environment and will help to disentangle physics from chemistry.



Methyl Formate

Glycolaldehyde

Acetic Acid

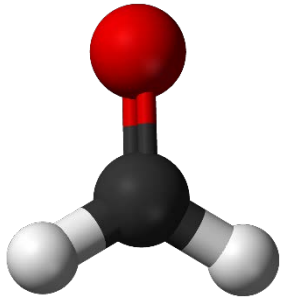
Mapping molecular emission - Conclusions

- We are beginning to really see the utility of using chemical maps to determine something about the formation chemistry

- Typically, the spatial extent and morphology of the distribution of molecules and NOT taken into consideration – they are all reactive and not predictive (more on that later)

- Yet the power of interferometric arrays are clearly demonstrated to determine possible chemical formation pathways.

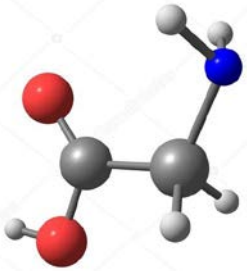
Outline



Let's start at the beginning…detection of Formaldehyde

The hunt for more complex molecules

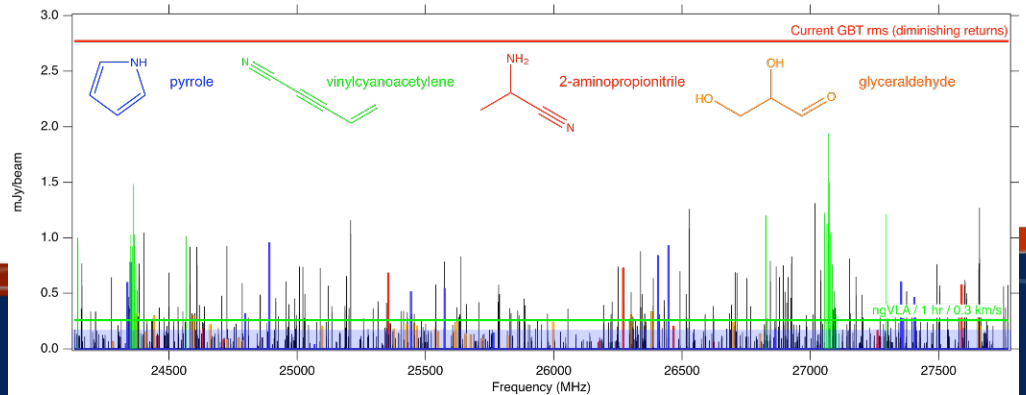
- Glycine
- Dihydroxyacetone
- Urea



Interstellar mapping campaigns

- Acetic acid
- Acetone
- Formic acid/methyl formate
- $C_2H_4O_2$ isomers

What are the limits to molecular complexity?



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.

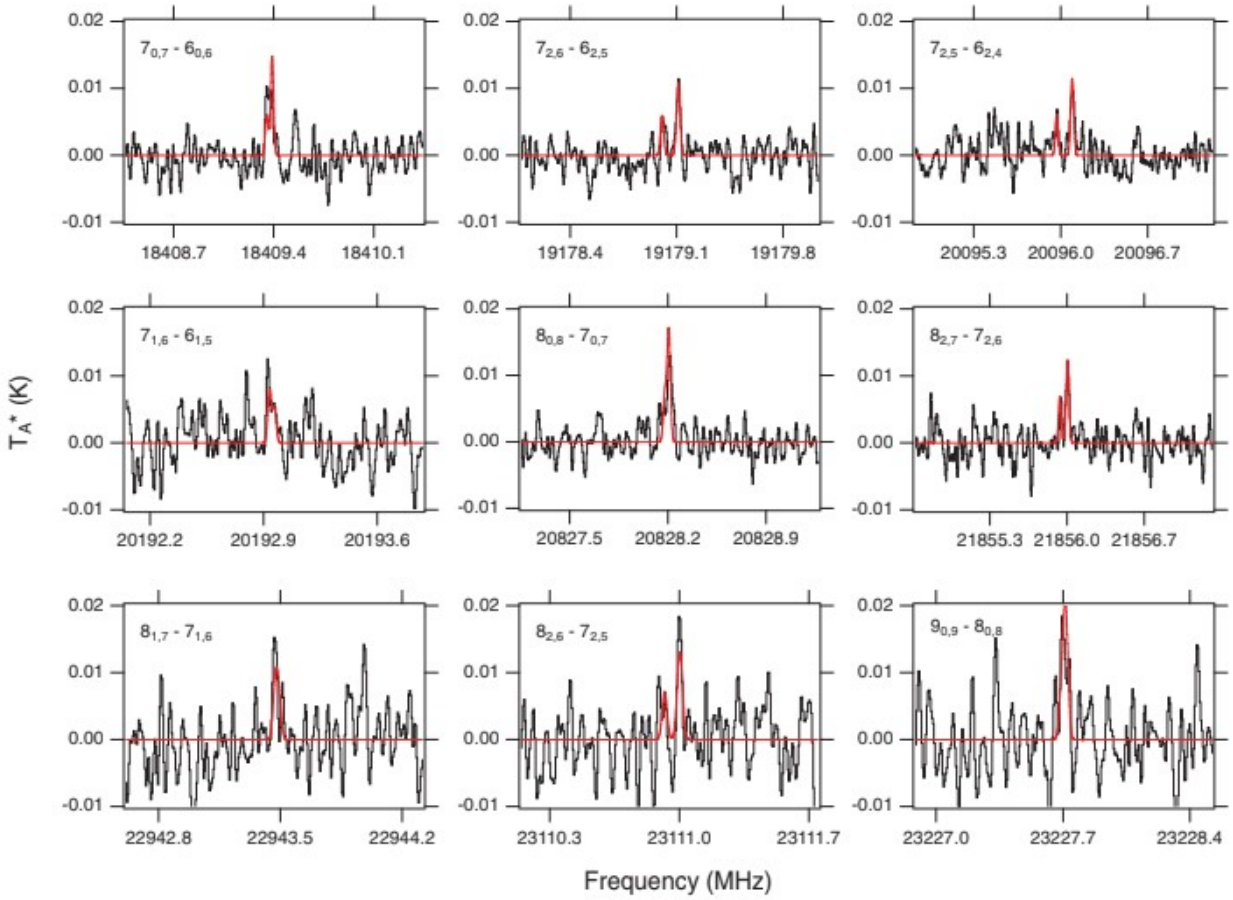
- Very wisely, looking at the proposal for the Green Bank Telescope…

> 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.*

Where we are today?

New molecule detections and a better understanding of the molecular makeup of the Galaxy continues to grow because of low frequency observations, new, innovative ways to detect molecules… and

- 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



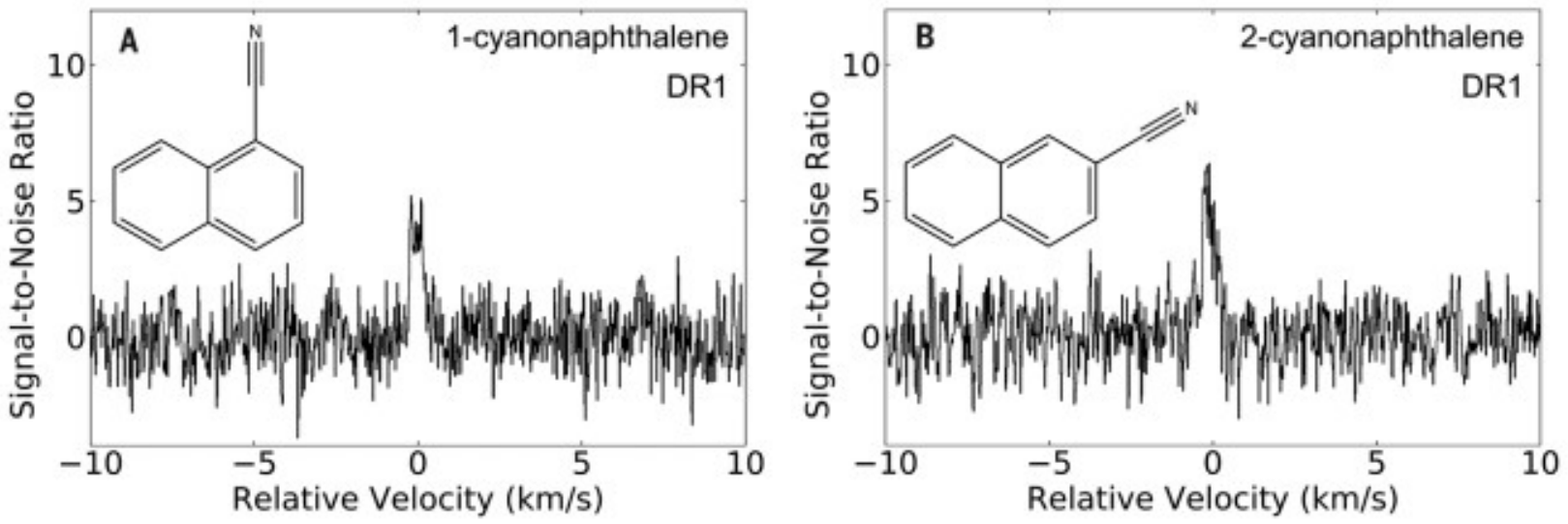
And a GBT Large Program

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

ASTROCHEMISTRY

Detection of two interstellar polycyclic aromatic hydrocarbons via spectral matched filtering

Brett A. McGuire[1,2,3]*, Ryan A. Loomis[2]†, Andrew M. Burkhardt[3]†, Kin Long Kelvin Lee[1,3], Christopher N. Shingledecker[4,5,6], Steven B. Charnley[7], Ilsa R. Cooke[8], Martin A. Cordiner[7,9], Eric Herbst[10,11], Sergei Kalenskii[12], Mark A. Siebert[11], Eric R. Willis[10], Ci Xue[10], Anthony J. Remijan[2], Michael C. McCarthy[3]



