

Molecular Discovery at Green Bank

Past, Present, and Future

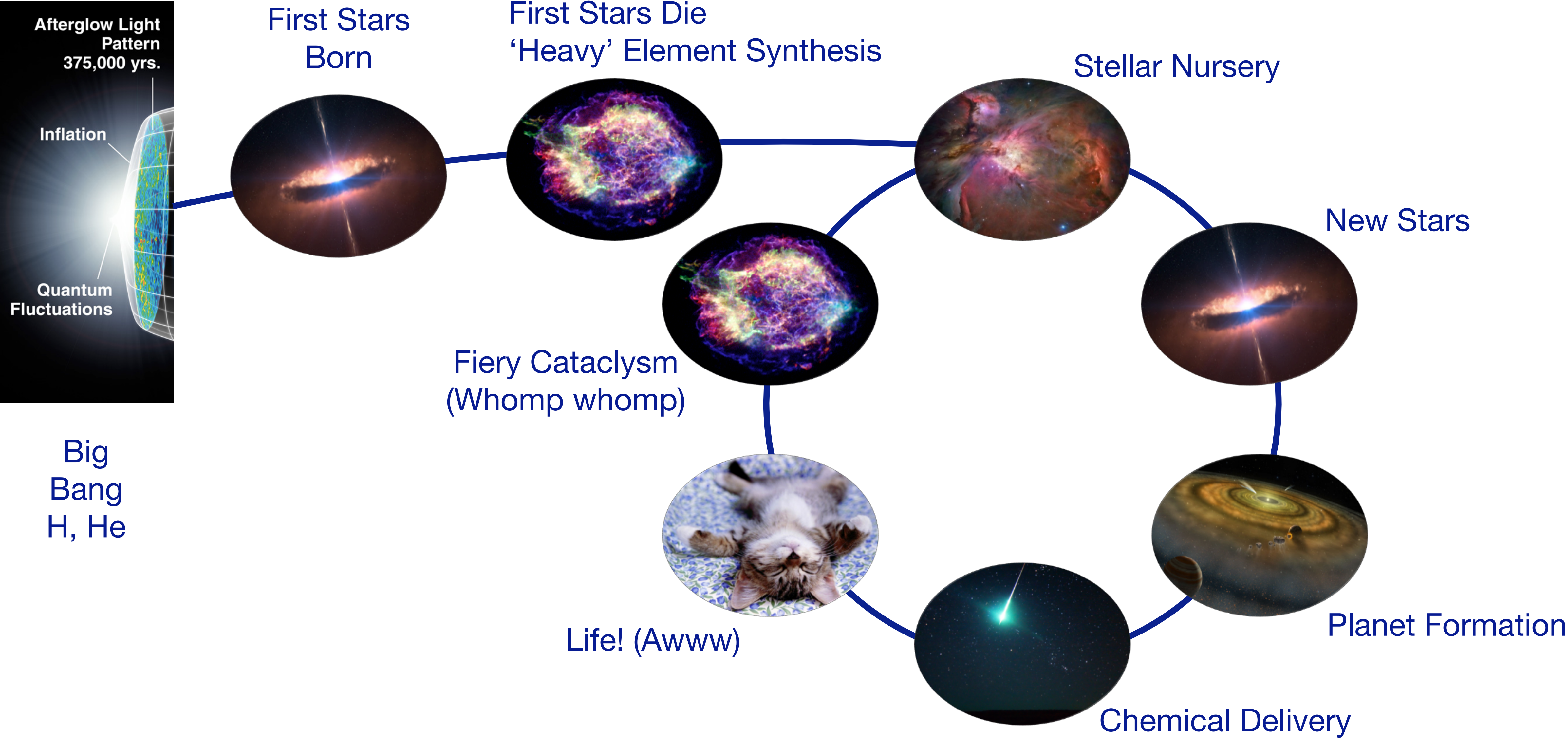


Brett A. McGuire
Department of Chemistry, Massachusetts Institute of Technology

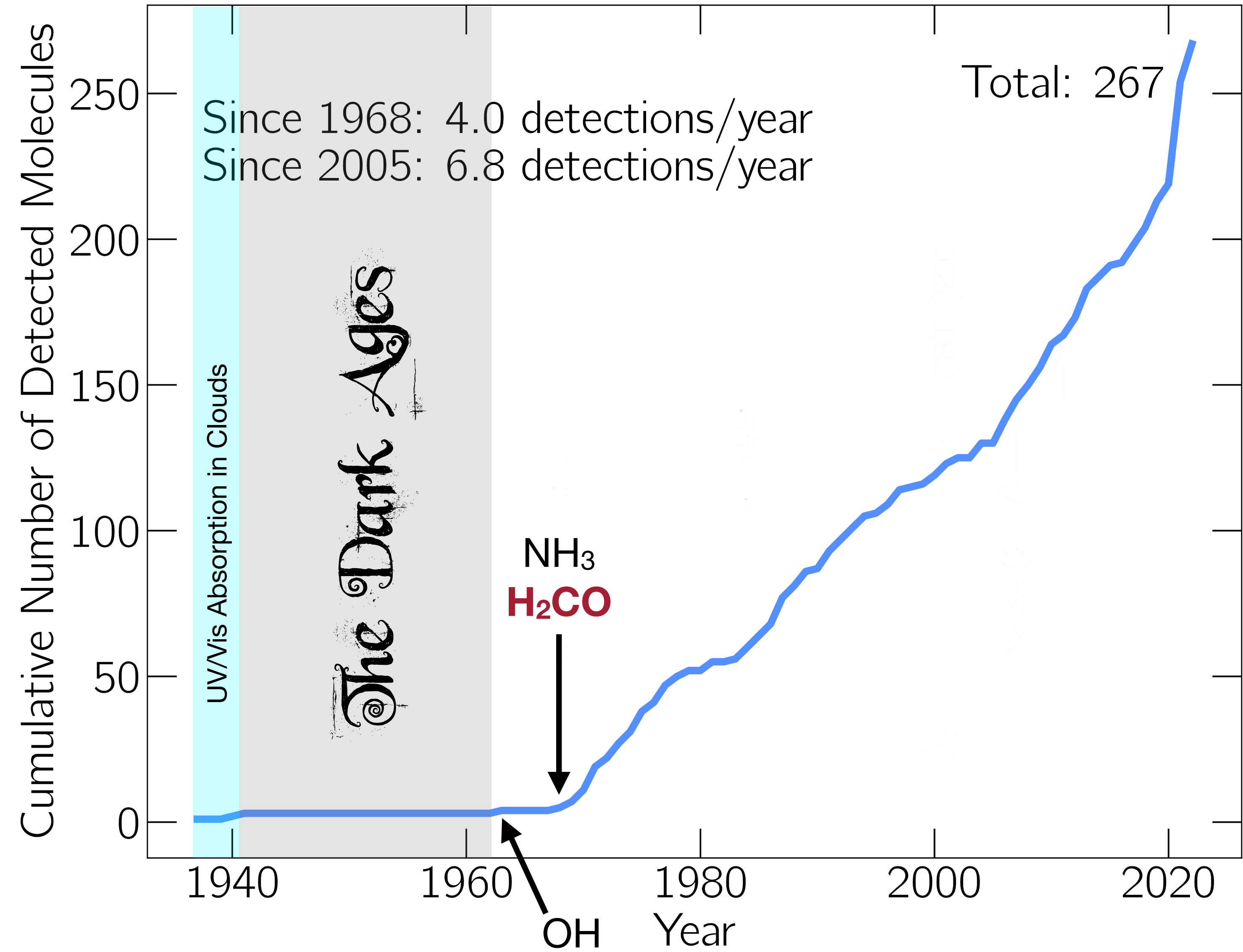


Astrochemistry *astrō'keməstrē* (n)
The study of molecules in space:
where they are, how they got there,
and what they are doing.

THE COSMIC CHEMISTRY LIFECYCLE



A BRIEF HISTORY OF MOLECULAR ASTRONOMY



Known Interstellar Molecules

2 Atoms		3 Atoms		4 Atoms		5 Atoms		6 Atoms		7 Atoms		8 Atoms		9 Atoms	
CH	NH	H ₂ O	MgCN	NH ₃	SiC ₃	HC ₃ N	C ₄ H ⁻	CH ₃ OH	CH ₃ CHO	HCOOCH ₃	CH ₃ OCH ₃	C ₈ H ⁻			
CN	SiN	HCO ⁺	H ₃ ⁺	H ₂ CO	CH ₃	HCOOH	CNCHO	CH ₃ CN	CH ₃ CCH	CH ₃ C ₃ N	CH ₃ CH ₂ OH	CH ₂ CHCH ₃			
CH ⁺	SO ⁺	HCN	SiCN	HNCO	C ₃ N ⁻	CH ₂ NH	HNCNH	NH ₂ CHO	CH ₃ NH ₂	C ₇ H	CH ₃ CH ₂ CN	CH ₃ CH ₂ SH			
OH	CO ⁺	OCS	AlNC	H ₂ CS	PH ₃	NH ₂ CN	CH ₃ O	CH ₃ SH	CH ₂ CHCN	CH ₃ COOH	HC ₇ N	HC ₇ O			
CO	HF	HNC	SiNC	C ₂ H ₂	HCNO	H ₂ CCO	NH ₃ D ⁺	C ₂ H ₄	HC ₅ N	H ₂ C ₆	CH ₃ C ₄ H	H ₂ CCCHCCH			
H ₂	N ₂	H ₂ S	HCP	C ₃ N	HOCN	C ₄ H	H ₂ NCO ⁺	C ₅ H	C ₆ H	CH ₂ OHCHO	C ₈ H	HCCCHCHCN			
SiO	CF ⁺	N ₂ H ⁺	CCP	HNCS	HSCN	SiH ₄	NCCNH ⁺	CH ₃ NC	<i>c</i> -C ₂ H ₄ O	HC ₆ H	CH ₃ CONH ₂	H ₂ CCHC ₃ N			
CS	PO	C ₂ H	AlOH	HOCO ⁺	HOOH	<i>c</i> -C ₃ H ₂	CH ₃ Cl	HC ₂ CHO	CH ₂ CHOH	CH ₂ CHCHO	10 Atoms				
SO	O ₂	SO ₂	H ₂ O ⁺	C ₃ O	<i>i</i> -C ₃ H ⁺	CH ₂ CN	MgC ₃ N	H ₂ C ₄	C ₆ H ⁻	CH ₂ CCHCN					
SiS	AlO	HCO	H ₂ Cl ⁺	<i>i</i> -C ₃ H	HMgNC	C ₅	HC ₃ O ⁺	C ₅ S	CH ₃ NCO	NH ₂ CH ₂ CN	11 Atoms				
NS	CN ⁻	HNO	KCN	HCNH ⁺	HCCO	SiC ₄	NH ₂ OH	HC ₃ NH ⁺	HC ₅ O	CH ₃ CHNH					
C ₂	OH ⁺	HCS ⁺	FeCN	H ₃ O ⁺	CNCN	H ₂ CCC	HC ₃ S ⁺	C ₅ N	HOCH ₂ CN	CH ₃ SiH ₃	12 Atoms				
NO	SH ⁺	HOC ⁺	HO ₂	C ₃ S	HONO	CH ₄	H ₂ CCS	HC ₄ H	HC ₄ NC	NH ₂ CONH ₂					
HCl	HCl ⁺	SiC ₂	TiO ₂	<i>c</i> -C ₃ H	MgCCH	HCCNC	C ₄ S	HC ₄ N	HC ₃ HNH	HCCCH ₂ CN	13+ Atoms				
NaCl	SH	C ₂ S	CCN	HC ₂ N	HCCS	HNCCC	CHOSH	<i>c</i> -H ₂ C ₃ O	<i>c</i> -C ₃ HCCH	CH ₂ CHCCH					
AlCl	TiO	C ₃	SiCSi	H ₂ CN	HNCN	H ₂ COH ⁺	HC ₃ O	CH ₂ CNH	MgC ₅ N	MgC ₆ H	14 Atoms				
KCl	ArH ⁺	CO ₂	S ₂ H		HCCS ⁺			C ₅ N ⁻	CH ₂ C ₃ N	C ₂ H ₃ NH ₂					
AlF	NS ⁺	CH ₂	HCS					HNCHCN		HOCHCHOH	15 Atoms				
PN	HeH ⁺	C ₂ O	HSC					SiH ₃ CN							
SiC	VO	MgNC	NCO					MgC ₄ H			16 Atoms				
CP	PO ⁺	NH ₂	CaNC					CH ₃ CO ⁺							
		N ₂ O	NCS					H ₂ CCCS			17 Atoms				
								CH ₂ CCH							
								HCSCCH			18 Atoms				
								C ₅ O							
								C ₅ H ⁺			19 Atoms				
								<i>c</i> -C ₅ H							
											20 Atoms				
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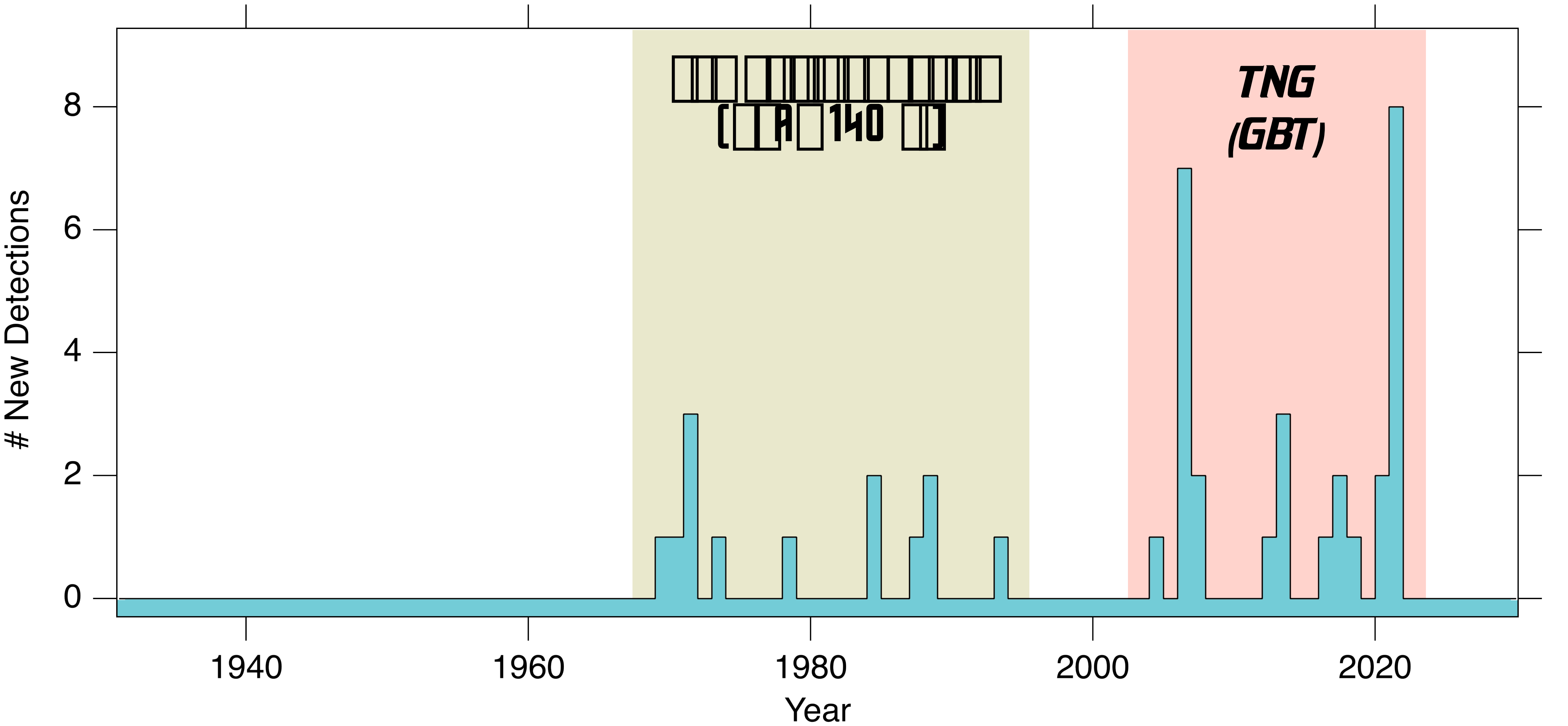
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CN	SiN	HCO ⁺	H ₃ ⁺	H ₂ CO	CH ₃	HCOOH	CNCHO	CH ₃ CN	CH ₃ CCH	CH ₃ C ₃ N	CH ₃ CH ₂ OH	CH ₂ CHCH ₃
CH ⁺	SO ⁺	HCN	SiCN	HNCO	C ₃ N ⁻	CH ₂ NH	HNCNH	NH ₂ CHO	CH ₃ NH ₂	C ₇ H	CH ₃ CH ₂ CN	CH ₃ CH ₂ SH
OH	CO ⁺	OCS	AlNC	H ₂ CS	PH ₃	NH ₂ CN	CH ₃ O	CH ₃ SH	CH ₂ CHCN	CH ₃ COOH	HC ₇ N	HC ₇ O
CO	HF	HNC	SiNC	C ₂ H ₂	HCNO	H ₂ CCO	NH ₃ D ⁺	C ₂ H ₄	HC ₅ N	H ₂ C ₆	CH ₃ C ₄ H	H ₂ CCCHCCH
H ₂	N ₂	H ₂ S	HCP	C ₃ N	HOCN	C ₄ H	H ₂ NCO ⁺	C ₅ H	C ₆ H	CH ₂ OHCHO	C ₈ H	HCCCHCHCN
SiO	CF ⁺	N ₂ H ⁺	CCP	HNCS	HSCN	SiH ₄	NCCNH ⁺	CH ₃ NC	c-C ₂ H ₄ O	HC ₆ H	CH ₃ CONH ₂	H ₂ CCHC ₃ N
CS	PO	C ₂ H	AlOH	HOCO ⁺	HOOH	c-C ₃ H ₂	CH ₃ Cl	HC ₂ CHO	CH ₂ CHOH	CH ₂ CHCHO		
SO	O ₂	SO ₂	H ₂ O ⁺	C ₃ O	/-C ₃ H ⁺	CH ₂ CN	MgC ₃ N	H ₂ C ₄	C ₆ H ⁻	CH ₂ CCHCN	10 Atoms	11 Atoms
SiS	AlO	HCO	H ₂ Cl ⁺	/-C ₃ H	HMgNC	C ₅	HC ₃ O ⁺	C ₅ S	CH ₃ NCO	NH ₂ CH ₂ CN	CH ₃ COCH ₃	HC ₉ N
NS	CN ⁻	HNO	KCN	HCNH ⁺	HCCO	SiC ₄	NH ₂ OH	HC ₃ NH ⁺	HC ₅ O	CH ₃ CHNH	HOCH ₂ CH ₂ OH	CH ₃ C ₆ H
C ₂	OH ⁺	HCS ⁺	FeCN	H ₃ O ⁺	CNCN	H ₂ CCC	HC ₃ S ⁺	C ₅ N	HOCH ₂ CN	CH ₃ SiH ₃	CH ₃ CH ₂ CHO	C ₂ H ₅ OCHO
NO	SH ⁺	HOC ⁺	HO ₂	C ₃ S	HONO	CH ₄	H ₂ CCS	HC ₄ H	HC ₄ NC	NH ₂ CONH ₂	CH ₃ C ₅ N	CH ₃ COOCH ₃
HCl	HCl ⁺	SiC ₂	TiO ₂	c-C ₃ H	MgCCH	HCCNC	C ₄ S	HC ₄ N	c-C ₃ HCCH	CH ₂ CONH ₂	CH ₃ CHCH ₂ O	CH ₃ COCH ₂ OH
NaCl	SH	C ₂ S	CCN	HC ₂ N	HCCS	HNCCC	CHOSH	c-H ₂ C ₃ O	MgC ₅ N	CH ₂ CHCCH	CH ₃ OCH ₂ OH	C ₅ H ₆
AlCl	TiO	C ₃	SiCSi	H ₂ CN	HNCN	H ₂ COH ⁺	HCSCN	CH ₂ CNH	CH ₂ C ₃ N	MgC ₆ H	C ₆ H ₄	NH ₂ CH ₂ CH ₂ OH
KCl	ArH ⁺	CO ₂	S ₂ H		HCCS ⁺			C ₅ N ⁻		C ₂ H ₃ NH ₂	CH ₃ CH ₂ OH	CH ₂ CCHC ₄ H
AlF	NS ⁺	CH ₂	HCS					HNCHCN		HOCHCHOH		
PN	HeH ⁺	C ₂ O	HSC					SiH ₃ CN	12 Atoms			
SiC	VO	MgNC	NCO					MgC ₄ H	C ₆ H ₆	1-C ₅ H ₅ CN	13+ Atoms	
CP	PO ⁺	NH ₂	CaNC					CH ₃ CO ⁺	n-C ₃ H ₇ CN	2-C ₅ H ₅ CN	C ₆ H ₅ CN	C ₉ H ₈
		N ₂ O	NCS					H ₂ CCCS	i-C ₃ H ₇ CN		HC ₁₁ N	2-C ₉ H ₇ CN
								CH ₂ CCH			c-C ₅ H ₄ CCH ₂	C ₆₀
								HCSCCH			1-C ₁₀ H ₇ CN	C ₆₀ ⁺
								C ₅ O			2-C ₁₀ H ₇ CN	C ₇₀
								C ₅ H ⁺				
								c-C ₅ H				