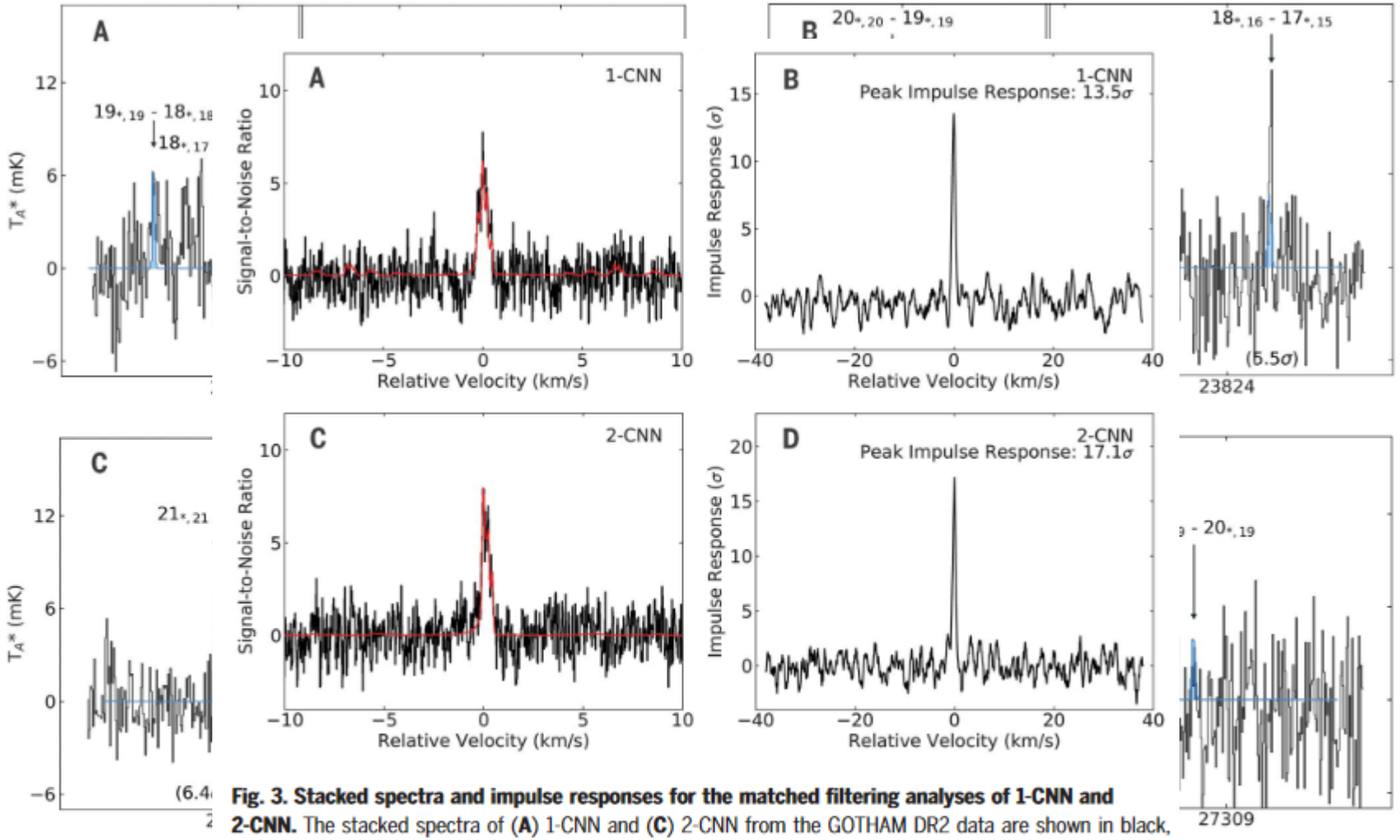


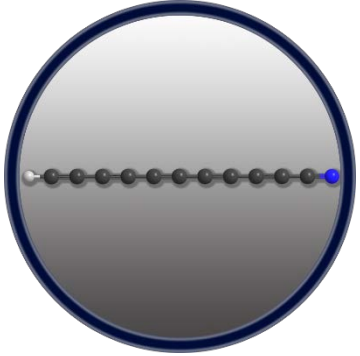
Fig. 3. Stacked spectra and impulse responses for the matched filtering analyses of 1-CNN and 2-CNN. The stacked spectra of (**A**) 1-CNN and (**C**) 2-CNN from the GOTHAM DR2 data are shown in black, overlaid with the line profile in red from the MCMC analysis of the DR2 data. The SNR is shown on a per-channel basis. Impulse response functions of the stacked spectra of (**B**) 1-CNN and (**D**) 2-CNN are shown, using the simulated line profiles as matched filters. The peak of the impulse response functions provides a minimum significance for the detections of 13.5σ and 17.1σ, respectively.

Fig. 2. GOTHAM DR2 spe transitions. (**A** to **D**) Obse of 1-CNN using the paramet blue. The *y* axis is the atm observations have not been adjusted for the systemic velocity of TMC-1 (5.8 km s^{-1}).

ow to a resolution of 14 kHz oring hyperfine structure, are Multiple closely spaced and are denoted by asterisks. Transitions with SNRs ≥4σ are labeled in parentheses beneath the spectra.

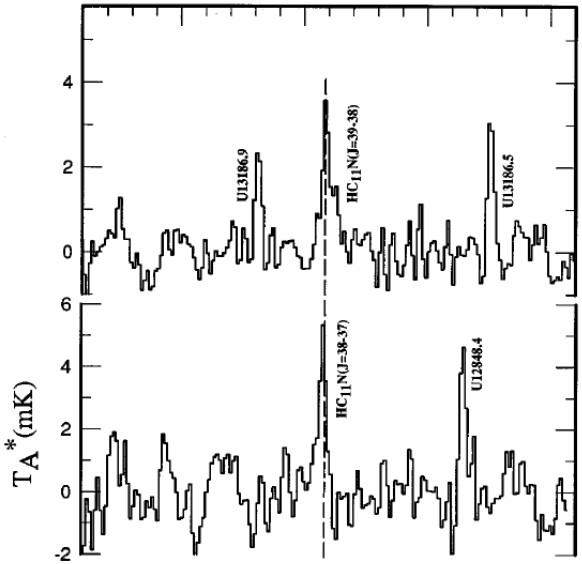
There and back again…

The curious case of $HC_{11}N$



The first *initial* claims for this molecule were in 1982 towards IRC+10216 and 1985 towards TMC-1.

The first multi-transition detection was by Bell et al. 1997



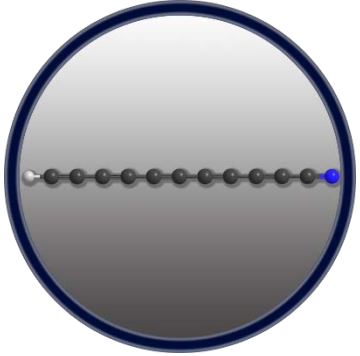
It should be noted that in some cases the observing frequency used differed slightly from the rest frequency (Table 1). For HC_5N, the observing frequency used was 13,313.338 MHz. More importantly, for the HC_9N $J = 22 \rightarrow 21$ and $23 \rightarrow 22$ lines, the observing frequencies were 12,782.766 and 13,363.790 MHz, respectively, and the differences between these and the rest frequencies in Table 1 were taken into account in determining velocities. For the $J = 38 \rightarrow 37$ line of $HC_{11}N$, the value obtained from the laboratory constants (12,848.731 MHz) was used both as an observing frequency and in determining the velocity listed in Table 1.

Three U lines are apparently present in the deep $HC_{11}N$ spectra (Fig. 1). For the reason mentioned earlier, we are unable to completely rule out the possibility that these are spurious features introduced by the correlator. If this is the

Yet, these two transitions were never seen again…

There and back again…

The curious case of $HC_{11}N$



It wasn't for a lack of trying though!

MNRAS 463, 4175–4183 (2016)
Advance Access publication 2016 September 12
doi:10.1093/mnras/stw2302

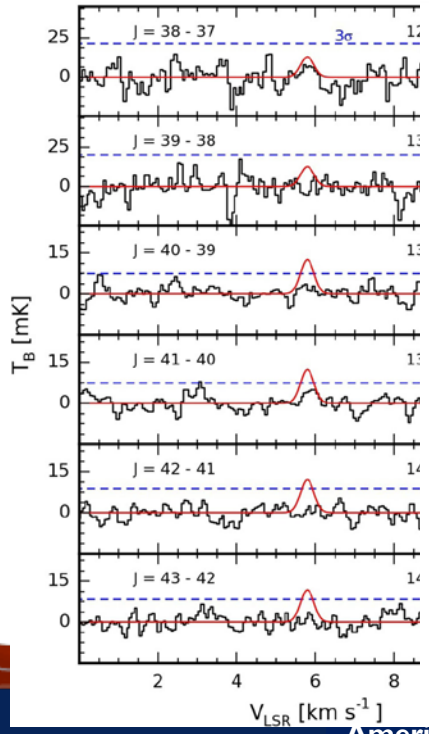
Non-detection of HC
of large carbon-chai

Ryan A. Loomis,[1]★ Chri
Brett A. McGuire,[4,5]† N
Shawn T. Booth,[6]‡ P. Bra

The Astrophysical Journal, 850:187 (7pp), 2017 December 1
https://doi.org/10.3847/1538-4357/aa970c

Deep K-band Observations of TMC-1 with the Green Bank Telescope: Detection of HC_7O, Nondetection of $HC_{11}N$, and a Search for New Organic Molecules

M. A. Cordiner[1,2], S. B. Charnley[1], Z. Kisiel[3], B. A. McGuire[4], and Y.-J. Kuan[5,6]
[1] Astrochemistry Laboratory and the Goddard Center for Astrobiology, NASA Goddard Space Flight Center, 8800 Greenbelt Road, MD 20771, USA



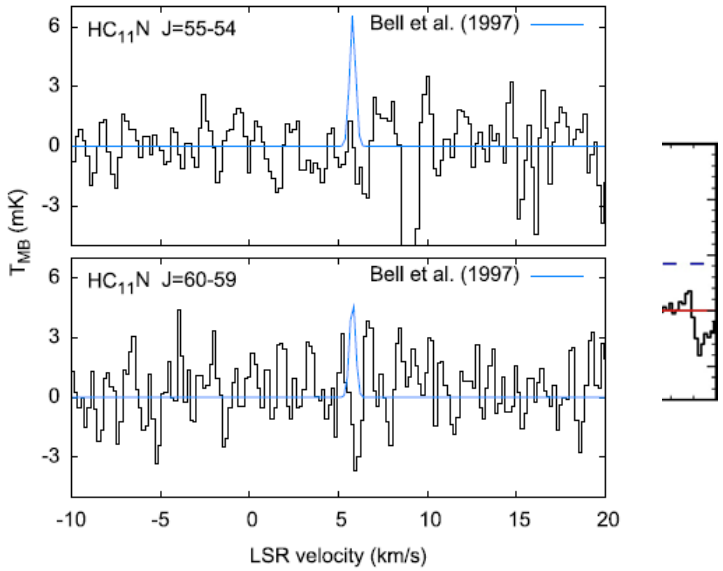
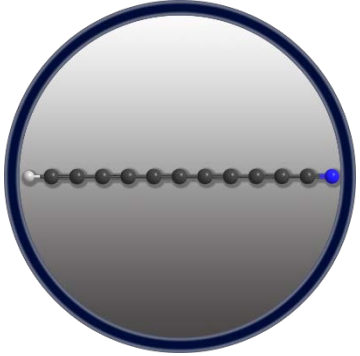


Figure 3. GBT K-band spectra surrounding two transitions of $HC_{11}N$. Predicted spectra based on the column density reported by Bell et al. (1997) are overlaid in blue.

10

There and back again…

The curious case of $HC_{11}N$



Until… finally!

An investigation of spectral line stacking techniques and application to the detection of $HC_{11}N$

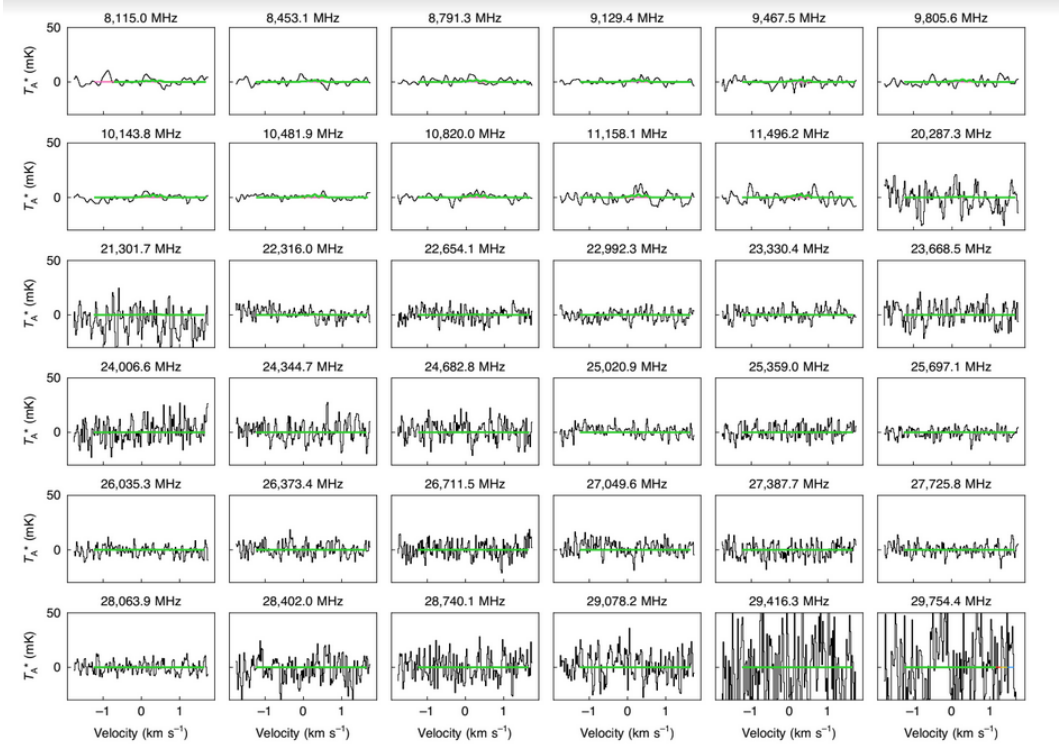
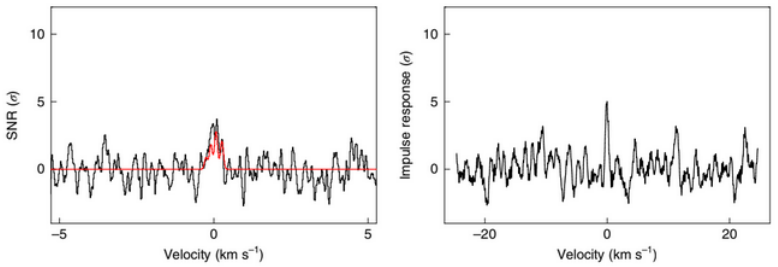


Fig. 6 | Individual line observations of $HC_{11}N$ in the GOTHAM data. The spectra (black) are displayed in velocity space relative to 5.8 km s^{-1}, and using the rest frequencies given in the top right of each panel. The best-fit model to the data, including all velocity components, is overlaid in green. Simulated spectra of the individual velocity components are shown in blue (5.63 km s^{-1}), yellow (5.79 km s^{-1}), red (5.91 km s^{-1}) and violet (6.03 km s^{-1}).



Spatial variations in cyanopolyyne chemistry. Previous spatially resolved observations of HC_3N, HC_5N and HC_7N towards TMC-1 have shown them to be spatially extended on scales large enough to fill the GBT beam at the frequencies probed by GOTHAM[36–38]. These observations were all taken at relatively coarse spatial resolution, however, and the detailed distribution of these species is unknown, as is the distribution of larger cyanopolyynes such as HC_9N. In particular, observations of cyanopolyynes at both high spectral and spatial resolution do not exist to date, making it difficult to spatially disentangle the four known velocity components in TMC-1.

The "old" tried and true way – still effective*

A&A 649, L15 (2021)
https://doi.org/10.1051/0004-6361/202141156

Astronomy & Astrophysics

LETTER TO THE EDITOR

Pure hydrocarbon cycles in TMC-1: Discovery of ethynyl cyclopropenylidene, cyclopentadiene, and indene*

J. Cernicharo[1], M. Agúndez[1], C. Cabezas[1], B. Tercero[2,3], N. Marcelino[1], J. R. Pardo[1], and P. de Vicente[2]

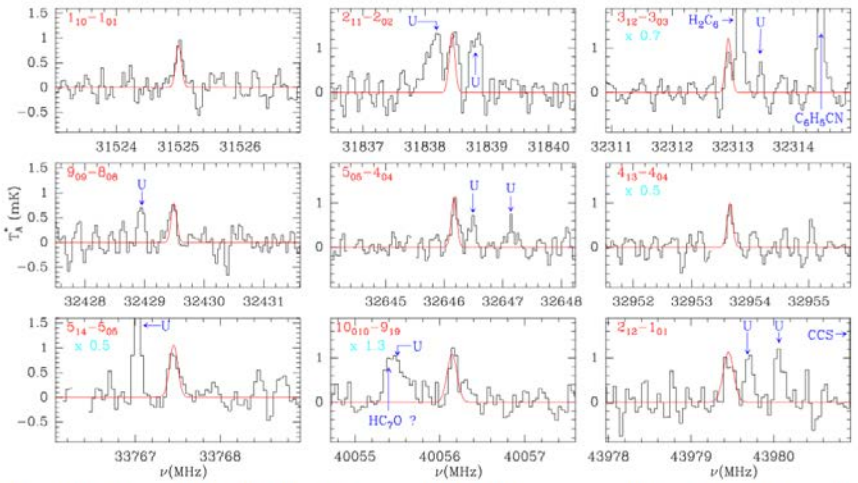


Fig. 2. Selected transitions of c-C_3HCCH in TMC-1. The abscissa corresponds to the rest frequency of the lines, assuming a local standard of rest velocity of the source of 5.83 km s^{-1}. Frequencies and intensities for the observed lines are given in Table A.1. The ordinate is the antenna temperature, corrected for atmospheric and telescope losses, in millikelvins. The quantum numbers for each transition are indicated in the upper left corner of the corresponding panel. The red lines show the computed synthetic spectrum for this species for T_r = 10 K and a column density of 3.1×10^{11} cm^{-2}. Cyan labels indicate the multiplicative factor applied to the model to match the intensity of the observed lines.

The Astrophysical Journal Letters, 929:L11 (9pp), 2022 April 10
https://doi.org/10.3847/2041-8213/ac6186

Precursors of the RNA World in Space: Detection of (Z)-1,2-ethenediol in the Interstellar Medium, a Key Intermediate in Sugar Formation

Víctor M. Rivilla[1,2], Laura Colzi[1,2], Izaskun Jiménez-Serra[1], Jesús Martín-Pintado[1], Andrés Megías[1], Mattia Melosso[3,4], Luca Bizzocchi[3], Álvaro López-Gallifa[1], Antonio Martínez-Henares[1], Sarah Massalkhi[1], Belén Tercero[5], Pablo de Vicente[6], Jean-Claude Guillemin[7], Juan García de la Concepción[1], Fernando Rico-Villas[1],