268 Molecules

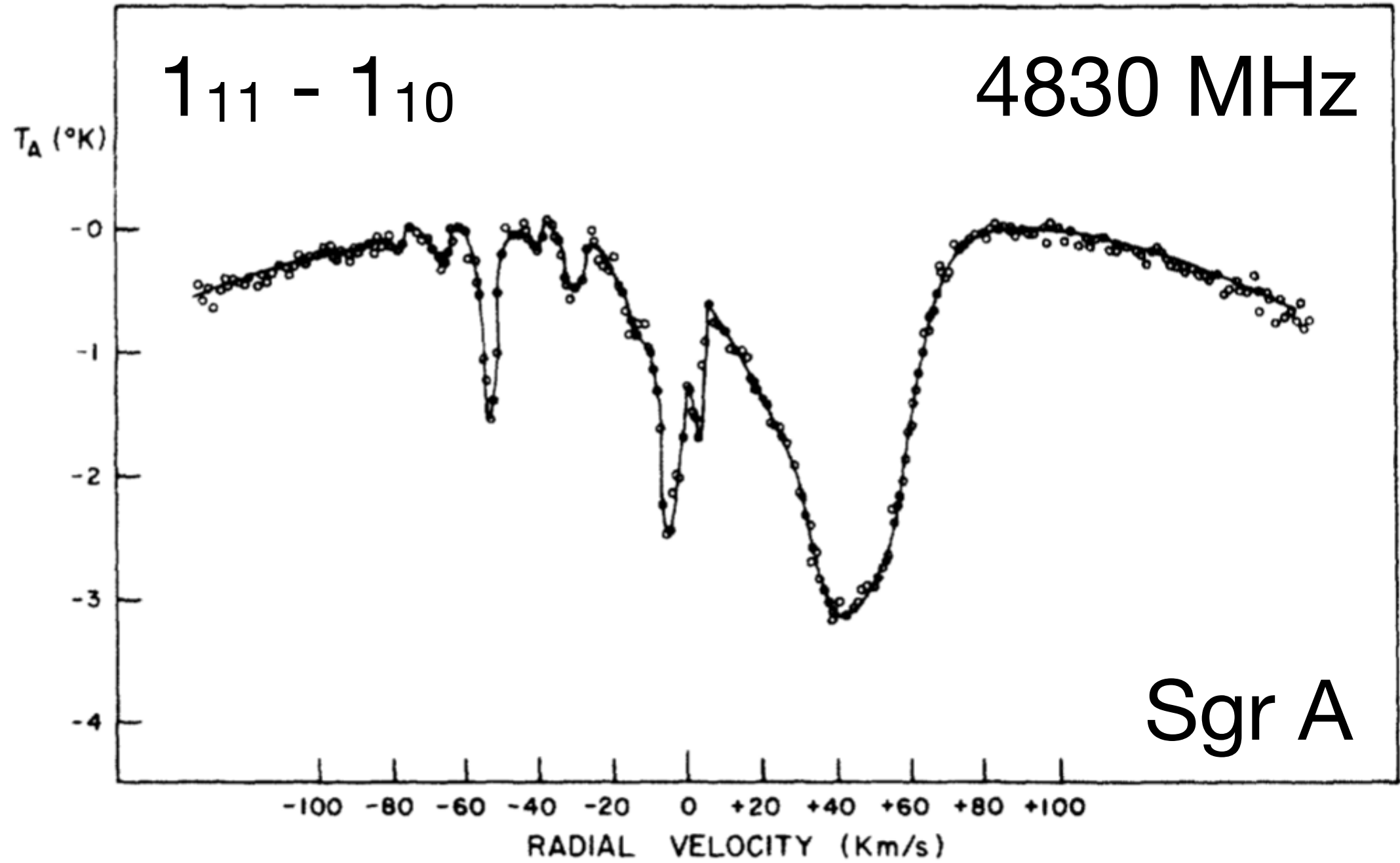
Last Updated: 14 Sep 2022

A SERIES OF FORTUNATE EVENTS



ONCE UPON A TIME





cm H absorption lines in these directions. We regard the close coincidence of the astronomical and laboratory rest frequencies as a strong argument in favor of the identification with H₂CO since we find no other molecule⁴ composed of astrophysically abundant elements that has a microwave line with a rest frequency that lies within our error bars. If some other molecule is found that has the astronomically measured rest frequency, a conclusive identification will require detection of other microwave transitions of either molecule.

Snyder's
Rules
v0.1

¹An example of a C function is
$$C(\alpha_c(t), \alpha(u)) = \int_{-L+\alpha_c(t)}^{\alpha_c(t)} dl (\alpha_c - l)(\alpha_c - L - l) \times \frac{\Gamma(1-l)\Gamma(1-\alpha(u))}{\Gamma(1-\alpha(u)-l)}$$

from unpublished work by A. Schwimmer and S. Pinsky.
²We only mention a few examples: S. Frautschi and B. Margolis CERN Preprint No. Th CERN 909 (to be published); G. Veneziano, Massachusetts Institute of Technology Preprint No. CTP 51 (to be published).

MICROWAVE DETECTION OF INTERSTELLAR FORMALDEHYDE

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and
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(Received 17 March 1969)

Interstellar formaldehyde (H₂CO) has been detected in absorption against numerous galactic and extragalactic radio sources by means of the 1₁₁-1₁₀ ground-state rotational transition at 4830 MHz. The absorbing regions often correspond in velocity with 18-cm OH features. H₂CO 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.

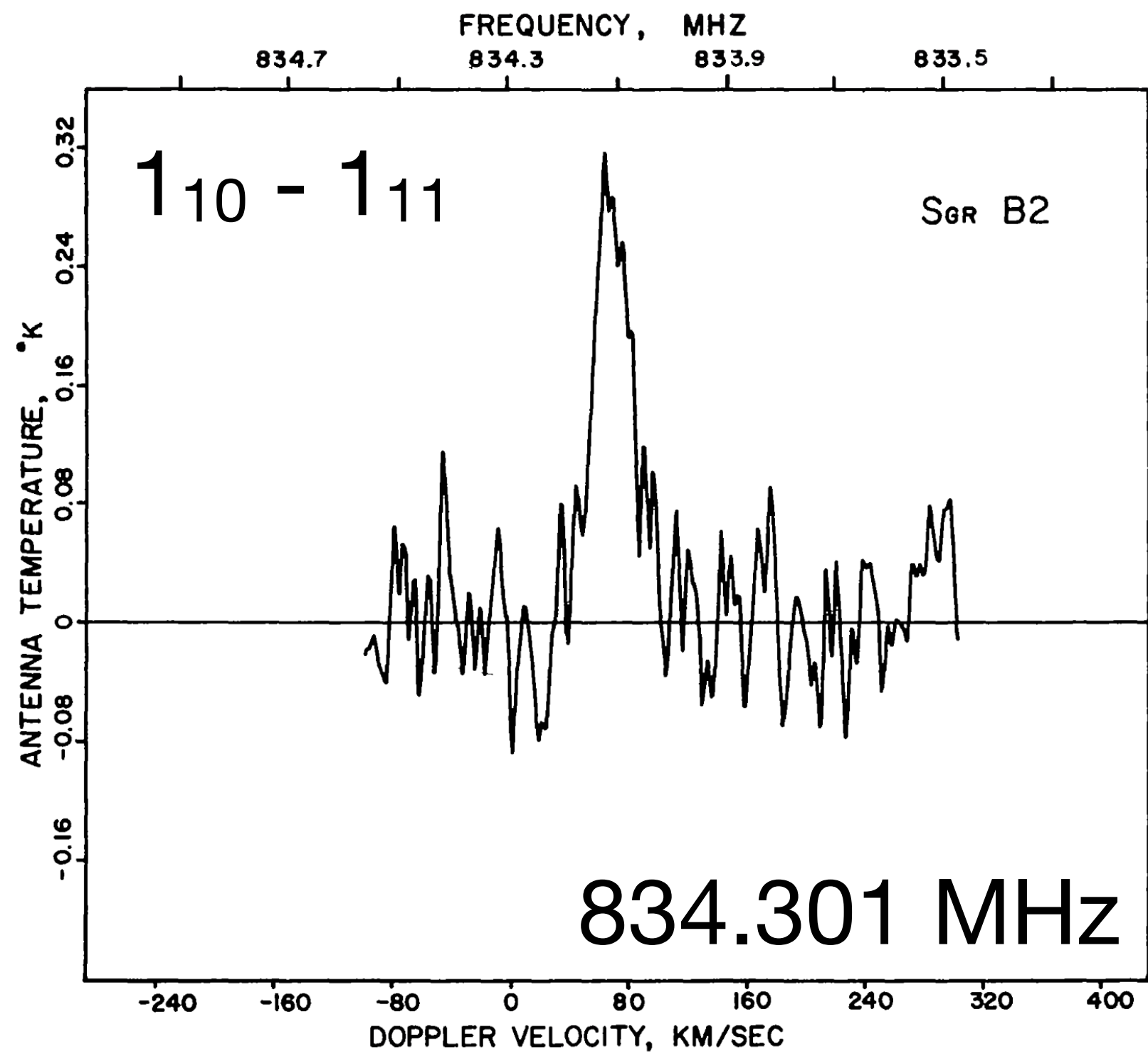
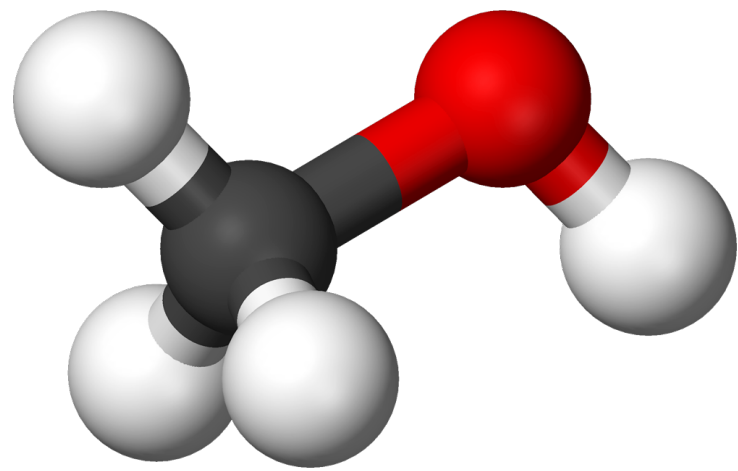
The 140-ft telescope of the National Radio Astronomy Observatory was used to detect the 1₁₁-1₁₀ transition of interstellar formaldehyde at 4830 MHz in absorption against numerous continuum radio sources. The 6₂₅-6₂₄, 13_{3,11}-13_{3,10}, and 21_{4,18}-21_{4,17} transitions¹ were also searched for but not detected. Due to the present widespread interest in interstellar molecules and because a detailed analysis of all of our data will take some time, in this Letter we briefly report a portion of our results.

The 140-ft telescope was equipped with a cooled parametric amplifier and a 400-channel autocorrelation receiver. Spectral resolutions of 1, 2, 4, 8, and 16 kHz were used. The system temperature and aperture efficiencies were about 100°K and 50%, respectively. The half-power width of the antenna beam was ~6.6'. The radiometer was operated with frequency switching in the first local oscillator. The oscillator was locked to a rubidium standard which had a long-term stability of 2 parts in 10¹¹.