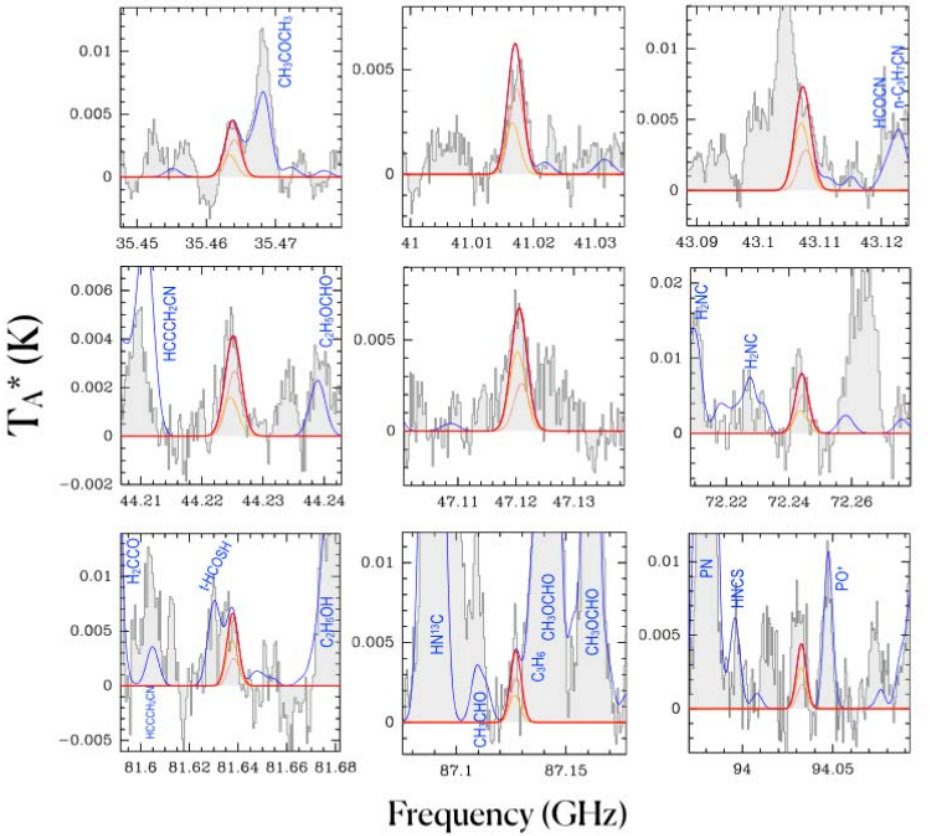
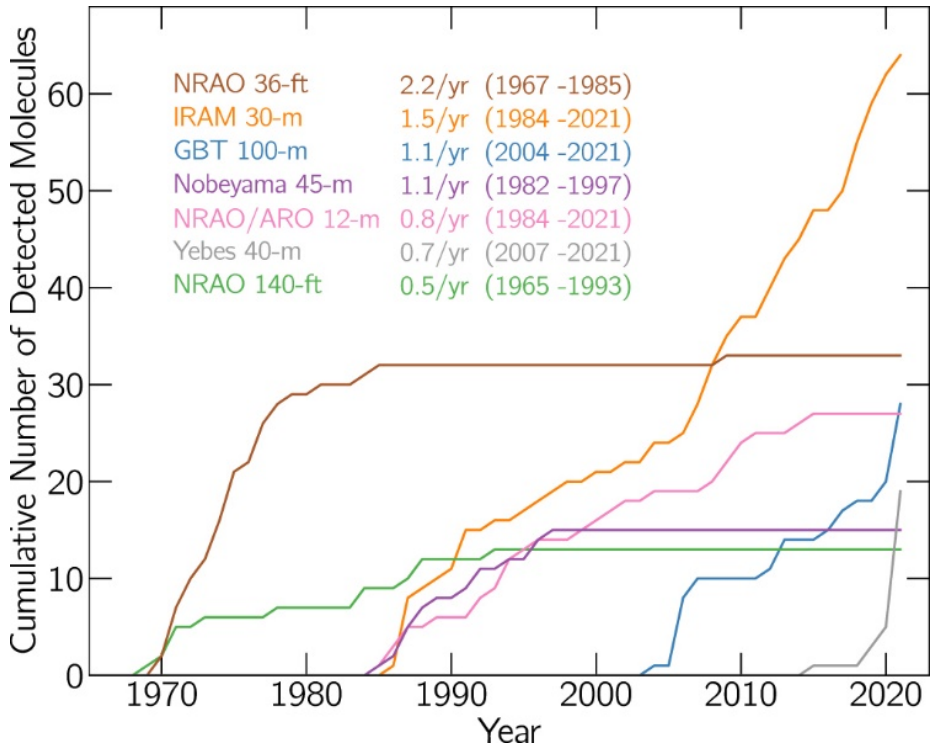


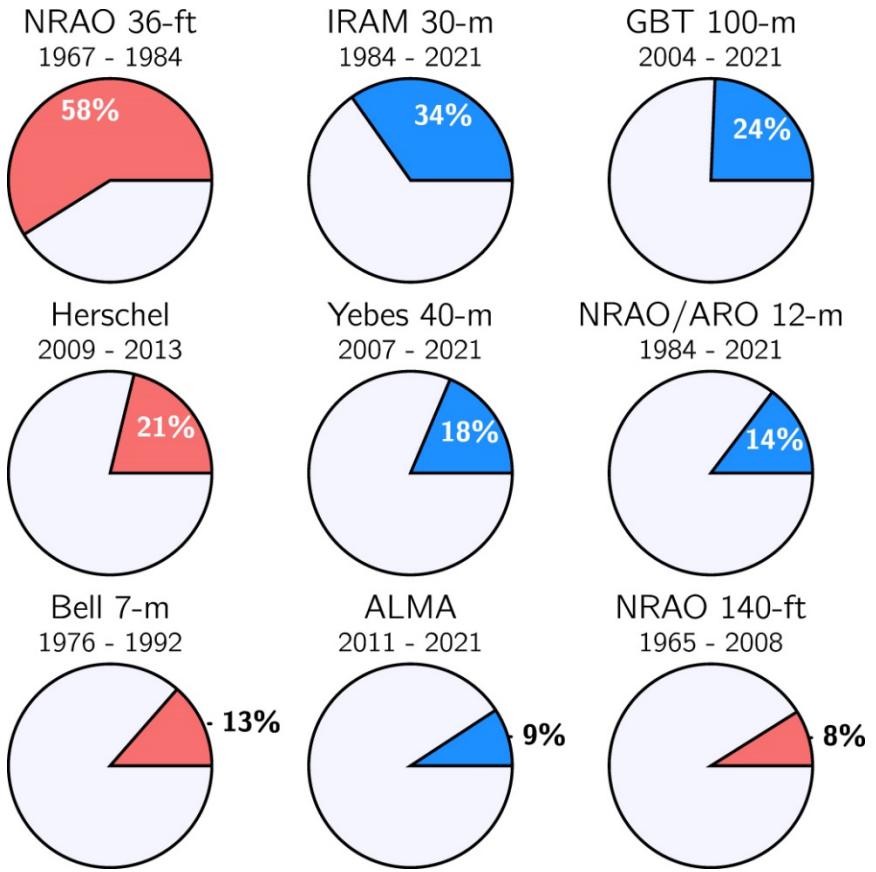
Figure 1. Selected unblended or slightly blended transitions of 1,2-ethenediol detected toward the G+0.693−0.027 molecular cloud. Note that each panel contains two 1,2-ethenediol transitions close in frequency that are not resolved (see Table 1), the individual contributions of which are shown with the yellow and salmon curves. The best LTE fit derived with MADCUBA for the 1,2-ethenediol emission is shown with a red curve. The blue curve represents the total emission considering all the species identified toward this molecular cloud.

(so long as you have a LOT of observing time!)

Overall impact of facilities on the detection of new molecules

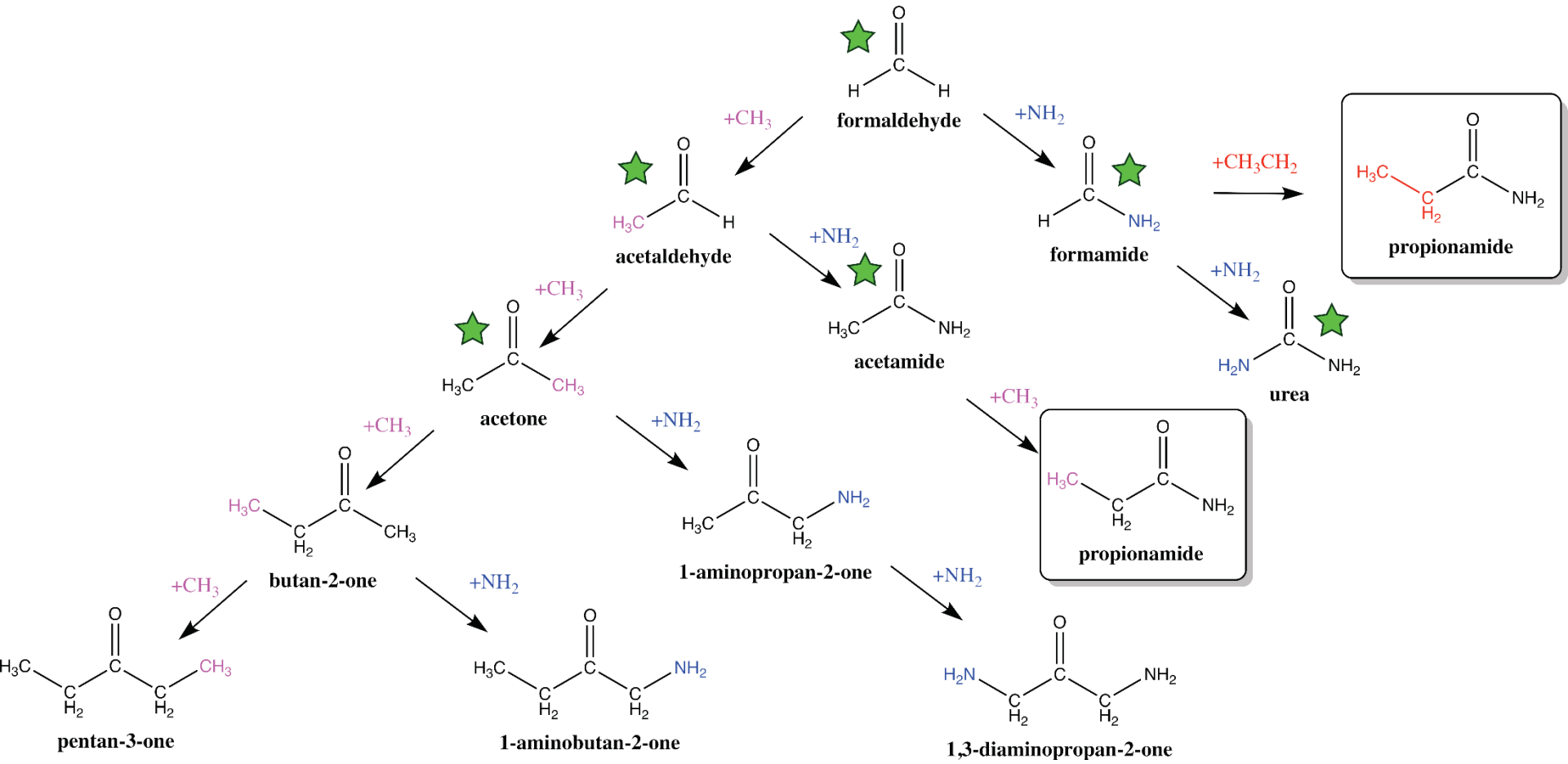


Cumulative number of detections per facility by year. For clarity, only those facilities with 10 or more total detections are shown. The detection rates for the facilities over selected time periods are highlighted.