The 4830-MHz line was detected in absorption against the following continuum sources: M17, W3, W3 (OH position), W49, NGC 2024, DR 21, W43, W44, W51, Sgr A, Sgr B2, W33, NGC

6334, Cas A, and 3C 123. The line was not detected in NML Cyg, DR 23, 3C 273, Orion A, W28, VY Cma, Virgo A, Taurus A, Cygnus A, Venus, and Jupiter. Figure 1 shows an H₂CO spectrum of the galactic center (Sgr A) in which numerous absorption features are present. This spectrum closely resembles the OH absorption spectrum in the same direction.² For features with half-power widths <30 kHz the hyperfine splitting³ must be considered. The hyperfine components of the line are not indicated in Fig. 1 since they are not resolved. Typical spectra contain between one and eight Doppler features. These features have full widths at half-maximum power (Δν) ranging from 15 to 500 kHz and peak antenna temperatures between 0.2 and 5°K. For sources in which no lines were detected the lower limits for detection are <0.5°K depending on linewidth. H₂CO emission was also sought adjacent to some of the continuum sources, but none is evident at the present stage of data reduction.

At least some of the observed features appear to originate in "typical" interstellar clouds (densities ~ 10 hydrogen atoms/cm³, kinetic temperatures 50-100°K), some of which are associated



Spectral data were processed with the NRAO 384-channel one-bit digital autocorrelator. To double the effective integration time, 192 channels were used on each receiver, and the final spectra represent the average of two orthogonal linear polarizations. The

alcohol.² After the successful detection in Sagittarius, we made a direct laboratory measurement of the 36-cm line in order to get an accurate value of the rest frequency and to investigate the possibility of unresolved hyperfine structure in the astronomical line.

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DETECTION OF METHYL ALCOHOL IN SAGITTARIUS

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AND

H. E. RADFORD
Smithsonian Astrophysical Observatory, Cambridge, Massachusetts
Received 1970 October 31

ABSTRACT

This Letter reports observations of radio line emission at 834 MHz (36 cm), due to a *K*-type doubling transition in methyl alcohol, in the directions of Sgr A and Sgr B2. Line widths and Doppler velocities compare favorably with other molecular spectra observed toward the galactic-center region.

I. INTRODUCTION

Methyl alcohol, CH_3OH , also called methanol or wood alcohol, is the simplest alcohol molecule. It brings a new level of complexity to molecular astronomy, for it is a molecule that exhibits a torsional motion called hindered internal rotation, a type of motion that has so far defied exact analysis by spectroscopists. This complexity also multiplies the number of low energy levels available to the molecule, makes some of them metastable, and provides new possibilities for infrared pumping.

We detected methyl alcohol by its *K*-type doubling line at 834 MHz (the counterpart of the 4830-MHz line of formaldehyde), using the 140-foot radio telescope at NRAO.¹ At this low frequency, the half-power beamwidth of the antenna is approximately 36 arc min, substantially larger than the beamwidths used in previous molecular observations of the galactic-center region. Even though the continuum temperatures toward the center are relatively large, greater than 100° K, the line appears in emission.

II. OBSERVATIONS

Figures 1 and 2 show the spectra for Sgr B2 and Sgr A obtained 1970 September 1-7. Baseline curvature, discussed below, has been removed by subtracting a fitted fourth-order polynomial. Because the emission spectra are weak and because of limited observing time, as possible. Table 1 gives the positions used, the antenna temperature maxima, line widths, and Doppler velocities with respect to the galactic center. Limits are given for four other radio sources in Table 2. The spectra were obtained with a crossed-dipole feed and a two-channel receiver. The system had a system temperature of $550^\circ \pm 50^\circ$ K. Aperture and the conversion factor from antenna temperature to flux density are ± 0.4 f.u. per ° K.

Spectral data were processed with the NRAO 384-channel one-bit digital autocorrelator. To double the effective integration time, 192 channels were used on each receiver, and the final spectra represent the average of two orthogonal linear polarizations. The results of cosine weighting of the autocorrelation data to accumulate the data, with a long off-axis beam, are described by Ball

¹ The NRAO 140-foot radio telescope, located at Green Bank, West Virginia, is operated by Associated Universities, Inc.

EXTRA, EXTRA! READ ALL ABOUT IT!



EXTRA, EXTRA! READ ALL ABOUT IT!

12

Boston Evening Globe Tuesday, November 10, 1970

Celestial mystery

Harvard scientists spot alcohol near Milky Way

By Victor K. McElheny
Globe Staff

Fresh from the discovery of two big, glowing clouds of poisonous methyl alcohol near the center of our Milky Way galaxy, three Harvard radio astronomers returned to West Virginia today to look for more of it.

This just-announced finding of alcohol in the distant heavens is not even the latest discovery of a molecule associated with life in the cosmos.

After alcohol was found at two points in the constellation Sagittarius (the Archer), a team headed by a University of Maryland researcher and including two of the Harvard group probed the cosmos and found formic acid.

radio frequencies. One of these is the molecule of hydrogen (H_2). Just last summer, a Navy research rocket equipped with instruments for studying ultraviolet light found some of this UV light from the direction of a star called Xi Persei absorbed by hydrogen molecules.

Other key molecules associated with life and the early atmosphere of a planet, such as methane and carbon dioxide, also do not show up at radio frequencies.

The team involved in the methyl alcohol work included Prof. A.E. Lilley and Drs. John A. Ball and Carl Gottlieb of the Harvard College Observatory.

Leading the work on for-

the discovery of hyde, the simplest of the compounds known as aldehydes.

This also set off the search for formic acid, the simplest of the acids containing carbon.

The idea of looking for the simplest chemicals of a class was a sort of "chemical intuition," according to Gottlieb. It gained strength when a flurry of searches for other compounds turned up nothing.

The laboratory tests by Radford gave the local team a rough idea where to search. Radford had precise measurements on some of the higher "transitions" in methyl alcohol and estimated where the lowest one would be.

After the September observations, the scientists

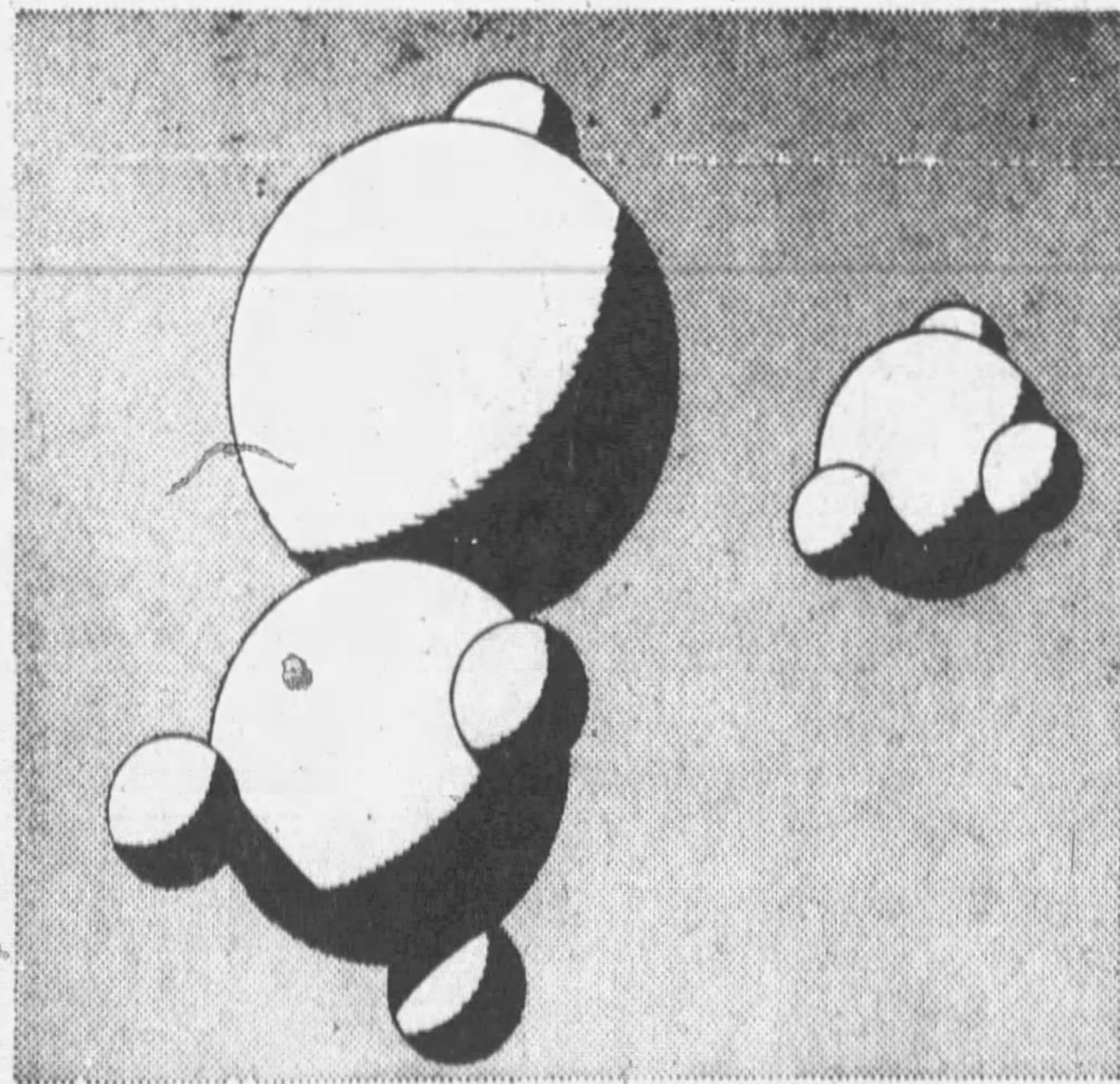
Methyl alcohol (CH_3OH), is better known as wood alcohol, or "torpedo juice," the substance in illegal liquor which temporarily or permanently blinded venturesome youths during Prohibition.

Staunton, Va., Leader, Wednesday, June 17, 1970 29

"Many space scientists are already speculating about the chemical implications of interstellar clouds of complex molecules and how they might fit into an evolutionary pattern of life throughout our galaxy," says Dr. Snyder.

"Of course, no one knows how far astronomers will be able to go with their detections of new molecules, but it doesn't appear as though the end is in sight."

A NEW SCIENCE IS BORN!



Do Clouds In Space Hold Secrets Of Life?

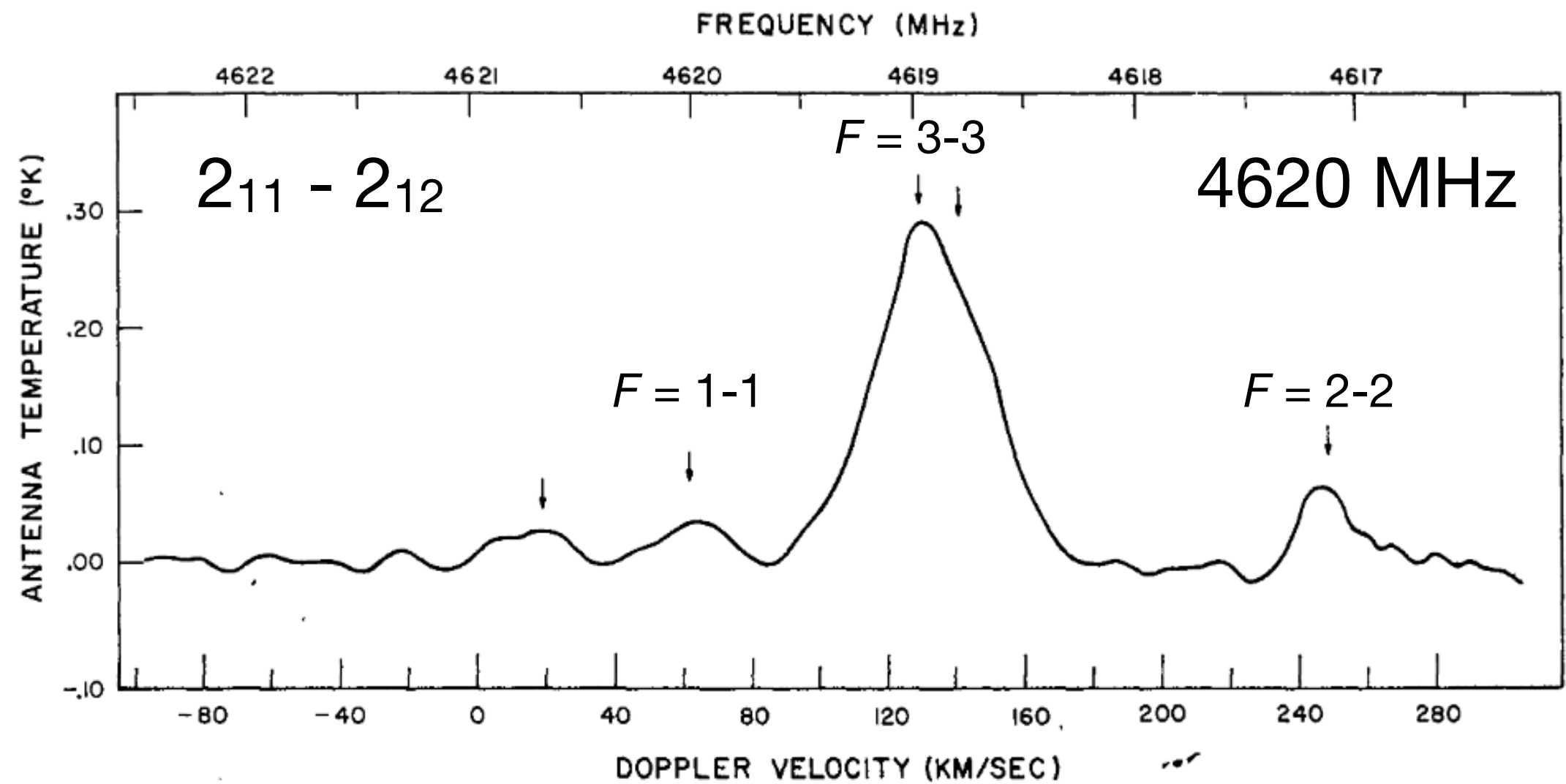
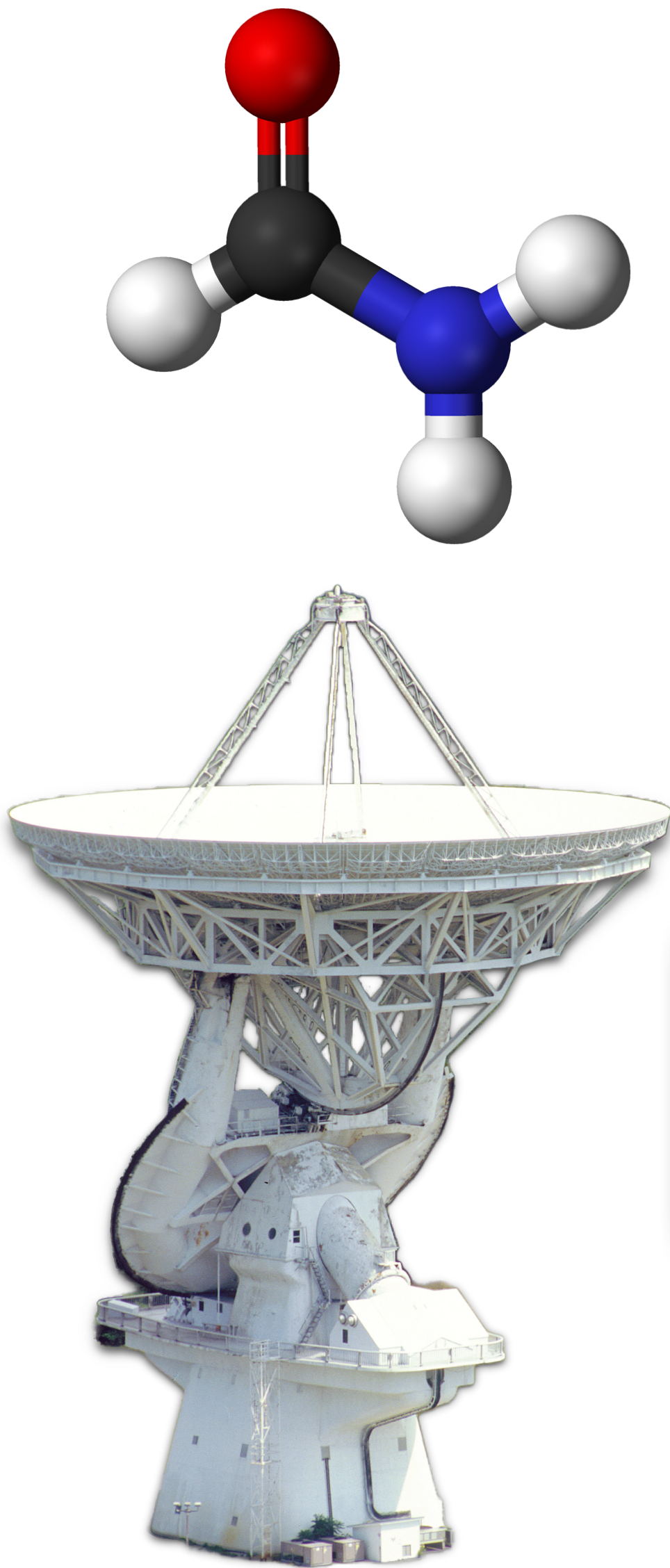
A new science is born!