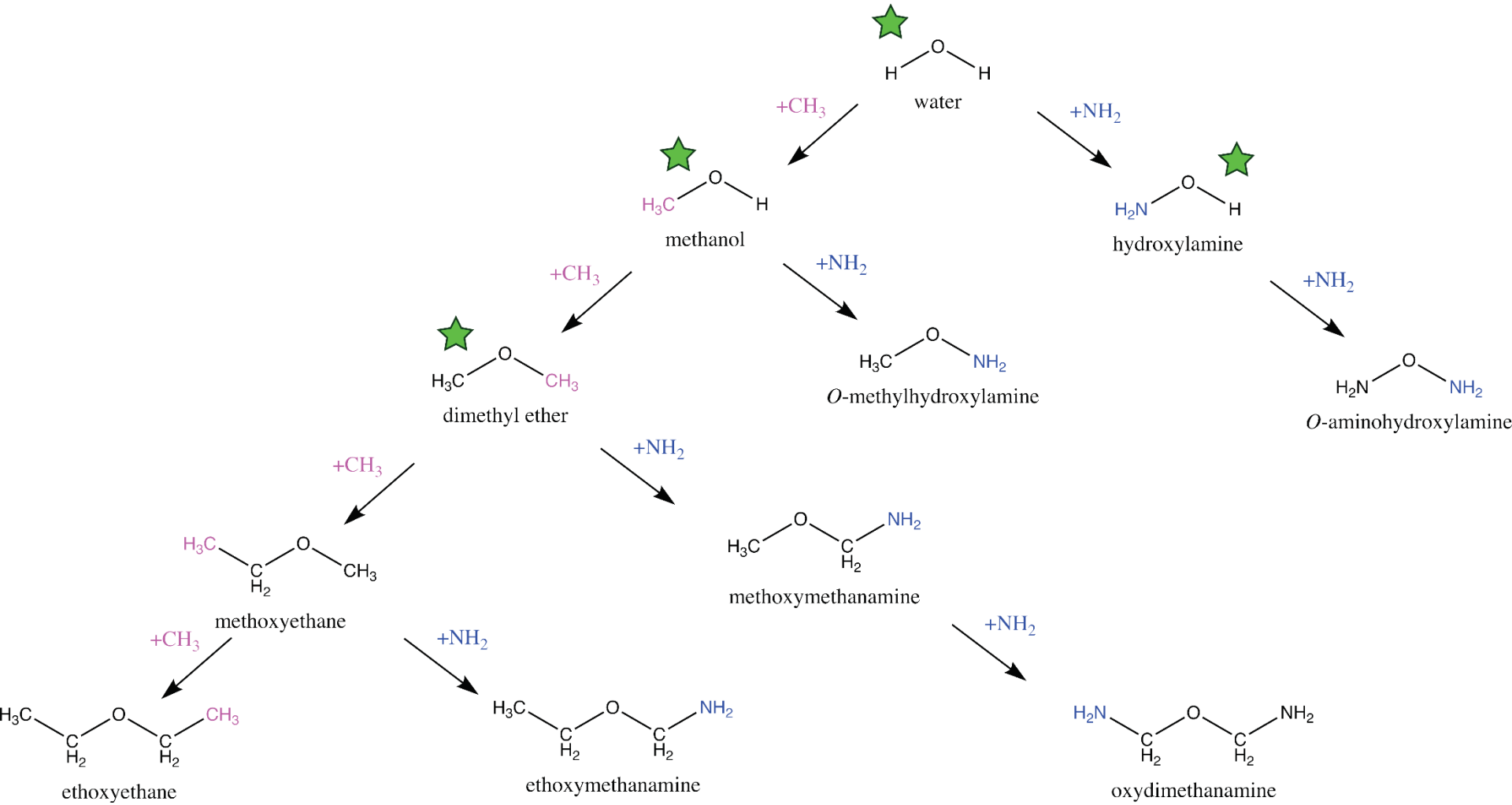


Percentage share of detections that a facility contributed (or is contributing) over its operational lifetime. For example, the NRAO 36 ft antenna accounted for 58% of all detections made during its operational lifetime. Facilities no longer in operation are colored red, and current facilities are in blue.

The Aldehyde Family



The Water Family?

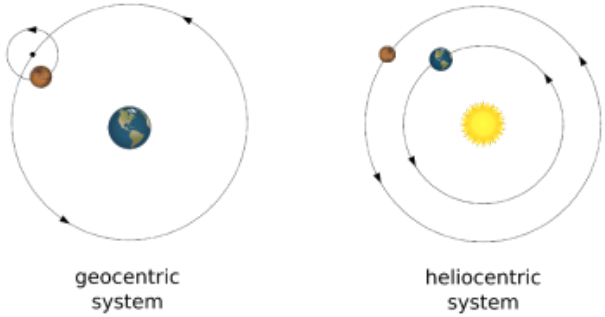


Adding Spatial Extent to Chemical Models?

Chemical maps are "expensive" and difficult to interpret…

- "What type of data do you want/need?"
  - Do morphological differences actually trace chemistry or physics?
    - *Or worse…just abundance?*
- Mapping isomeric "families" may help to constrain chemical formation models (maybe)
  - What does the "non-detection" of some isomers tell us? Perhaps just the spectra is enough…
- Moving beyond adding "epicycles" to chemical models
  - Do we/should we fundamentally change how we approach chemical modeling of molecules in astronomical environments?

Adding Spatial Extent to Chemical Models?



"One significant advantage of simplicity is the clear focus it gives you. This level of clarity makes it easier for you to produce the results you're after."

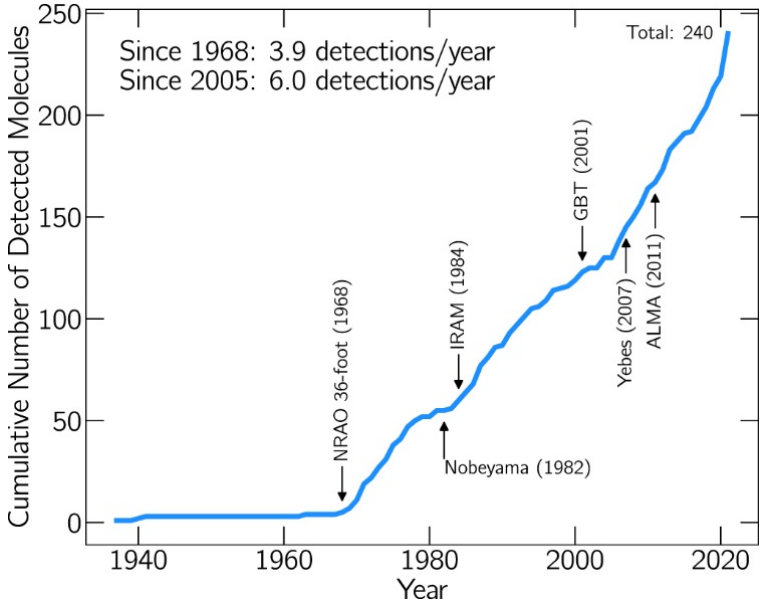
GOAL/CHALLENGE:

Determine a global formation pathway for a chemical family that is consistent with both the spectroscopic detections and morphological diversity in a given astronomical environment.

How do we get there?

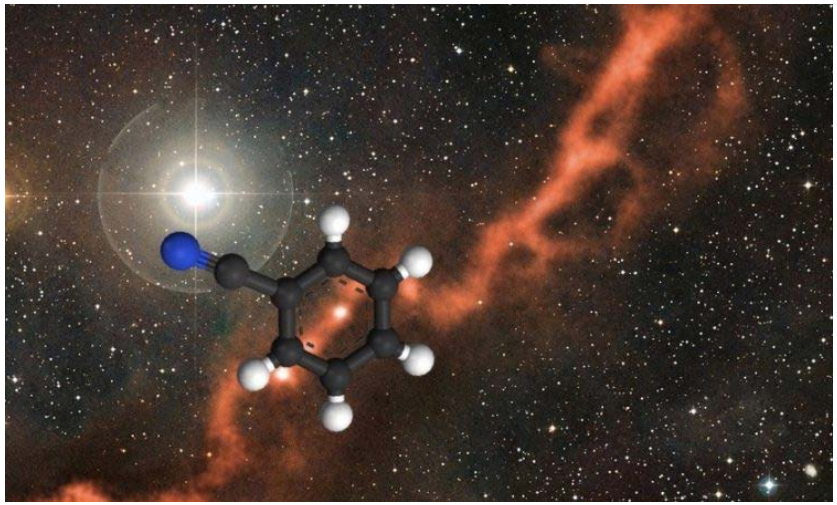
I have no idea…

Astrochemistry Research – Continuing a Legacy…



Total number of molecular detections per year since 1968. Reproduced from McGuire et al. 2022 – and still growing!

From the simplest, to the most complex, the modern field of radio astrochemistry is uncovering a molecular complexity previously unheard of just 50 years ago.



LES: "Formaldehyde was the first polyatomic organic molecule found in space. This discovery revealed the vast amount of gas and dust that is found between the stars and marked the start of an exciting branch of chemistry broadly known as "astrochemistry"."

www.nrao.edu
science.nrao.edu
public.nrao.edu

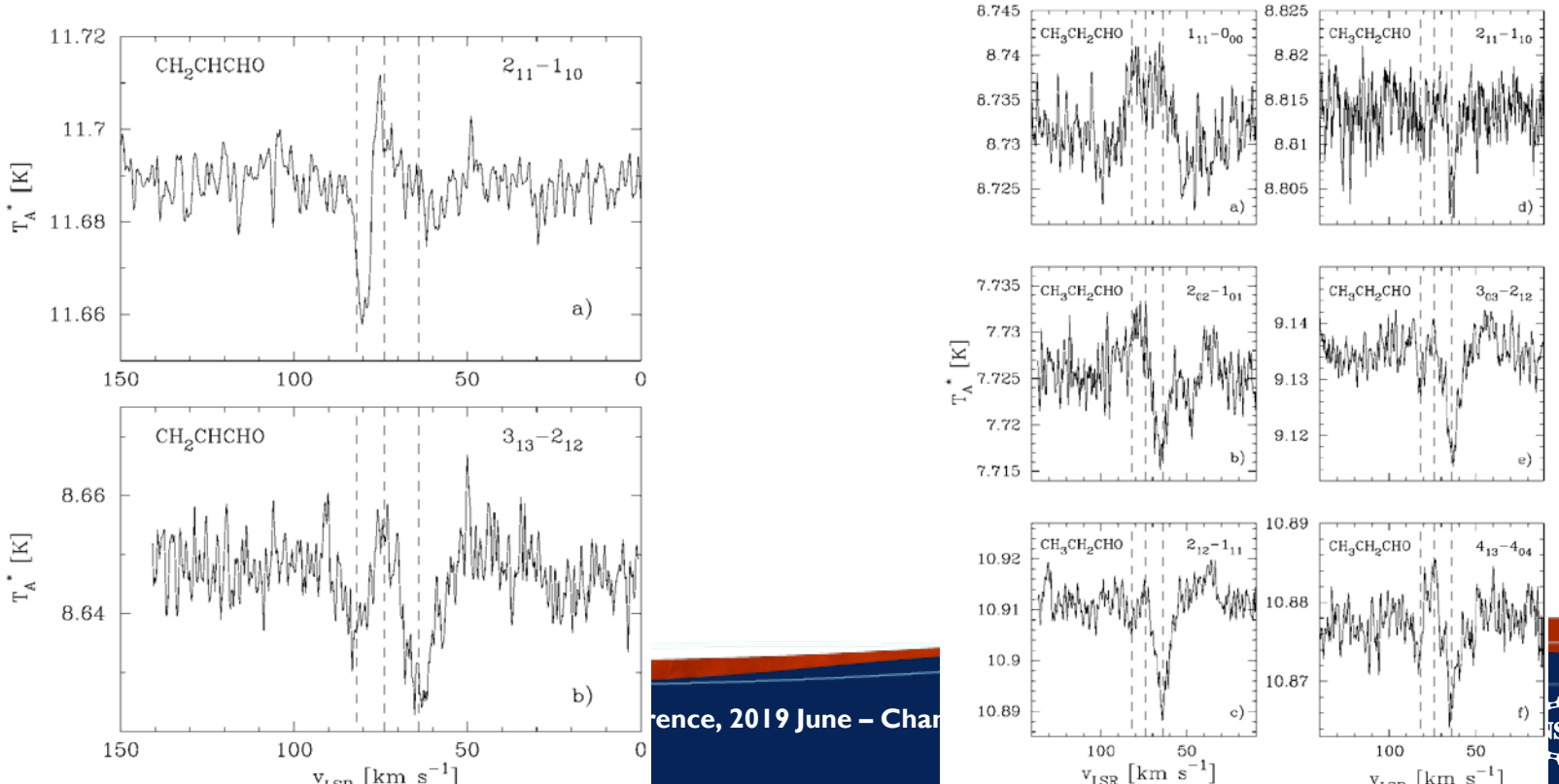
The National Radio Astronomy Observatory is a facility of the National Science Foundation operated under cooperative agreement by Associated Universities, Inc.

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

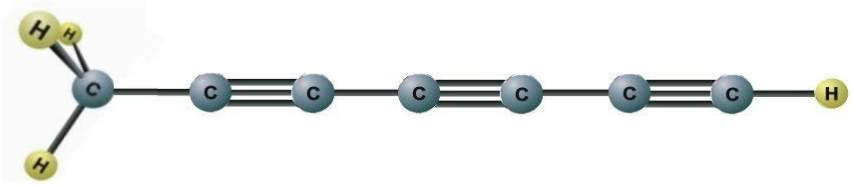
(Hollis et al. 2004, ApJ, 610, L21)



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

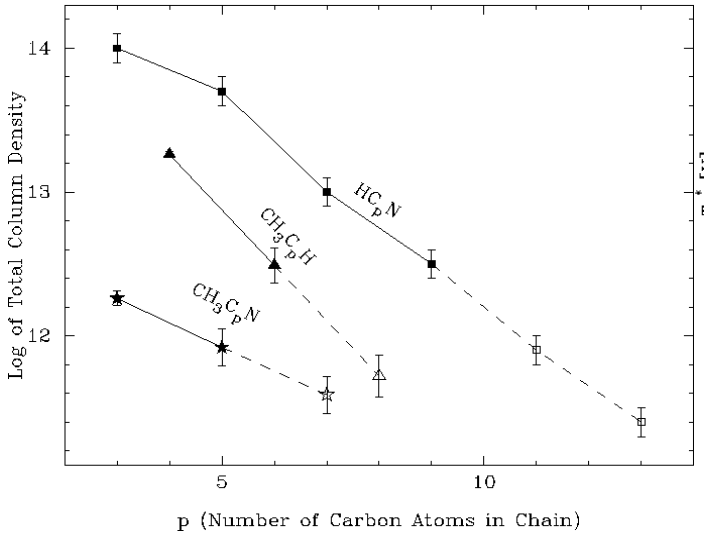
(Remijan et al. 2006, ApJ, 643, L37)

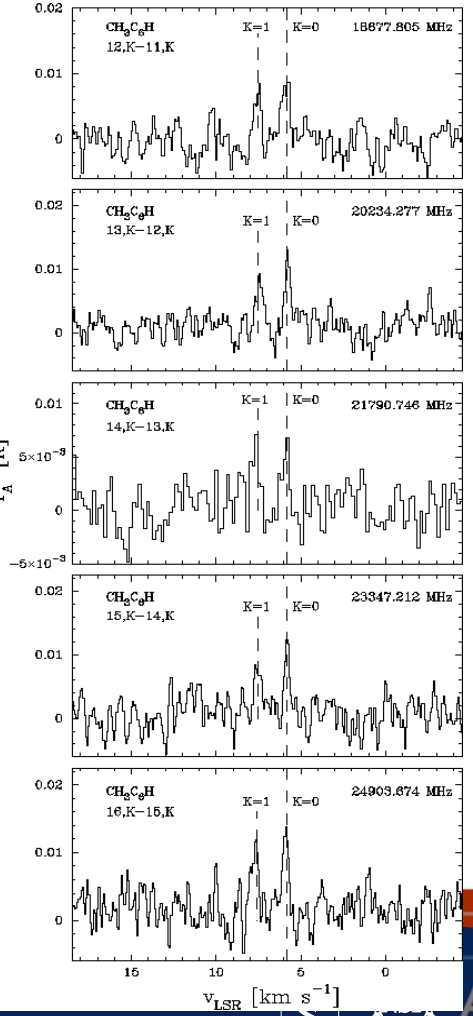
In this work, we identified interstellar methyltriacetylene (CH_3C_6H) using the GBT toward the dark Taurus Molecular Cloud (TMC-1).



METHYLTRIACETYLENE

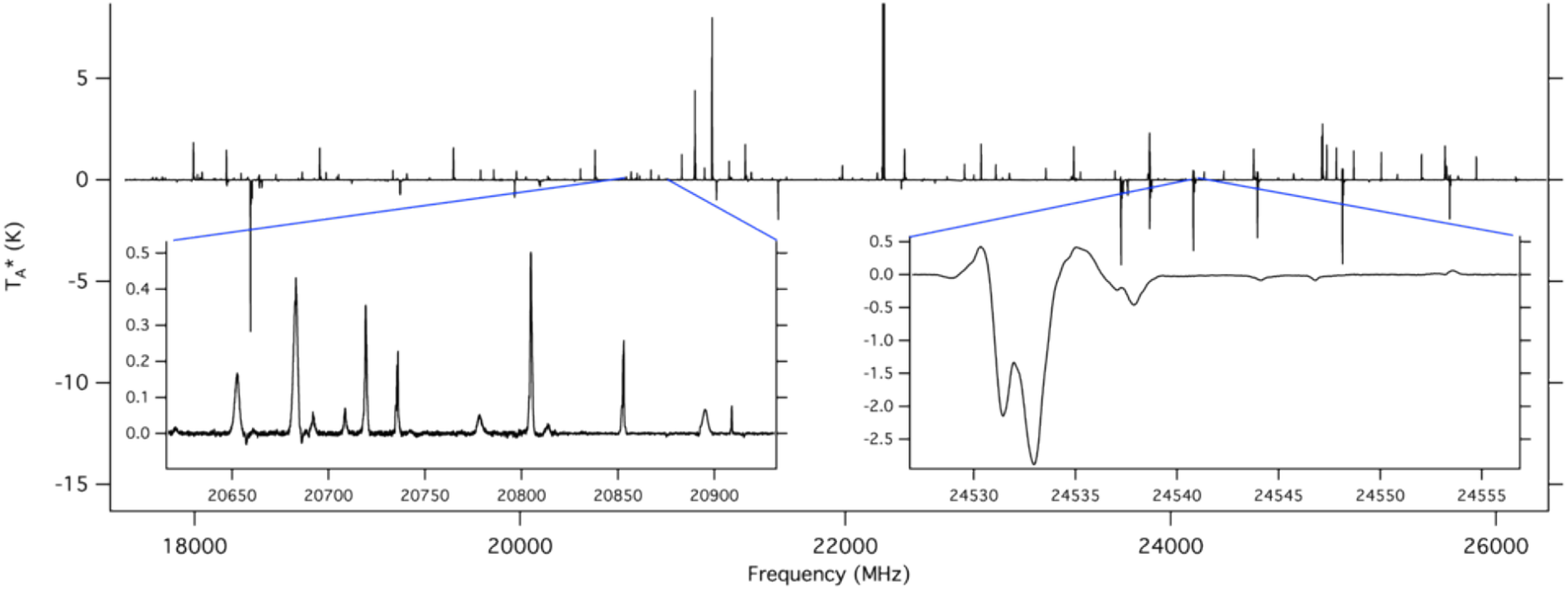
Strong correlations are found among the values of the three different carbon-chain slopes when total column densities of sequence members are plotted against the number of carbon atoms in the carbon chain. This result suggests that the formation chemistry for all these carbon-chain sequences is common.