Astrochemistry . . . and it promises a treasure chest of new understanding about the origins of Earth and life.

hydroxyl free radicals. These are being studied in an emerging new branch of astronomy called "astro-chemistry" or more correctly "astromolecular radio spectroscopy," says Dr. Snyder.

Astonished astronomers found they had a new science on their hands, "astrochemistry," the chemistry of the thin matter of outer space. What's more, the molecules they were detecting might also be on the high-road to life. They were beginning to point in the same direction as that shown by the chemists working with their made-up primitive mixtures in the laboratory.

It looked as if the chemists might not be kidding themselves. Did that mean that, if we looked harder and in more detail, we might find such important compounds as amino acids, the building blocks of proteins? -Isaac Asimov



$$\tau = \frac{2(\ln 2)^{1/2} \lambda^2 A_{ul}}{8\pi^{3/2} \Delta\nu_l} \frac{g_u}{g_l} N_l \left[1 - \exp\left(-\frac{h\nu}{kT_R}\right) \right],$$

$$N_l = \frac{N g_l \exp(-E_l/kT_R)}{Q_R},$$

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MICROWAVE DETECTION OF INTERSTELLAR FORMAMIDE

R. H. RUBIN AND G. W. SWENSON, JR.
University of Illinois Observatory

AND

R. C. BENSON, H. L. TIGELAAR, AND W. H. FLYGARE
Noyes Chemical Laboratory, University of Illinois, Urbana

Received 1971 August 6

ABSTRACT

Formamide was detected by its microwave emission from the $2_{11} \rightarrow 2_{12}$ rotational transition at ~ 4620 MHz in the direction of Sgr B2 and possibly Sgr A. There is evidence that all three of the $\Delta F = 0$ hyperfine components are present. The astronomical rest frequencies are in good agreement with laboratory measurements.

I. INTRODUCTION

Formamide (NH_2CHO), the simplest molecule containing the amide linkage, was detected in the direction of Sgr B2 at 6.5 cm. This is the first interstellar molecule found that contains H, C, N, and O all in the same molecule. The observations were made 1971 March 23 with the 140-foot telescope at the NRAO.¹ The molecule was detected by emission from its K -type doubling transition $2_{11} \rightarrow 2_{12}$. The rotational-energy levels of formamide exhibit hyperfine splitting due to the coupling of the electric-quadrupole moment of the ^{14}N nucleus with the electronic-charge distribution. For Sgr B2 the $F = 2 \rightarrow 2$ and $F = 1 \rightarrow 1$ hyperfine components were clearly resolved, while the strongest component, $F = 3 \rightarrow 3$, was blended with the H112 α line. For Sgr A, since the bandpass did not include the $F = 2 \rightarrow 2$ component, the detection is less certain, but the $F = 3 \rightarrow 3$ line is probably present and blended with the H112 α line.

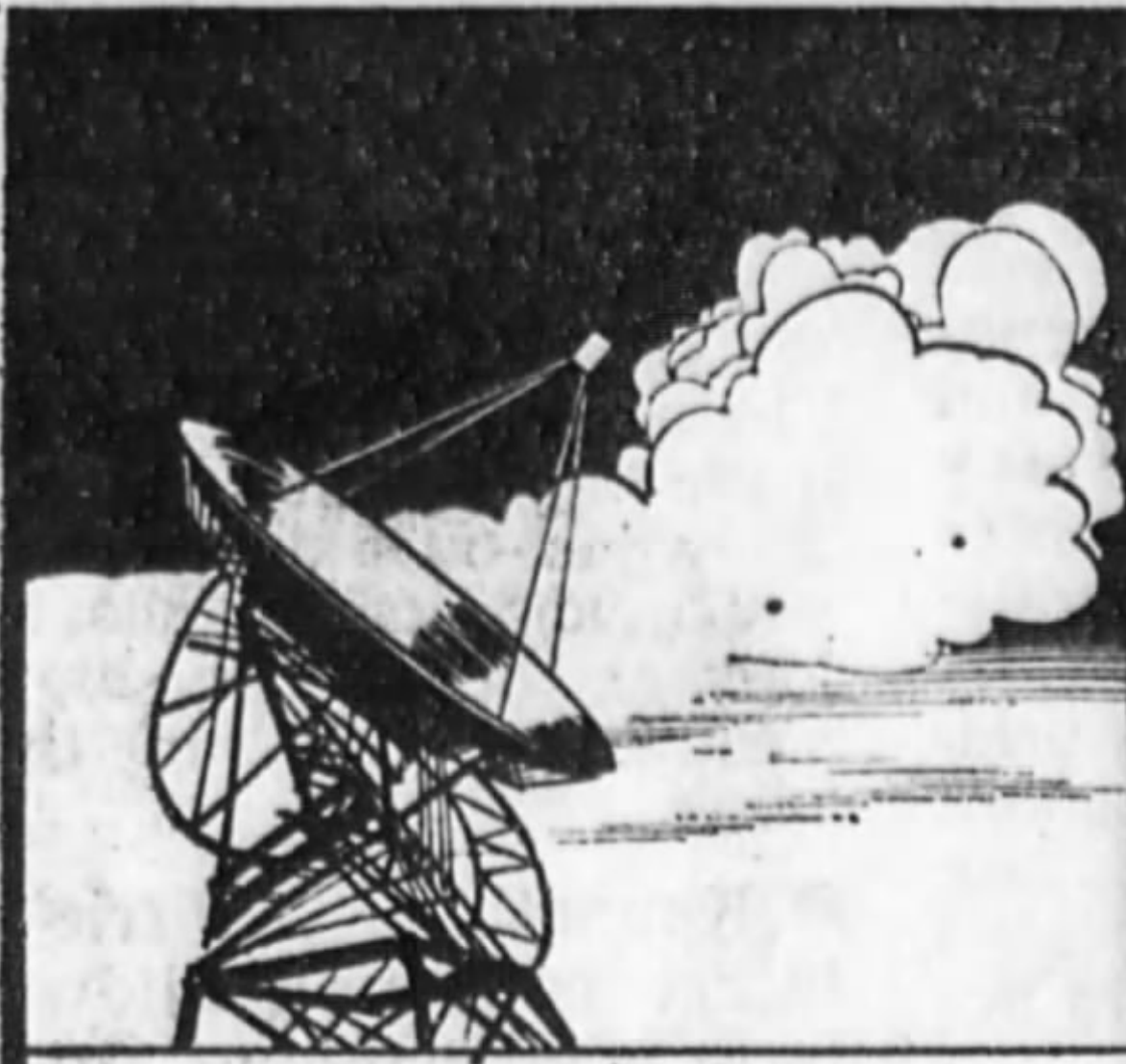
II. LABORATORY MEASUREMENTS

The energy levels of the lowest rotational states in the absence of hyperfine splitting are shown in Figure 1. To the right of the energy-level diagram is a schematic indicating the hyperfine splittings of the 2_{11} and 2_{12} levels. Both $\Delta F = 0$ and $\Delta F = \pm 1$ transitions are allowed, but since the ($\Delta F = \pm 1$, $\Delta J = 0$)-transitions are about 3 times less intense than the weakest ($\Delta F = 0$, $\Delta J = 0$)-transition, only the $\Delta F = 0$ components are expected to be observed.

The rest frequencies of the $F = 2 \rightarrow 2$, $F = 3 \rightarrow 3$, and $F = 1 \rightarrow 1$ absorption transitions were measured in the laboratory, using a standard high-resolution microwave spectrometer employing 5-kHz Stark modulation (Flygare *et al.* 1969). The full widths at half-intensity were ~ 80 kHz. The measured rest frequencies are: $F = 2 \rightarrow 2$ 4617.118 ± 0.02 , $F = 3 \rightarrow 3$ 4618.970 ± 0.02 , and $F = 1 \rightarrow 1$ 4619.988 ± 0.02 MHz. There is excellent agreement between the experimental relative intensities of the above lines and the theoretical intensities of 23:42:15. The parameter $3(B - C)$ may be obtained from the measured $F = 1 \rightarrow 1$ and $F = 2 \rightarrow 2$ components and the centrifugal distortion correction of -123 kHz (Kurland and Wilson 1957). Thus, $3(B - C) = 4618.676 \pm 0.02$ MHz, which was obtained independently of the quadrupole coupling constants. The parameter $B - C$ is then 1539.559 ± 0.02 MHz, which is useful in calculating the rigid-rotor frequencies of $K = 1$ doublets in $^{14}\text{NH}_2\text{CHO}$.

¹ The National Radio Astronomy Observatory is operated by Associated Universities, Inc., under contract with the National Science Foundation.

FRONTIERS OF SCIENCE



THE DISCOVERY, IN 1970, OF COMPLEX MOLECULES IN INTERSTELLAR SPACE STARTED A "GOLDRUSH" IN THE SKY.

BY APRIL, 1971, RADIOASTRONOMERS HAD FOUND MORE THAN A DOZEN, INCLUDING THE FOUR-ELEMENT, SIX-ATOM FORMAMIDE (HCONH_2).

FORMAMIDE

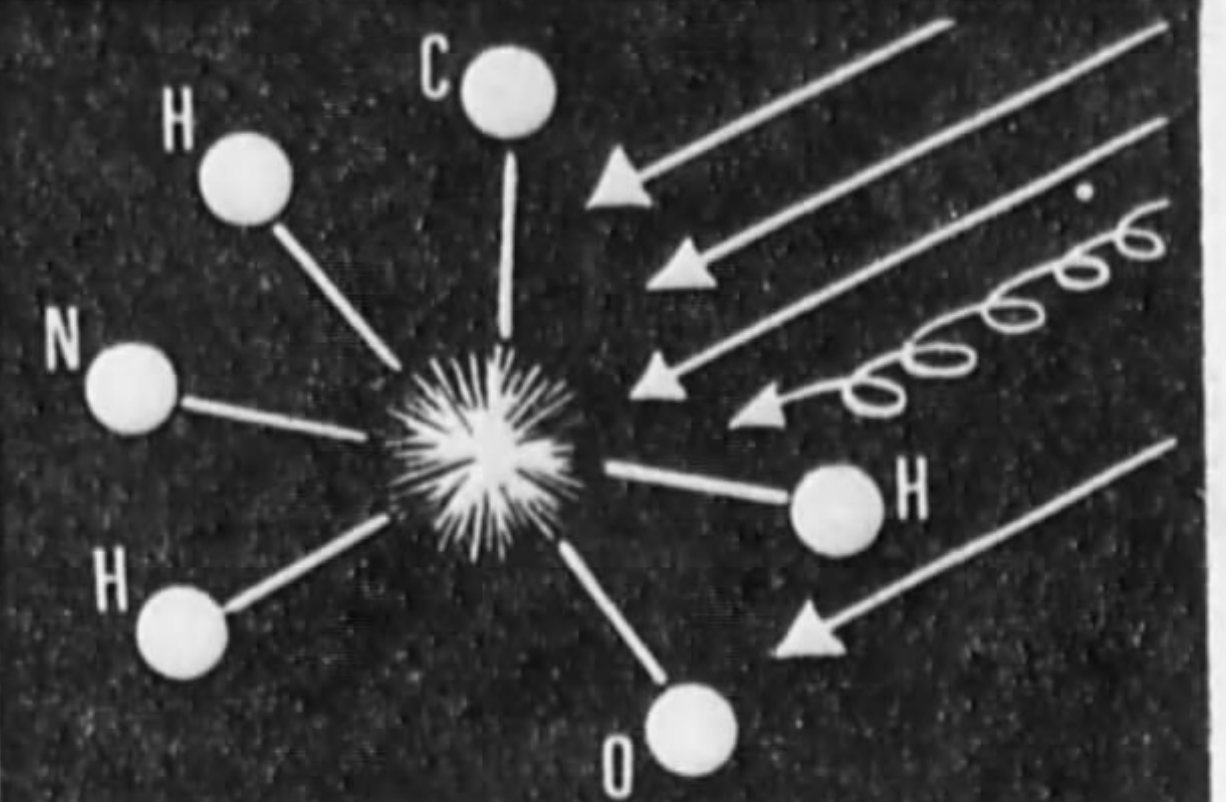
A "Frontiers of Science" illustration in Wednesday's "Herald" showing the components of a formamide molecule was not intended to be a formal molecular diagram.

Such a diagram would have shown a double bond between the carbon and oxygen atoms. The nitrogen, with two hydrogen atoms attached, would have been bonded to the carbon. The third hydrogen atom also would have been bonded to the carbon.

ALTHOUGH FORMAMIDE PLAYS NO ROLE IN ANY TERRESTRIAL LIFE FORM, IT IS THE NEAREST MOLECULE YET FOUND IN SPACE TO THE AMINOACIDS, THE BASIC BUILDING BLOCKS OF LIFE.



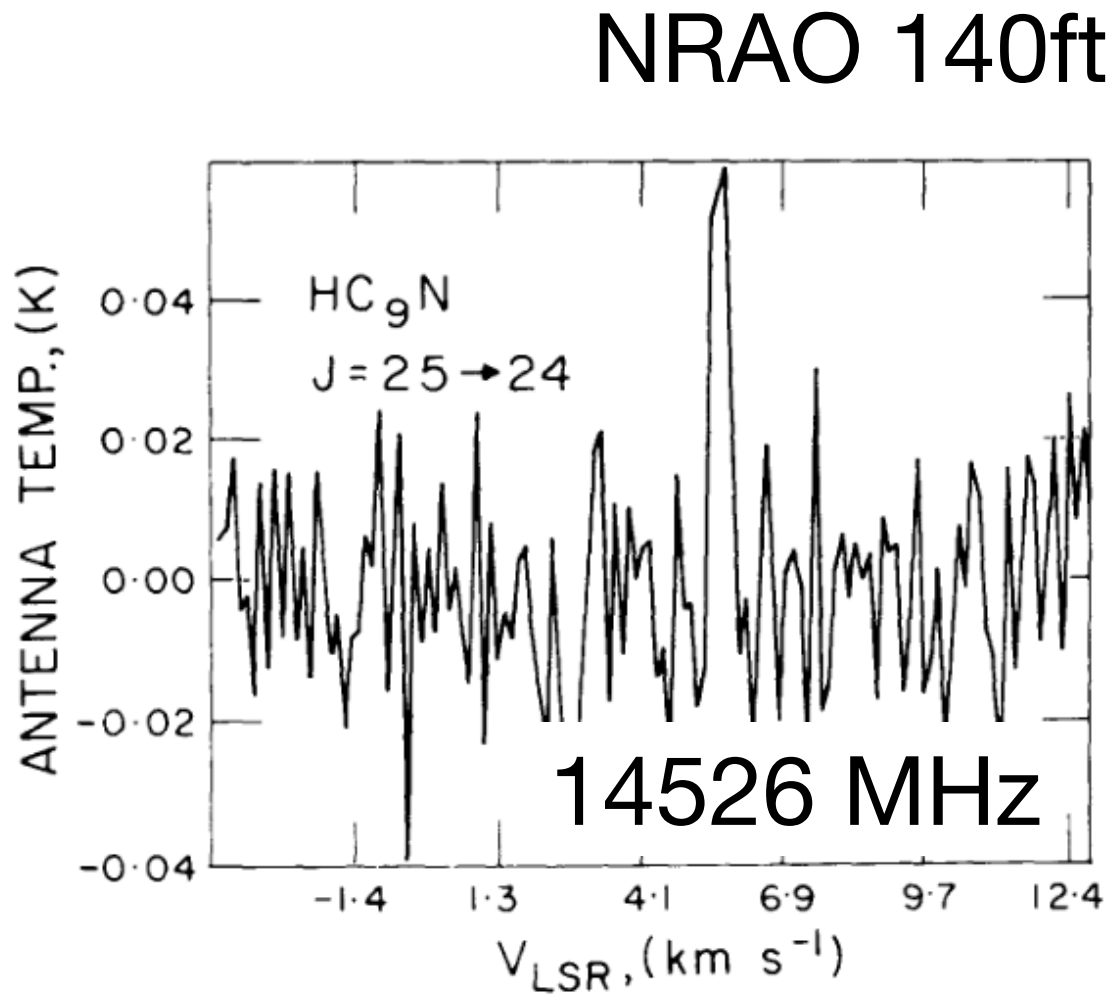
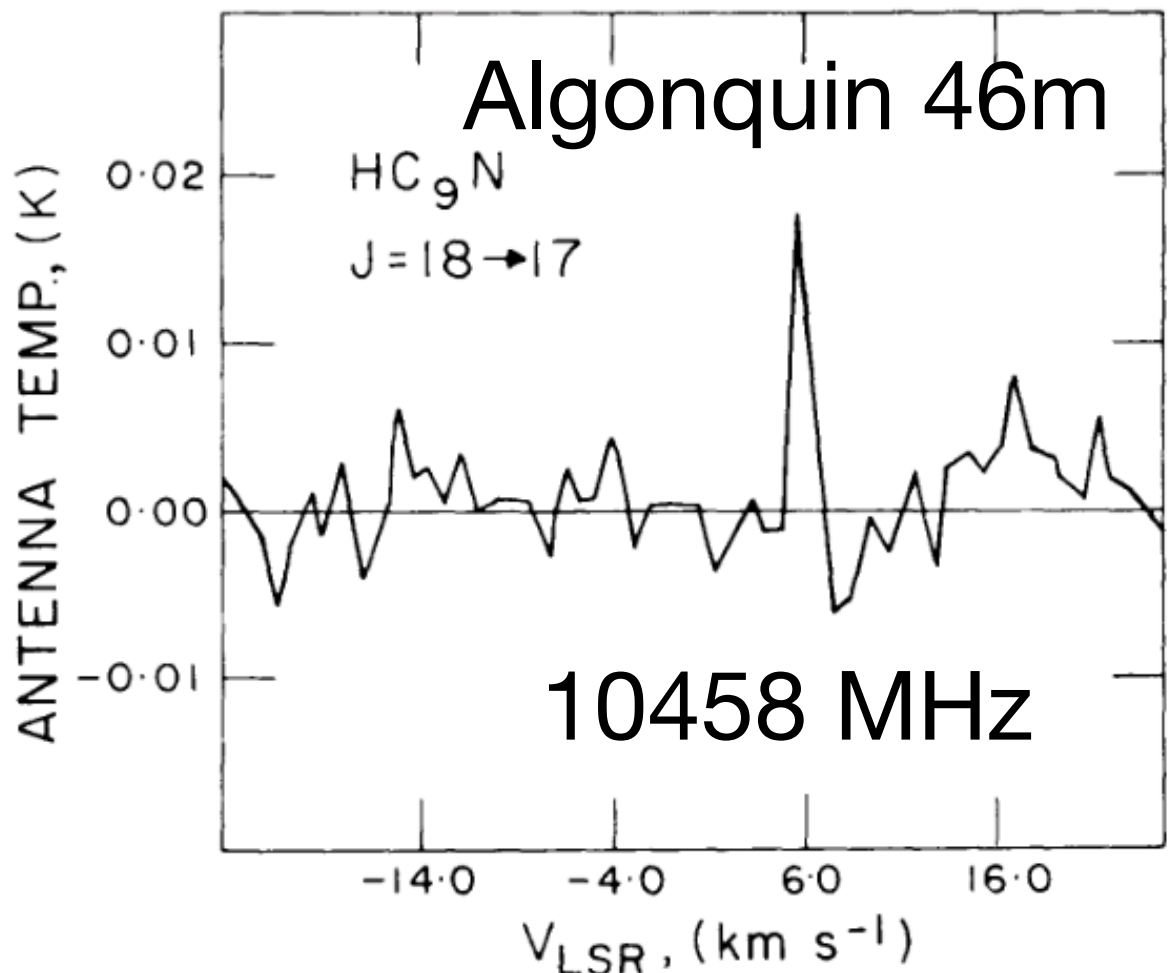
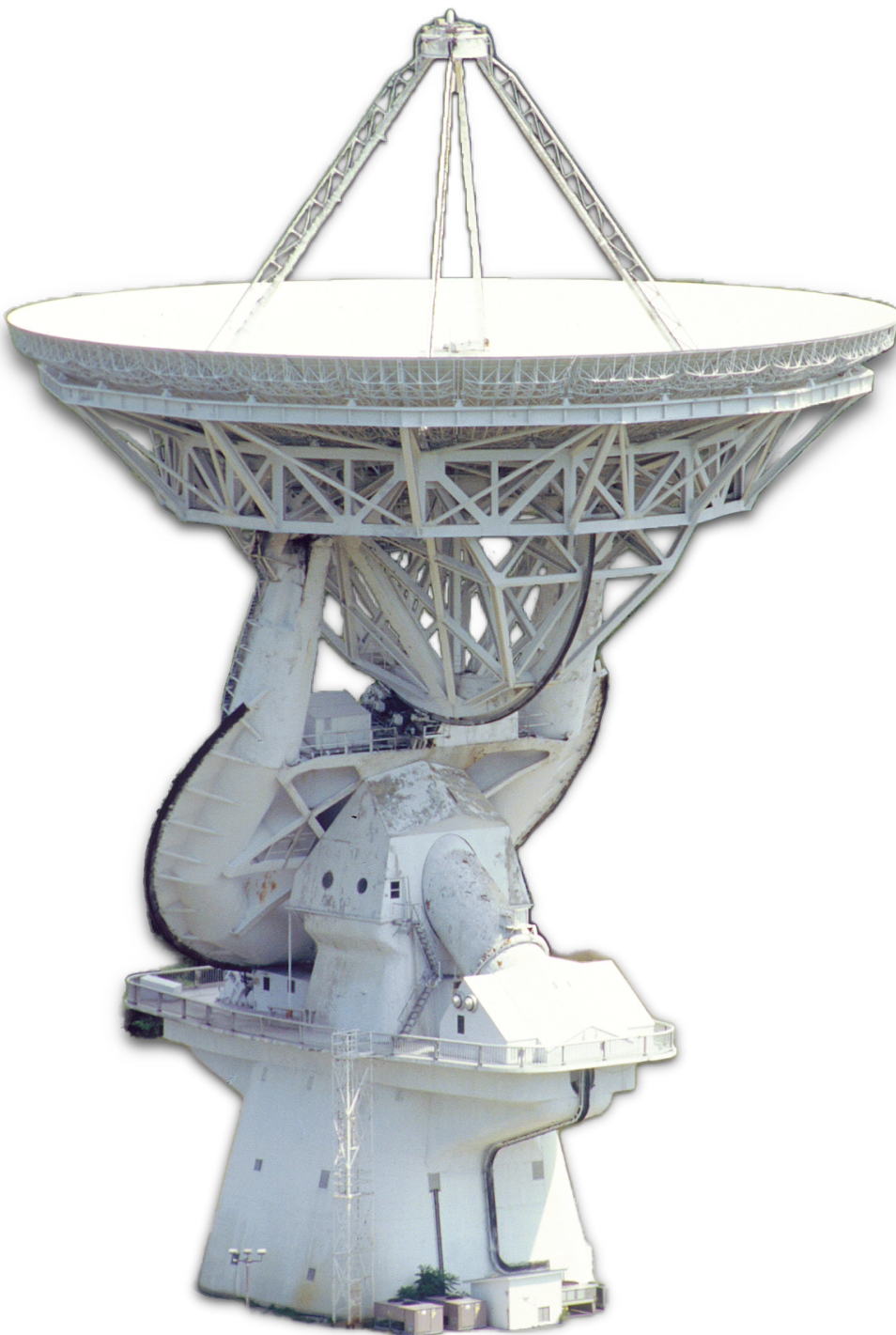
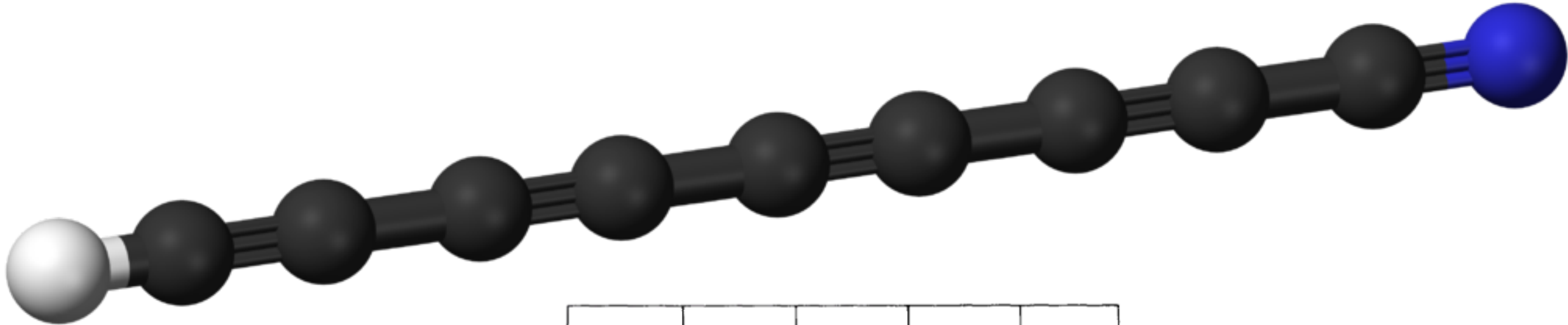
GOLDMINE IN THE SKY (3)



WHILE EXCITED OVER THIS DISCOVERY, ASTRONOMERS ARE STILL PUZZLED HOW SUCH MOLECULES CAN SURVIVE THE FIERCE, DISINTEGRATING BOMBARDMENT OF ULTRAVIOLET AND COSMIC RAYS IN SPACE. 515-3

OK, WHO LET THE WEIRDO IN?

Broten et al. 1978 *ApJ* 223, L105



THE ASTROPHYSICAL JOURNAL, 223:L105-L107, 1978 July 15
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THE DETECTION OF HC₉N IN INTERSTELLAR SPACE

N. W. BROTEN, T. OKA, L. W. AVERY, AND J. M. MACLEOD
Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa

AND

H. W. KROTO
School of Molecular Sciences, University of Sussex, Brighton
Received 1978 March; accepted 1978 May 10

ABSTRACT

With a molecular weight of 123 amu, and 11 atoms, HC₉N (cyano-octatetra-yne) is the heaviest and largest molecule yet detected in interstellar space. The $J = 18 \rightarrow 17$ and $J = 25 \rightarrow 24$ transitions have been observed in Heiles's Cloud 2 by using a molecular constant obtained by extrapolation from the lighter cyanopolyne molecules. The column density is estimated to be 3.2×10^{12} cm⁻², down by a factor of 4 from that of HC₃N in the same source.

Subject headings: interstellar: molecules — molecular processes

I. INTRODUCTION

The recent detections of the long linear molecules HC₃N and HC₇N in appreciable abundance in the dark dust cloud Heiles's Cloud 2 (MacLeod, Avery, and Broten 1978; Krotto *et al.* 1978) have prompted us to undertake a search for the next member of the series, cyano-octatetra-yne (H—C≡C—C≡C—C≡C—C≡C—C≡N). In contrast to the situation for HC₃N and HC₇N, where laboratory frequencies were available (Alexander, Krotto, and Walton 1976; Kirby, Krotto, and Walton 1978), HC₉N has not yet been made in the laboratory. In view of the very long integration times anticipated for the search, an accurate method of estimating the value of the molecular constant B_0 had to be developed. The procedure we used is described by Oka (1978) and involves extrapolation of the molecular constants which have been measured for the lighter molecules HCN, HC₃N, HC₅N, and HC₇N. Using our calculated B_0 for HC₉N, we predicted the frequency of the $J = 18 \rightarrow 17$ and $J = 25 \rightarrow 24$ transitions and subsequently detected both of these transitions in the molecular ridge in Heiles's Cloud 2. We believe this to be the first interstellar molecule detected on the basis of a calculated rotational constant with no previous spectroscopic study.

With a molecular weight of 123 amu, HC₉N now replaces HC₇N as the heaviest known interstellar molecule.

II. OBSERVATIONS AND DETERMINATION OF B_0

Our predicted value for B_0 was 290.523 MHz, yielding a predicted frequency for the $J = 18 \rightarrow 17$ transition of 10458.8 MHz. Observations at this frequency were carried out with the 46 m telescope of the Algonquin Radio Observatory¹ in 1977 June, August, October, and November. The system temperature was 120 K, the telescope beamwidth was 2'7, and the beam

efficiency was $\eta_B = 0.65$. A dual bank spectrometer was used in the total power mode, with frequency resolutions of 30 kHz and 10 kHz (0.86 km s⁻¹ and 0.29 km s⁻¹). The observing techniques used are summarized by Avery *et al.* (1976).

Observations were made at only one position in Heiles's Cloud 2, near the peak of the HC₃N ridge. This position was $\alpha(1950) = 04^h38^m38^s$, $\delta(1950) = 25^\circ35'00''$. The total on-source observing time was 25 hours, yielding a channel-to-channel rms noise of 3.1 mK (30 kHz filters) and 5.7 mK (10 kHz filters).

A spectral line of 20 mK antenna temperature was detected at a rest frequency of 10458.634 MHz, with an assumed radial velocity of 5.8 km s⁻¹ (based on HC₃N and HC₇N velocities at this position). The observed line is shown in Figure 1a, and its parameters are listed in Table 1. We identified this line with the $J = 18 \rightarrow 17$ transition of HC₉N. Using a centrifugal distortion constant $D_0 = 1.01$ Hz, estimated from $D_0(\text{HC}_3\text{N}) = D_0(\text{HC}_7\text{N}) \times [B_0(\text{HC}_3\text{N})/B_0(\text{HC}_7\text{N})]^2$, we obtained a revised estimate for B_0 :

$$B_0 = 290.5183 \pm 0.0002 \text{ MHz},$$

where the bulk of the uncertainty arises from an uncertainty of ± 0.25 km s⁻¹ in V_{LSR} .

Using the above value of B_0 , we calculated the expected laboratory frequency of the $J = 25 \rightarrow 24$ transition to be 14525.850 ± 0.012 MHz.