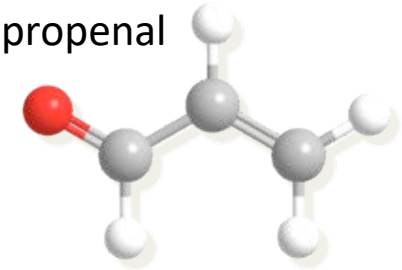


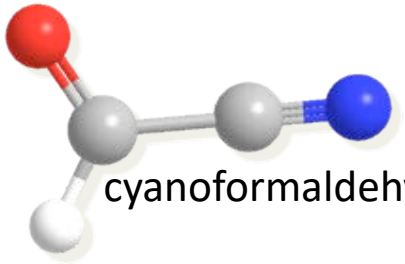
PRebiotic Interstellar MOlecular Survey

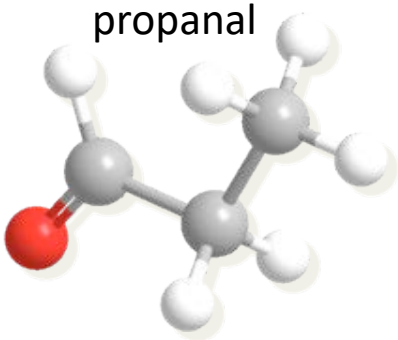
- One of the earliest "Large" programs on the GBT
- Target: Sgr B2(N-LMH)
- Coverage: 40.4 GHz of Bandwidth from 300 MHz - 50 GHz
- Noise level of ~2 mK
- Publicly available with no proprietary period

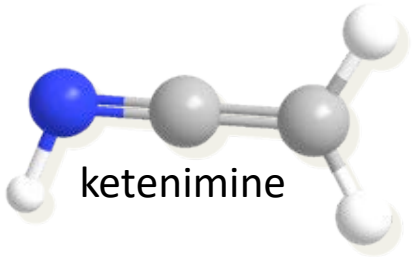


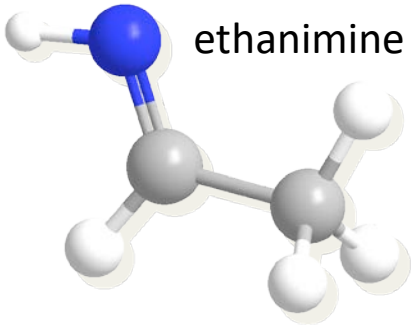
(Some) New Molecule Detections

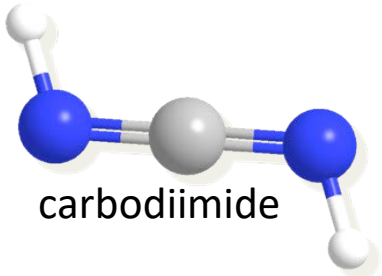

propenal

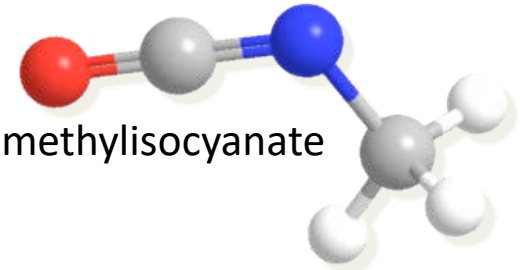

cyanoformaldehyde

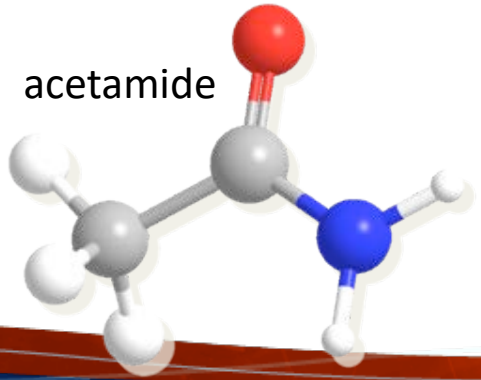

propanal

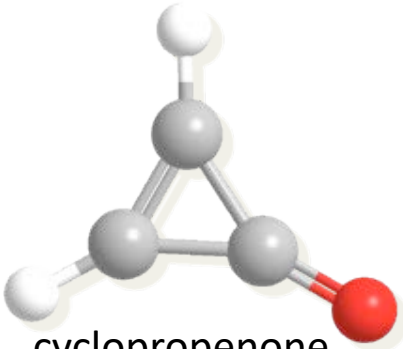

ketenimine

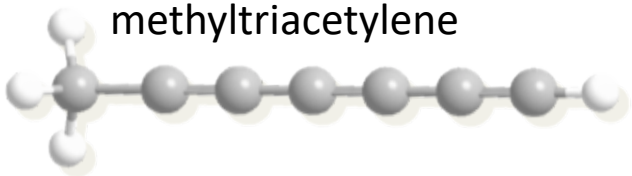

ethanimine


carbodiimide

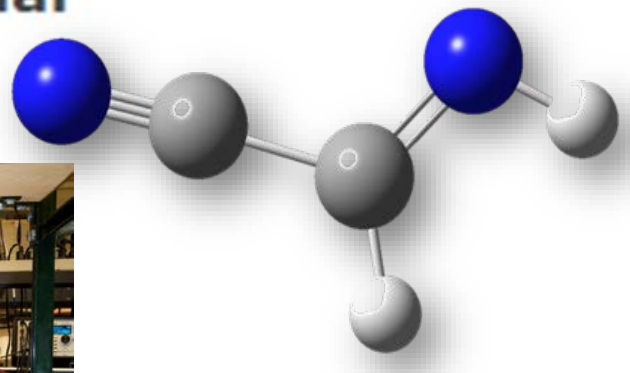

methylisocyanate

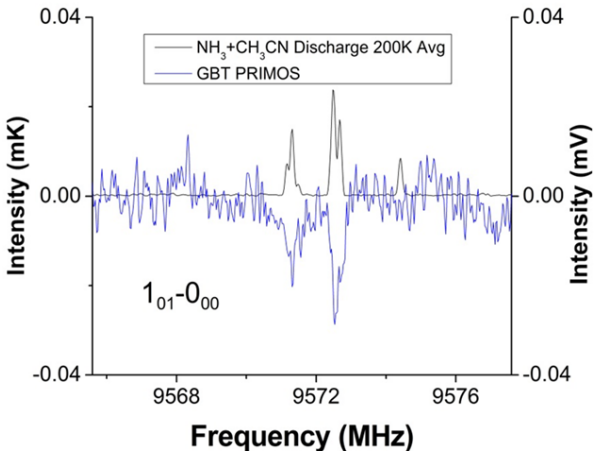

acetamide

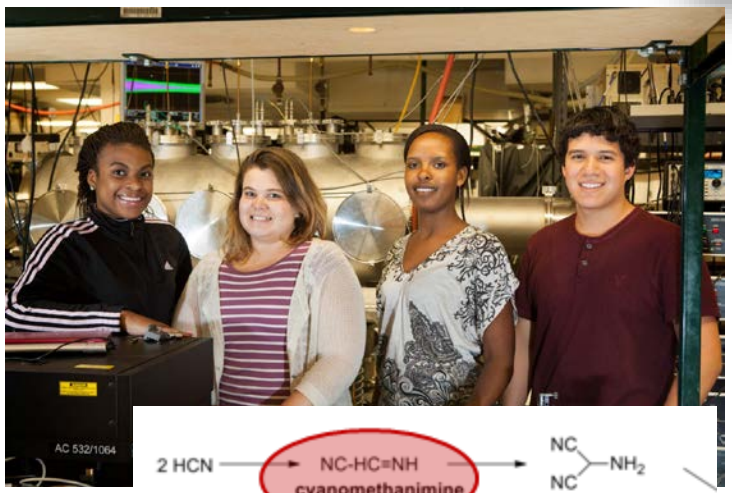

cyclopropenone

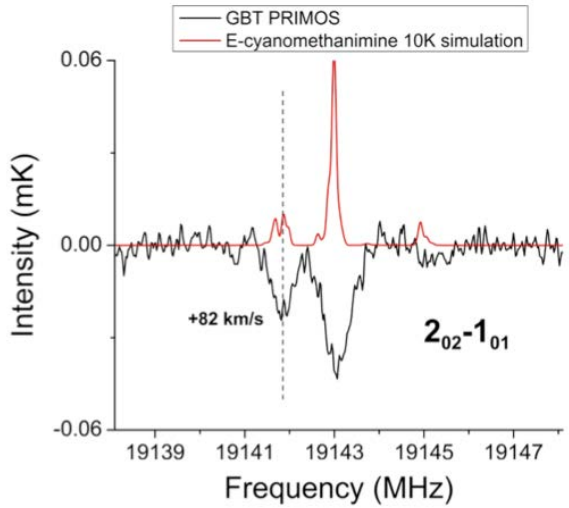

methyltriacetylene

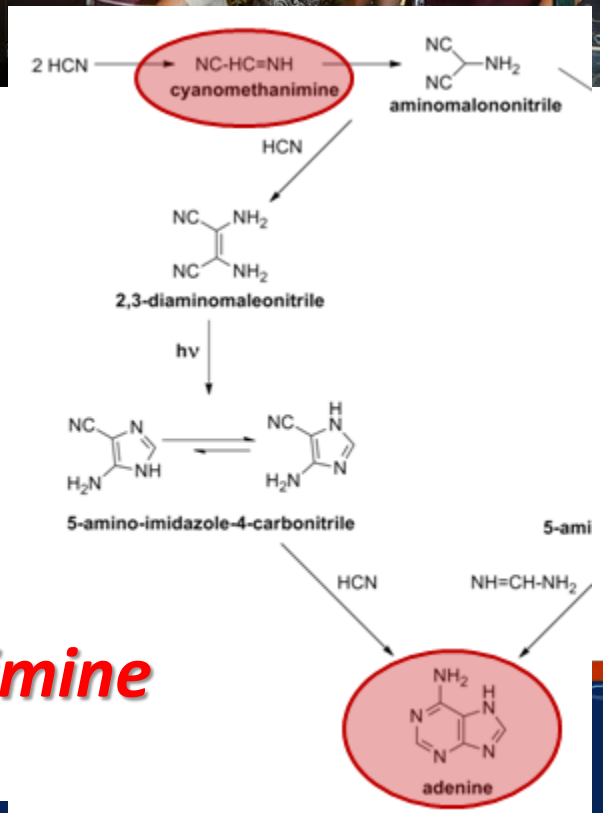
Student Team Discovers New Interstellar Molecule During Summer Program









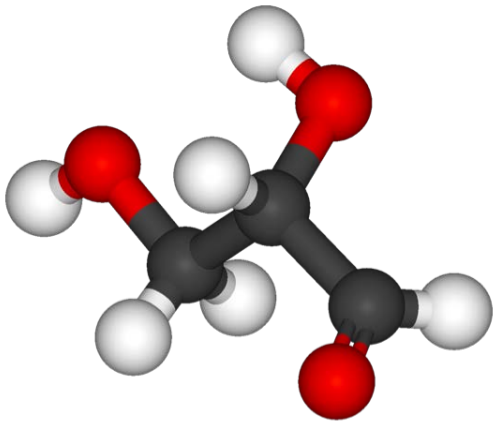


- **Precursor to prebiotic oligomers of HCN**
- **Formation of adenine using only addition of HCN**
  - **Adenine is a nucleobase with a variety of roles in organic chemistry including cellular respiration.**
  - **energy-rich adenosine triphosphate (ATP)**
  - **Protein synthesis, as a chemical component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