The 43 m radio telescope at the National Radio Astronomy Observatory,² Green Bank, West Virginia, was used to search for this transition in 1977 November. A dual channel parametric amplifier gave a system temperature of ~ 130 K. The beamwidth was $\sim 2'2$ and the beam efficiency ~ 0.65 . The 384-channel Mark II auto-correlation spectrometer was used in the parallel mode, with a total bandwidth of 1.25 MHz. This gave a

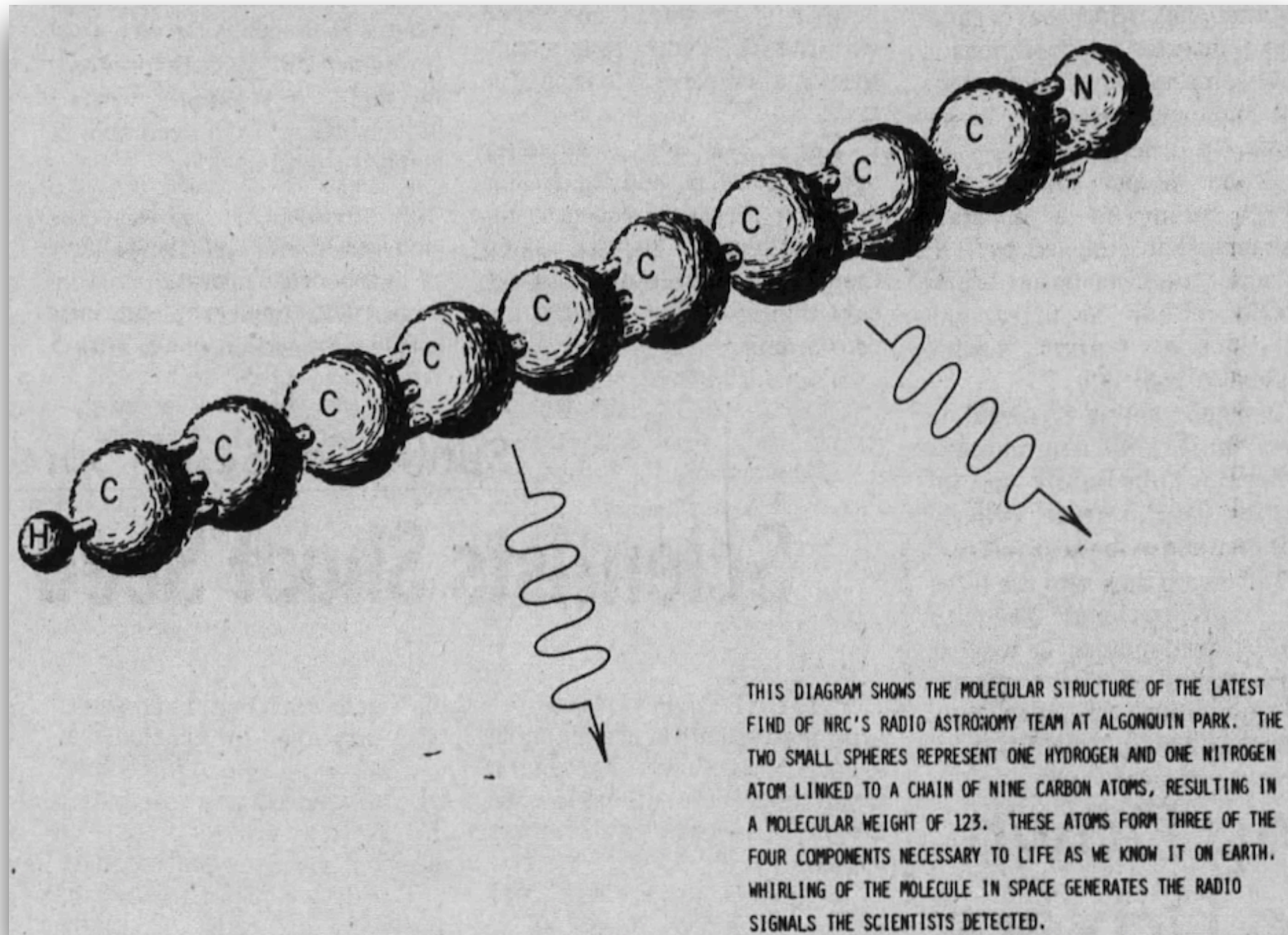
² Operated by Associated Universities, Inc., under contract with the National Science Foundation.
NRCC 16756

L105

The Whitehorse Star, Wednesday, January 4, 1978, Page 19

The Clue To Life?

"Heavy" Molecules Discovered In Space



More important than weight alone is the now-increased awareness that since molecules of such size exist in space, somewhere in the dark, mysterious dust clouds between the stars may be a real amino acid—the basic building block of life.

The three heavy molecules have all been detected within one such cloud located approximately 350 light years from Earth in the constellation Taurus.

Dr. Lorne Avery at the Algonquin Radio Observatory and NRC's Dr. John MacLeod at the National Radio Astronomy Observatory in Green Bank, West Virginia, made the recent observations on HC₉N.

Dr. Takeshi Oka provided the frequency clues in the search. This latest discovery is an extension of earlier laboratory work by Dr. Harry Kroto of the University of Sussex, England.

J. Am. Chem. Soc. **1987**, 109, 359–363

359

The Formation of Long Carbon Chain Molecules during Laser Vaporization of Graphite

J. R. Heath,[†] Q. Zhang, S. C. O'Brien,[†] R. F. Curl, H. W. Kroto,^{*†} and R. E. Smalley

Contribution from the Rice Quantum Institute and Department of Chemistry, Rice Houston, Texas 77251. Received July 16, 1986

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C₆₀ species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for

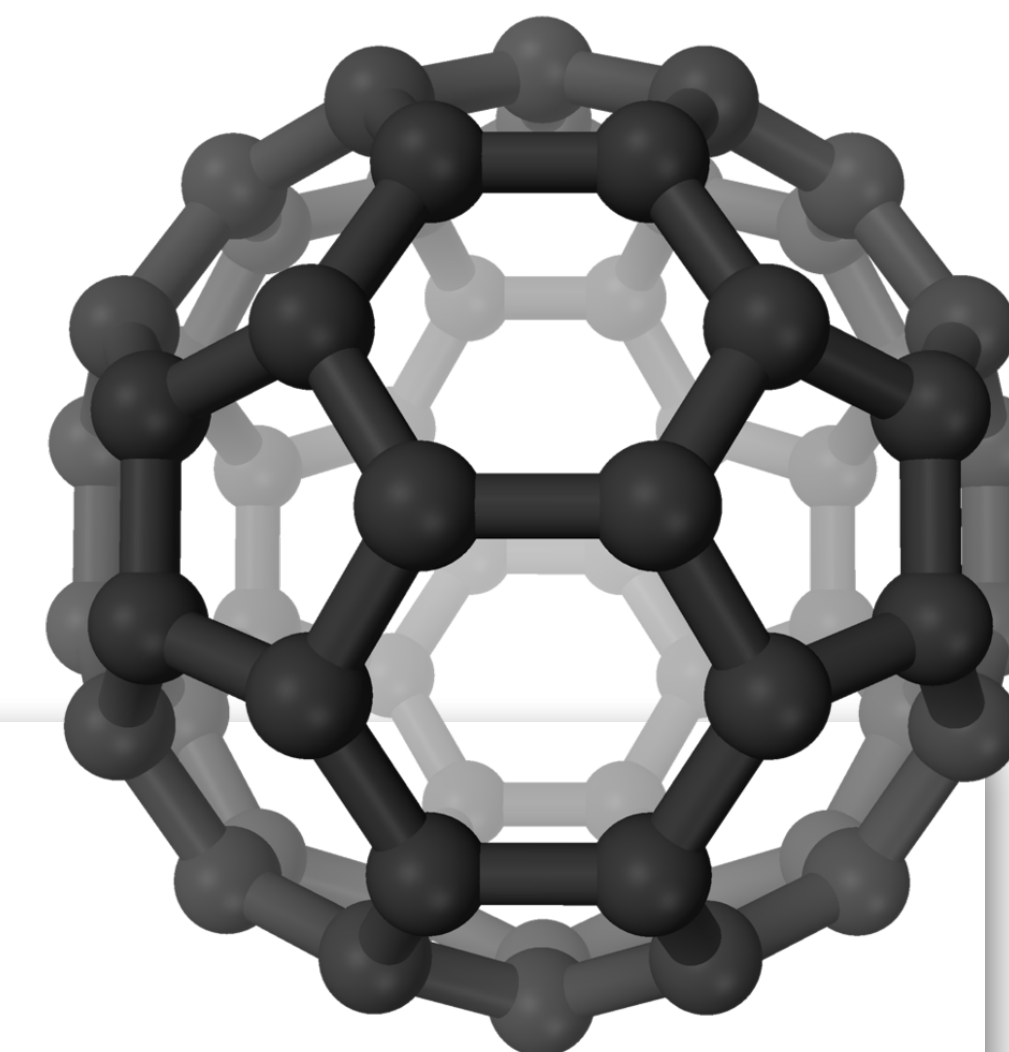
tion of interstellar molecules. Even more speculatively, C₆₀ or a derivative might be the carrier of the diffuse interstellar lines⁹.

C₆₀: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl
& R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells¹, graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-



B-6 Richmond Times-Dispatch, Thursday, October 30, 1986

ONE ★ *Scientist sees 'Bucky' as a stellar performer*

By Beverly Orndorff
Times-Dispatch science writer

Appropriately, the carbon molecule is called "buckminsterfullerene" because its 60 carbon atoms may form a hollow soccer-ball-like, geodesic structure akin to those designed by the late inventor R. Buckminster Fuller. The molecule's discoverer sometimes refers to it as "bucky."

It may be a highly inert, stable molecule and it may be abundant in space, where it could account for certain unexplainable features of interstellar dust clouds that scientists have known about for 30 or more years.

So far, however, the molecules have been observed only in supersonic vapor streams from a laboratory laser device, Dr. R.E. Smalley em-

phasized here this week, and those first observations were reported less than a year ago in the British science journal *Nature*. Dr. Smalley is a chemist at Rice University in Houston.

At this point, practically everything about the unusual carbon molecule is conjecture, Dr. Smalley stressed in an interview. "We don't have it in a bottle yet," he said.

On the other hand, he continued, in the year since the "bucky" molecule of carbon was reported, no counter conjectures about its shape and properties have been advanced by other chemists, and that itself is rather unusual, according to Dr. Smalley.

Dr. Smalley gave the opening address this week at an international symposium on the physics and chem-

istry of small clusters of atoms, which are small assemblages of a few to a few hundred atoms. The study of small atomic clusters has become a highly active area of research within the past few years, partly because such research may shed light on some fundamental questions about the properties of solids and liquids, and partly because such research may lead to new kinds of materials.

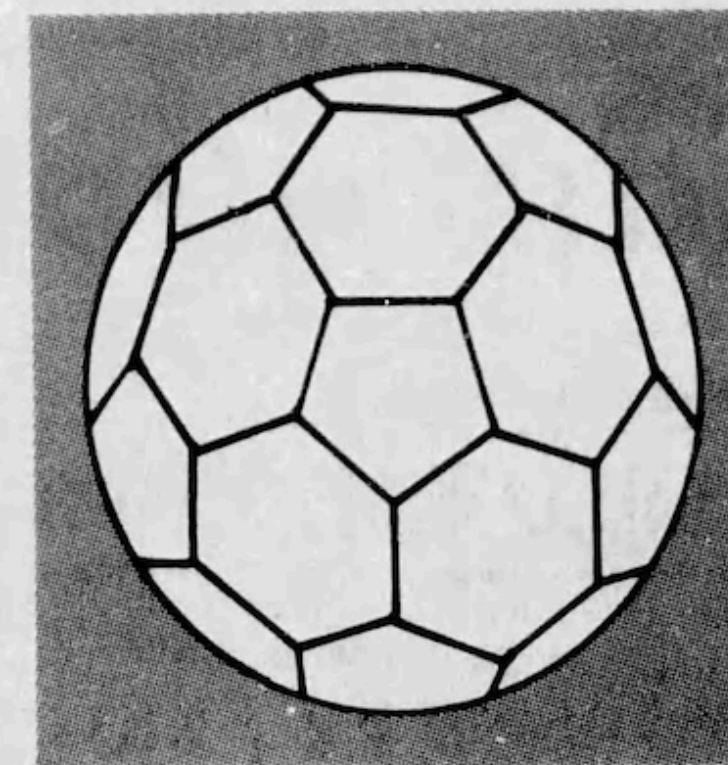
The conference, at the Sheraton Hotel through Saturday, was being attended by more than 100 scientists from about two dozen countries. Its sponsors include the National Aeronautics and Space Administration, the National Science Foundation, the U.S. Department of Energy, the Air Force Office of Scientific Research, the National

Academy of Sciences, and the Virginia Commonwealth University, where a group of physicists are among world leaders in small cluster research.

Dr. Purusottam Jena, the VCU physics professor who is the confer-

ence's president, has arisen within the past few years largely because scientists have learned only recently how to produce them under controlled conditions. At Rice University, the carbon clusters are being produced by a laser that vaporizes a graphite sample.

It's possible, he continued, that "bucky" molecules have been produced in great quantities in space, especially in carbon-rich stars. It's also possible, he suggested, that rich supplies of "bucky" molecules in interstellar dust clouds may account for peculiar light absorption patterns that astronomers have recognized in such clouds for several decades.



Staff graphic

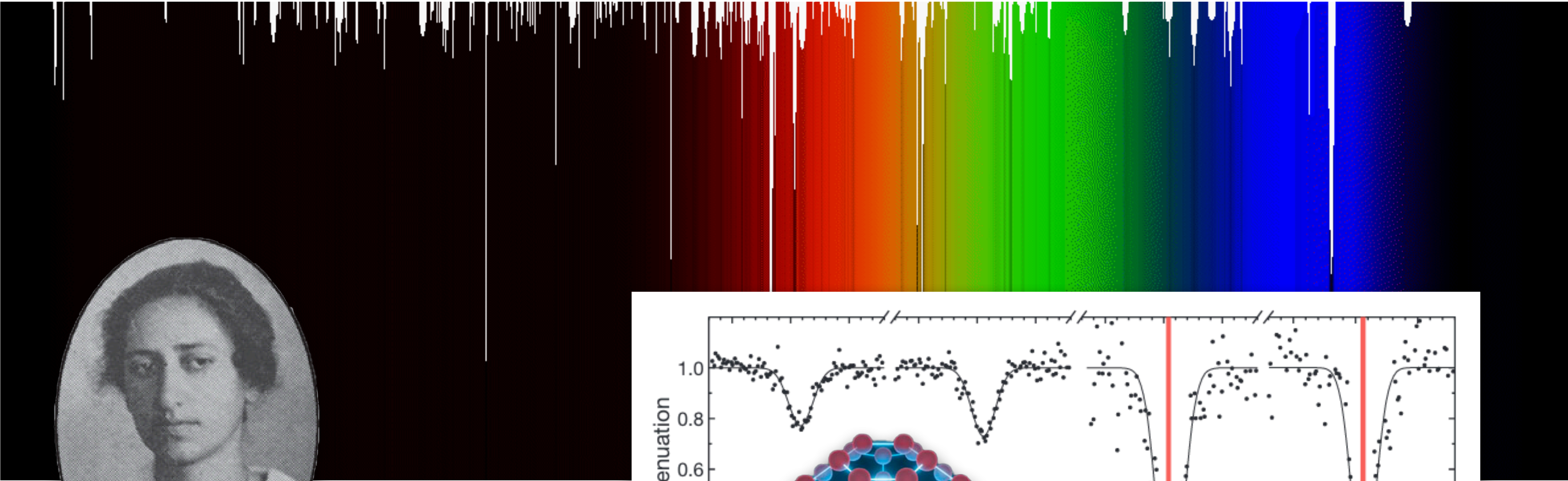
New carbon molecule

Has soccer-ball-like structure

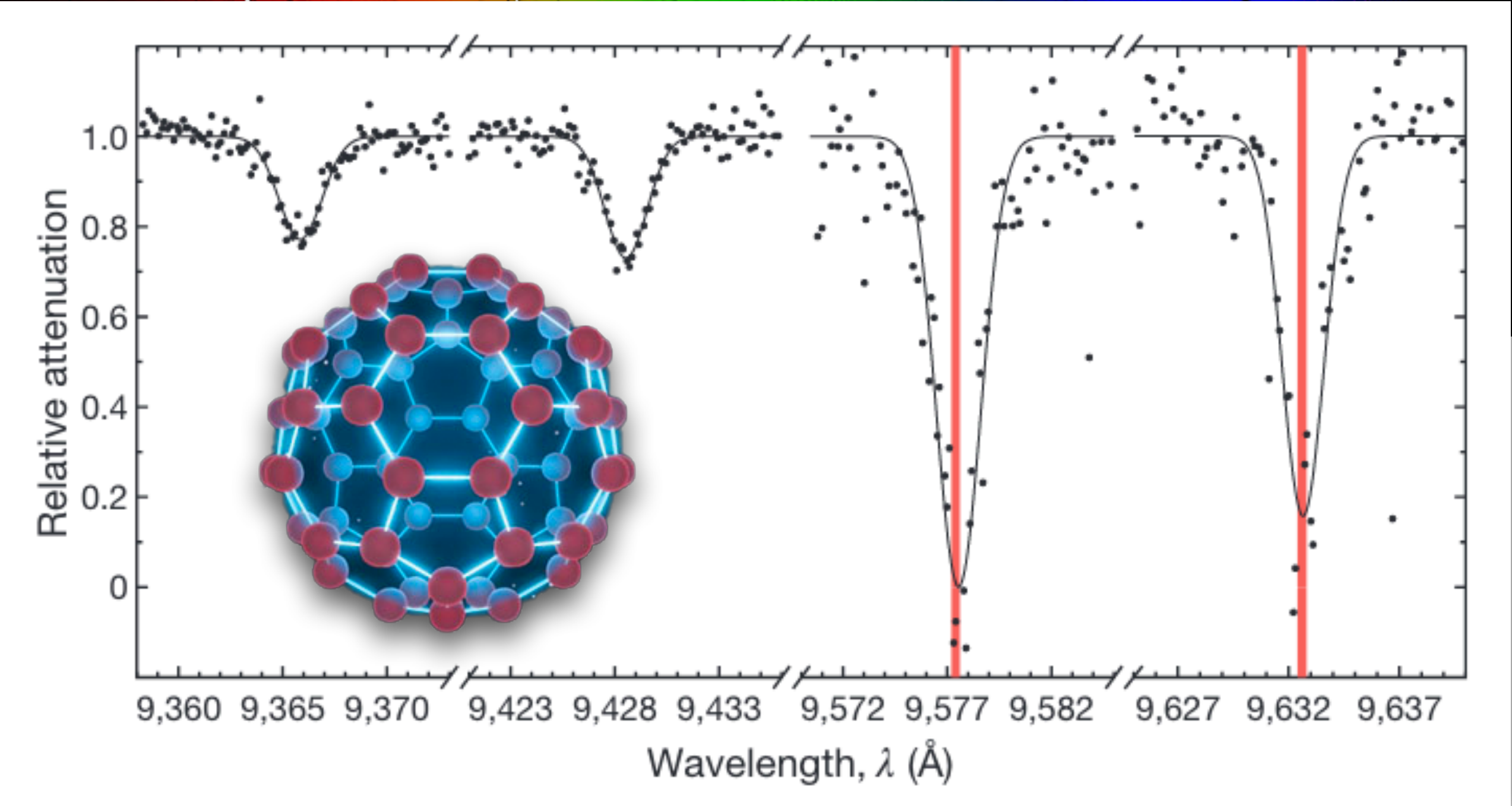
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A SPECTROSCOPIC MYSTERY

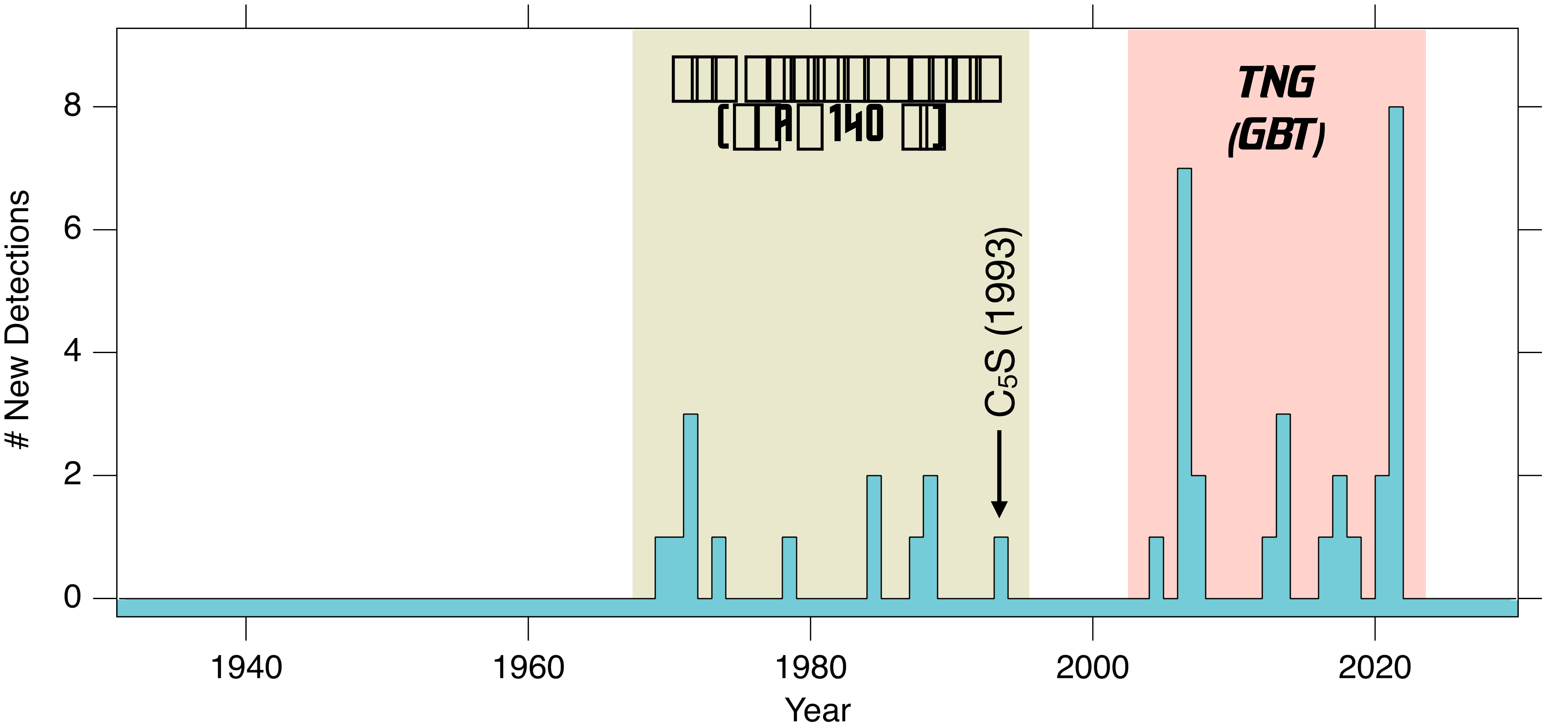
Campbell et al. 2015 *Nature* 523, 322



Mary Lea Heger



A SERIES OF FORTUNATE EVENTS



A SINGLE (UN)FORTUNATE EVENT

ONE ★ PRINTED IN COLOR

Richmond Times-Dispatch

Thursday, November 17, 1988

Richmond, Virginia 23219

138th Year, No. 322

★ 25 cents



1979 file photo

AIMED AT THE SKY — This huge radiotelescope at Green Bank, W.Va., was built in 1961-62 for less than \$1 million. It searched the skies for the "forests," not the "trees."

Telescope topples; probe begun

© New York Times Service

In a mysterious accident that may have set back astronomical research by years, the 300-foot radiotelescope at Green Bank, W.Va., collapsed Tuesday night in a tangle of twisted metal girders.

The instrument, operated by the government's National Radio Astronomy Observatory, was one of the most powerful radiotelescopes in the world.

Built in 1962, the dish antenna had been a part of major discoveries, including the finding that pulsating super-dense stars, pulsars, are created in the debris of exploding stars.

Dr. George A. Seielstad, assistant director of the observatory, said the collapse occurred without warning about 10 p.m. Tuesday while the telescope was in operation. No one was injured.

"There was no wind, the weather was fine, and operation was normal up to the moment of the collapse," Seielstad said.

"At this point we have no idea what may have caused the accident. Since the components are in such a twisted mess, it may take engineers a long

Continued on page 8, col. 1



Associated Press

ALL CAME TUMBLING DOWN — Wesley Sizemore, a worker at the National Radio Astronomy Observatory, takes pictures of the twisted remains of the huge dish.

By 1995, the \$75 million telescope should be ready to map the undiscovered universe by listening to the radio waves of outer space instead of peering into it.

TWO ★

Phoenixlike, telescope to rise from pile of metal

CHARLESTON, W.Va. (AP) — Scientist George Seielstad stood numb as he looked upon the wreckage of his "one of a kind" radiotelescope set in a valley of the rugged Allegheny Mountains.

The telescope, which is as long as a football field, had collapsed during a cool November night in 1988, the result of metal fatigue after 26 years of searching the heavens from a special "radio quiet zone" about 220 miles west of Washington.

"I was speechless and felt total disbelief. That telescope was one of a kind," said Seielstad, director of the National Radio Astronomy Observatory at Green Bank.

But the heap of twisted metal has given scientists a stellar opportunity. Designs are almost complete for a bigger, better radiotelescope to tower 35 stories above and 330 feet around isolated Deer Creek Valley.

By 1995, the \$75 million telescope should be ready to map the undiscovered universe by listening to the radio waves of outer space instead of peering into it.

nals from far beyond the Milky Way and helped unlock the secrets to pulsars and quasars.

The new telescope's blueprints show innovations never attempted in such a large scientific instrument, according to the National Science Foundation, which is funding the project.

The telescope will be designed to receive more and clearer signals with a solid surface of about 2,000 individually controlled panels to counteract the sagging effects of gravity as the telescope moves.

The panels will maintain an even surface, keeping radio waves in focus as they're transmitted to a computer for analysis.

The physical structure of the old dish blocked radio waves like, as one scientist explained, specks of dirt on a windshield that go unnoticed until the sun shines on them.

The telescope also will be fully movable, allowing it to point anywhere in the northern sky. The original telescope only moved up and down and relied on the Earth's rota-

Local radio and television stations can be picked up by the valley's 500 residents, but the stations' signals are carefully regulated. Many residents have cable television. An AM radio station operates in the quiet zone at a frequency that doesn't interfere with the observatory's studies.

The mountains of the Monongahela National Forest also shield the sensitive instruments from troublesome radio "noise" caused by anything from car engines to toasters.

"It makes this a unique spot on Earth and is the equivalent of a national park except we're protecting radio frequency space," Seielstad said. "It's one of West Virginia's jewels."

The original telescope's collapse sent tremors through the scientific community.

"It was like a friend had died," said Jay Lockman, an astronomer at the observatory's office in Charlottesville. "You don't know what you've had until it's gone."

Officials credit Sens. Jay Rocke-

A PATH FORWARD ... EVENTUALLY

The Atlanta Journal-Constitution

DIXIE LIVING

Sunday, March 26, 2000 M3

By Bob Dart
COX WASHINGTON BUREAU

Green Bank, W.Va.

The world's largest machine on dry land seems out of place in the rugged isolation of Deer Creek Valley. But this patch of scarce flatland, sparsely populated and surrounded by the Allegheny Mountains, is the ideal home for the gleaming white, two-acre radio telescope that looms above neighboring farms.

For four decades, this remote Pocahontas County hamlet has been "the center of American radio astronomy," explains Mark McKinnon, deputy site director of the National Radio Astronomy Observatory facility at Green Bank.

Shielded by the mountains from earthly interference such as radio stations, Green Bank's sensitive telescopes have explored distant galaxies by collecting radio waves since 1958. Now construction crews are nearing completion on a colossal new telescope packed with high-tech improvements. It could let astronomers examine uncharted reaches of the universe, and perhaps alter our conceptions of time and space and creation.

The Green Bank Telescope will be "the largest dynamic structure on Earth," says McKinnon. The only bigger machines are aircraft carriers and similar-size ocean vessels.

The project has taken more than a decade to complete. It began shortly after the collapse of Green Bank's 26-year-old radio telescope in late 1988. U.S. Sen. Robert Byrd (D-W.Va.), famous for looking after the home folks, quickly persuaded Congress to appropriate \$75 million to begin building a much bigger replacement.

After considerable complications and delay, the new GBT — weighing 16 million pounds and standing as tall as the Washington Monument — is to be completed this summer.

Having watched the telescope take shape like a monstrous roller coaster, its neighbors are curious about what it will find, and thankful for the dollars that its

THE GIANT TELESCOPE NEXT DOOR

A remote hamlet in the mountains of West Virginia is a portal to the edges of the universe

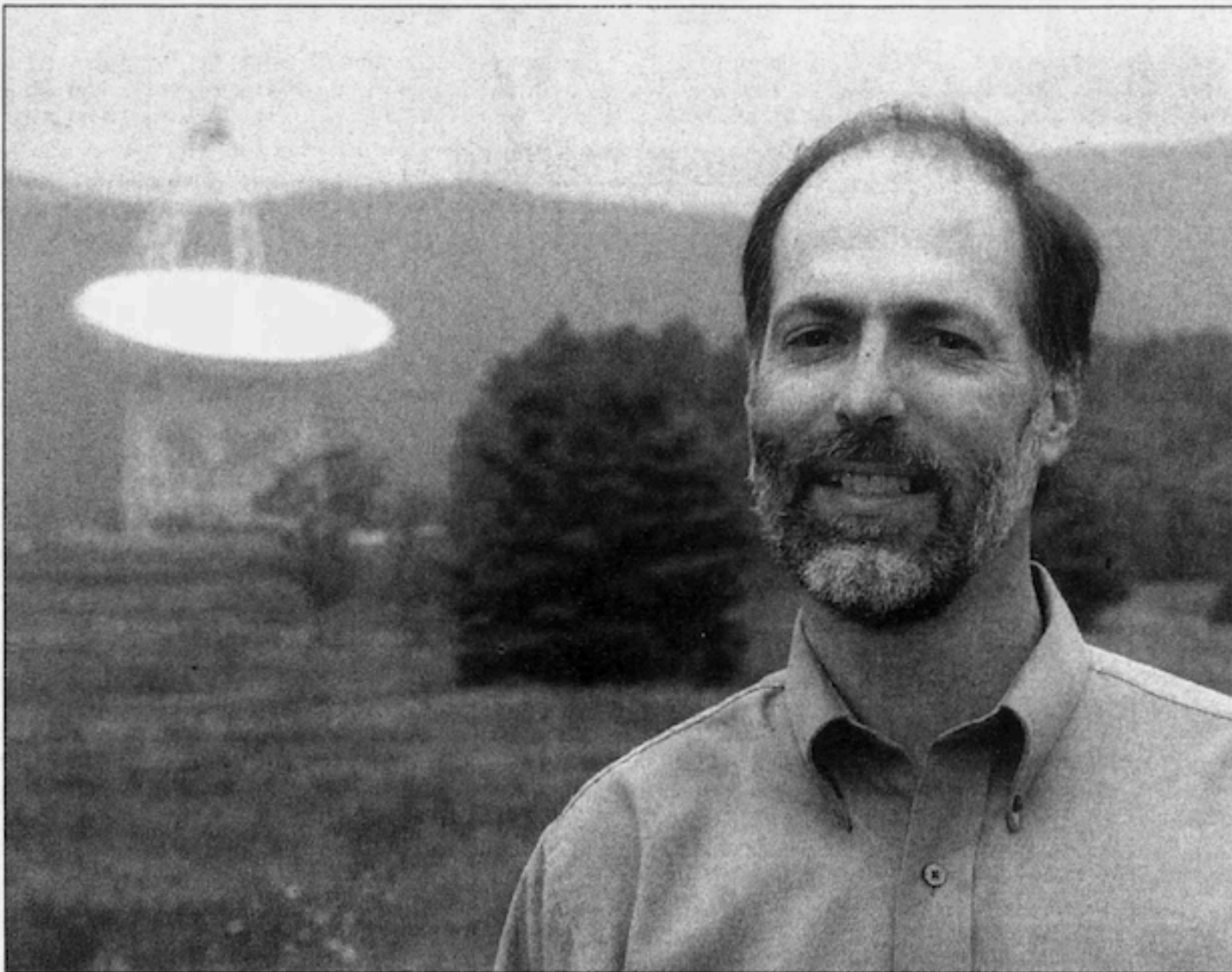
The Salt Lake Tribune TRAVEL Sunday, September 9, 2001

"It's pretty cool," said Katie Aguilera, who recently led a group of 12- and 13-year-olds looking for an adventure on a rainy day. "It feels like we are walking into Star Wars."