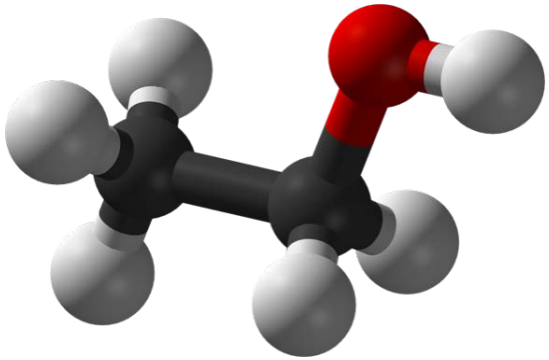
E-Cyanomethanimine

Zaleski et al. 2013 ApJ, 765, L9

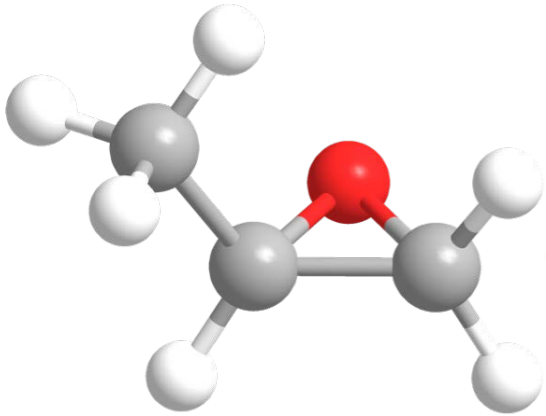
GBT Observations reveal the first signal from a chiral molecule



glyceraldehyde



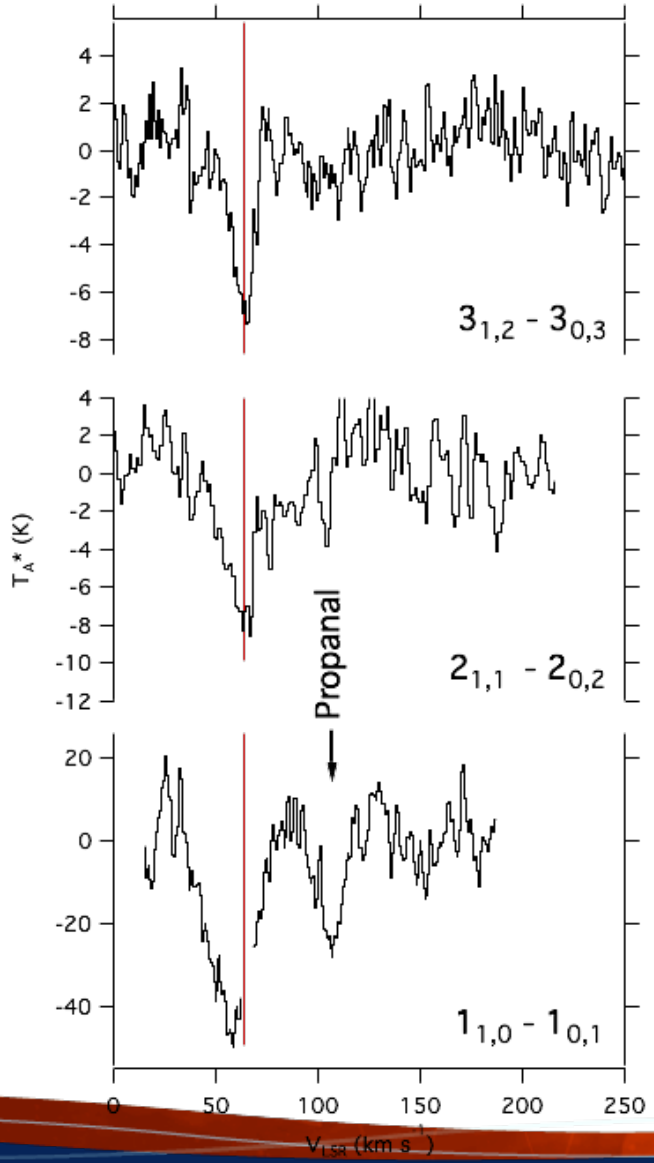
deuterated ethanol



propylene oxide

Joint GBT/Parkes Detection

GBT Observations reveal the first signal from a chiral molecule

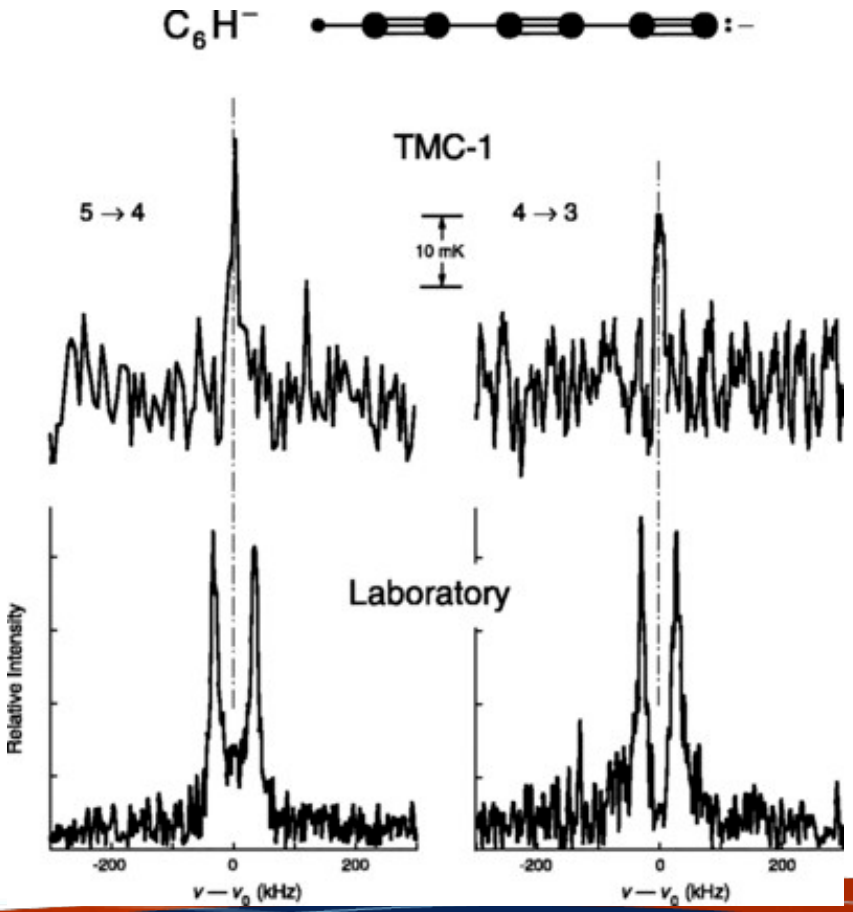


One of the most surprising and unanticipated discoveries was the first detection of interstellar anions toward the dark cloud TMC-1

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.

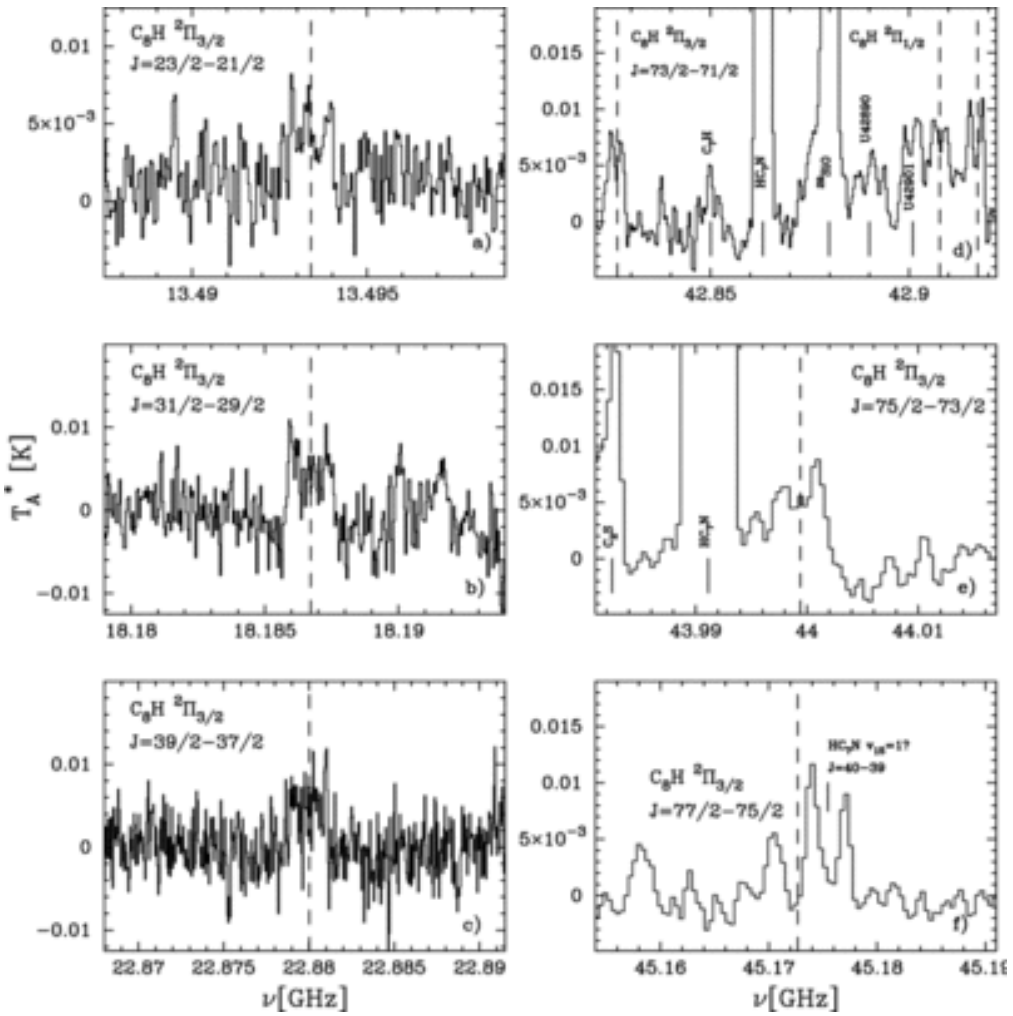


Soon after the discovery of C_6H^-…

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



Detection of large molecules – an aside.

- With all the progress made in mapping the distribution of large molecules with ALMA and the arrays that have come before it, ALMA has not provided the