Sunday, August 27, 2000

Pensacola News Journal



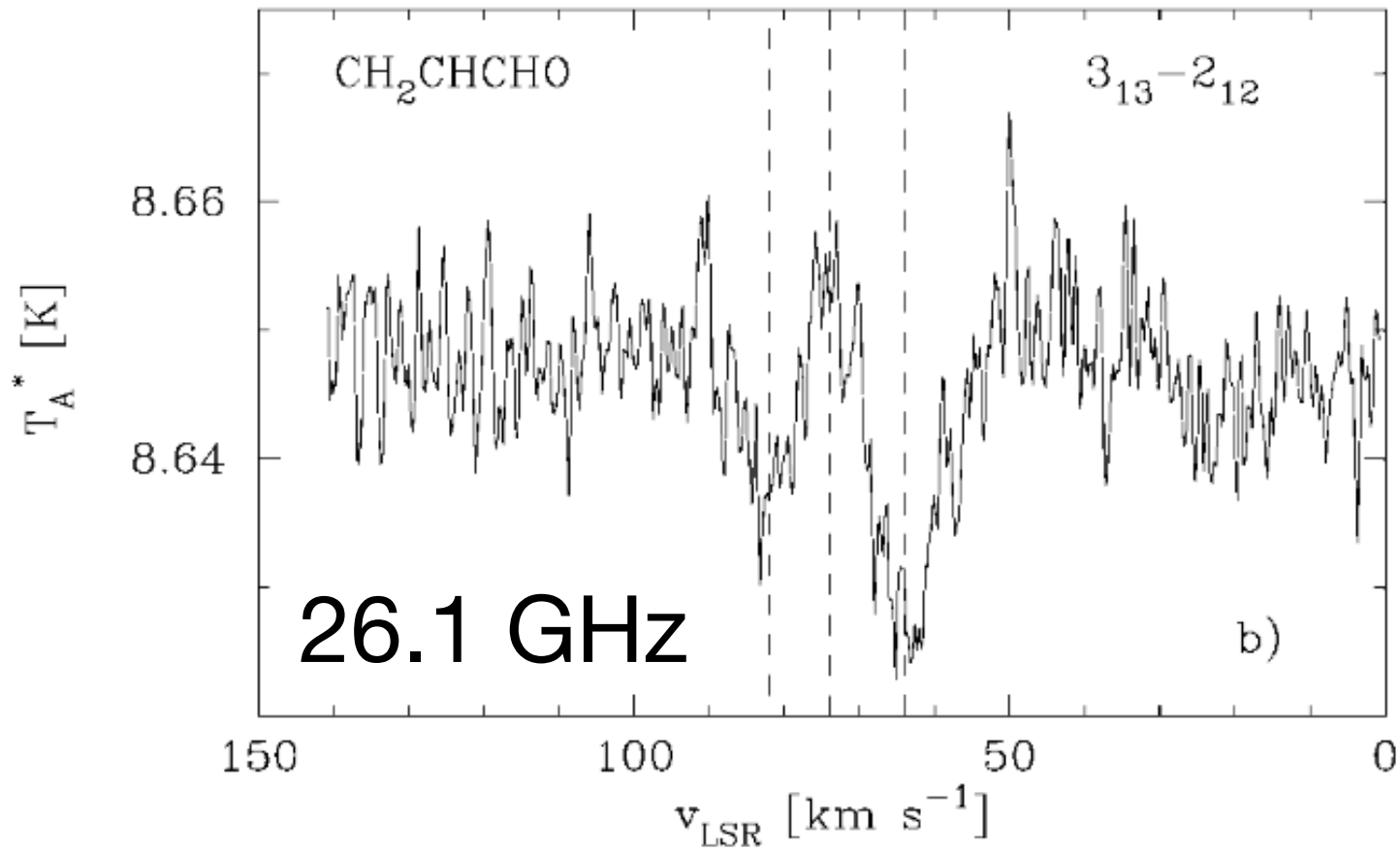
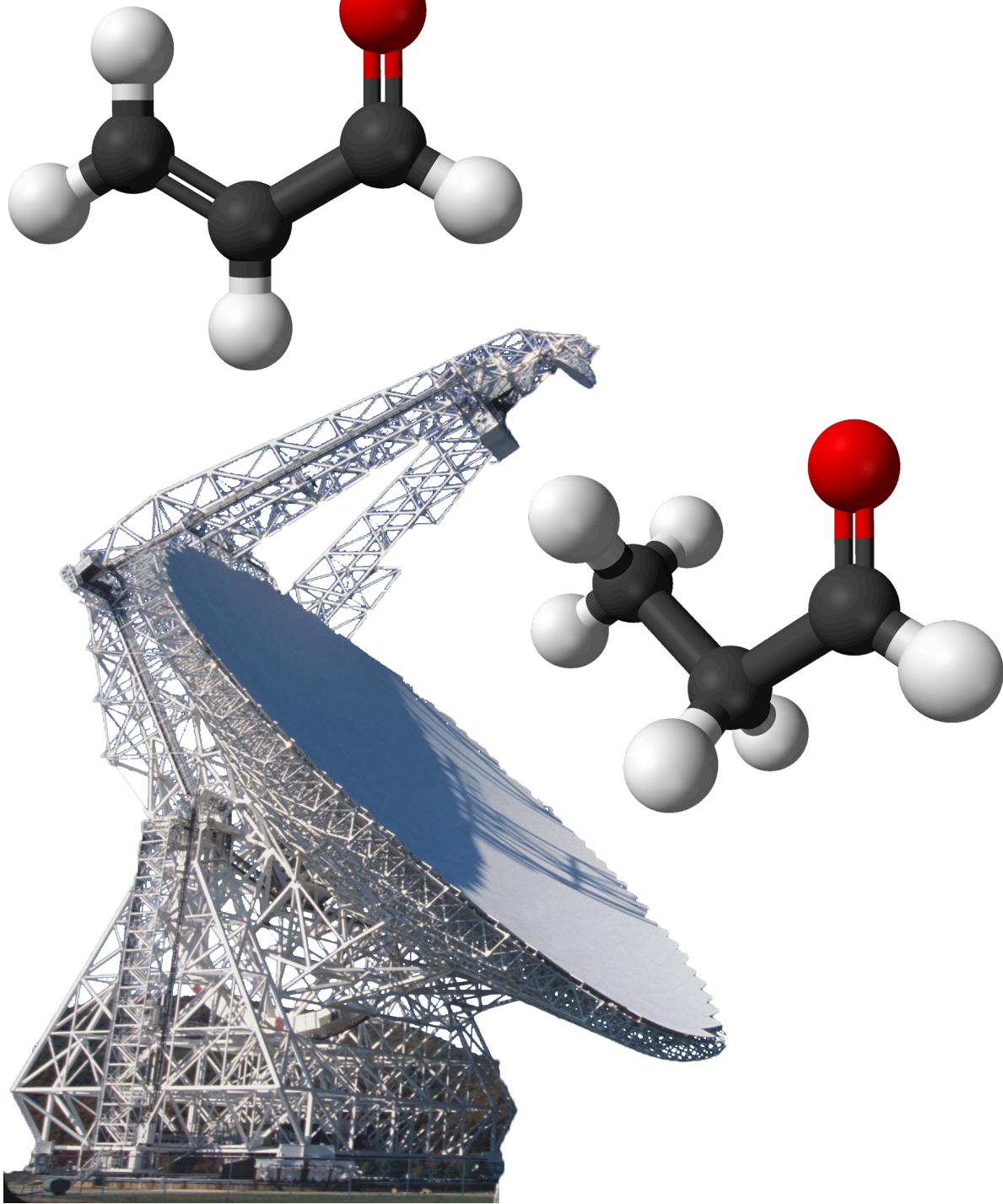
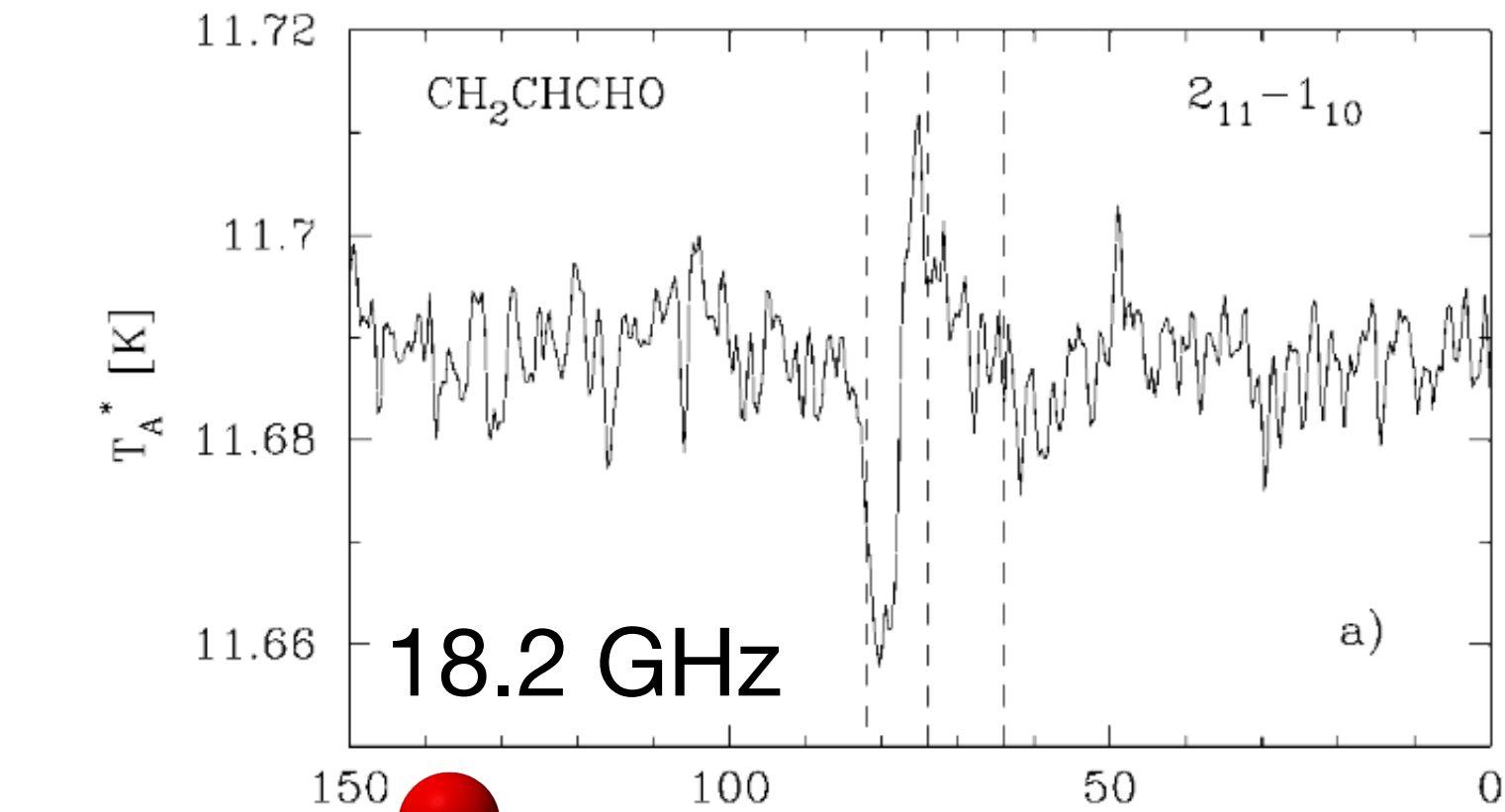
JON C. HANCOCK/Associated Press photo

Phillip R. Jewell, assistant director of the National Radio Astronomy Observatory, stands in front of the newest radio telescope in Green Bank, W. Va. It is the largest fully steerable radio telescope.



PLAYER 2 HAS ENTERED THE CHAT

Hollis et al. 2004 *ApJ* 610, L21



Star-Telegram | Monday, June 28, 2004

Monday

NBA rules prevent Mavericks officials from being able to talk specifically about speculation that they're working on a trade for Los Angeles Lakers center Shaquille O'Neal, but — and you can read into this what you wish — Mavericks owner Mark Cuban does not claim that O'Neal illegally steps across the foul line while shooting free throws.

Scientists announce the discovery of two new molecules in the center of the Milky Way: propenal and propanal. These are not considered to be as significant parts of the Milky Way as the previously discovered chocolate and caramel.

Chocolate



Caramel

THE ASTROPHYSICAL JOURNAL, 610:L21–L24, 2004 July 20
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GREEN BANK TELESCOPE DETECTION OF NEW INTERSTELLAR ALDEHYDES: PROPENAL AND PROPANAL

J. M. HOLLIS,¹ P. R. JEWELL,² F. J. LOVAS,³ A. REMIJAN,^{1,4} AND H. MØLLENDAL⁵

Received 2004 April 26; accepted 2004 June 9; published 2004 June 17

ABSTRACT

The new interstellar molecules propenal (CH_2CHCHO) and propanal ($\text{CH}_3\text{CH}_2\text{CHO}$) have been detected largely in absorption toward the star-forming region Sagittarius B2(N) by means of rotational transitions observed with the 100 m Green Bank Telescope (GBT) operating in the range from 18 GHz ($\lambda \sim 1.7$ cm) to 26 GHz ($\lambda \sim 1.2$ cm). The GBT was also used to observe the previously reported interstellar aldehyde propynal (HC_3CHO) in Sagittarius B2(N), which is a known source of large molecules presumably formed on interstellar grains. The presence of these three interstellar aldehydes toward Sagittarius B2(N) strongly suggests that simple hydrogen addition on interstellar grains accounts for successively larger molecular species: from propynal to propenal and from propenal to propanal. Energy sources within Sagittarius B2(N) likely permit the hydrogen addition reactions on grain surfaces to proceed. This work demonstrates that successive hydrogen addition is probably an important chemistry route in the formation of a number of complex interstellar molecules. We also searched for but did not detect the three-carbon sugar glyceraldehyde ($\text{CH}_2\text{OHCHOHCHO}$).

Subject headings: ISM: abundances — ISM: clouds — ISM: individual (Sagittarius B2(N-LMH)) — ISM: molecules — radio lines: ISM

1. INTRODUCTION

The large molecules found to date in interstellar clouds suggest a grain chemistry that favors aldehyde production. Consistent with this, we (Hollis et al. 2000) successfully detected interstellar glycolaldehyde (CH_2OHCHO) and suggested that it might result from the polymerization of two formaldehyde molecules (H_2CO) analogous to the early stage of the sugar synthesis (formose) reaction studied in the laboratory by investigators of prebiotic chemistry. Additionally, laboratory experiments have shown that subjecting interstellar ice analogs at ~ 16 K to ionizing radiation dosages that simulate interstellar cloud ages (Moore et al. 2001) results in solid-phase hydrogen addition reactions (Hudson & Moore 1999). The combination of the prevalence of interstellar aldehydes and the likelihood of subsequent hydrogen addition reactions with aldehydes prompted a successful search for interstellar ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) by Hollis et al. (2002). The detection of interstellar ethylene glycol, which differs in constituent atoms from glycolaldehyde by two hydrogen atoms, suggested that ethylene glycol is the product of two successive low-temperature hydrogen addition reactions with glycolaldehyde on grain surfaces or in grain ice mantles. As a consequence of these successes, we were motivated to search for the more complex sugar glyceraldehyde ($\text{CH}_2\text{OHCHOHCHO}$), which may result from the polymerization of three formaldehyde molecules. Additionally, we searched for simpler aldehydes, specifically propenal (CH_2CHCHO) and propanal ($\text{CH}_3\text{CH}_2\text{CHO}$), which could be the result of simple hydrogen addition reactions with the known interstellar aldehyde propynal (HC_3CHO ; Irvine et al. 1988; Turner 1991).

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² National Radio Astronomy Observatory, P.O. Box 2, Green Bank, WV 24944-0002.

³ Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

⁴ National Research Council Resident Research Associate.

⁵ Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway.

2. OBSERVATIONS AND RESULTS

Observations of propynal, propenal, and propanal and attempts to detect glyceraldehyde were made in 2004 February 25–April 17 with the NRAO⁶ 100 m Robert C. Byrd Green Bank Telescope (GBT). Table 1 lists the rotational transitions of the molecules sought. The transition quantum numbers, types, calculated rest frequencies, lower level energies (E_l), and line strengths (S) are listed in the first five columns. The GBT K-band receiver is divided into two frequency ranges with separate feed/amplifier sets covering 18–22.4 and 22–26.5 GHz. The GBT spectrometer was configured in its eight intermediate-frequency (IF), 200 MHz, three-level mode, which allows observing four 200 MHz frequency bands simultaneously in two polarizations through the use of offset oscillators in the IF. This mode affords 24.4 kHz channel separation. Antenna temperatures are on the T_A^* scale (Ulich & Haas 1976) with estimated 20% uncertainties. GBT half-power beamwidths can be approximated by $\theta_{\nu} = 720^\circ/\nu$ (GHz). Observations ranged between 18 and 26 GHz, corresponding to $\theta_{\nu} \sim 40^\circ$ and $\theta_{\nu} \sim 28^\circ$, respectively. The Sgr B2(N-LMH) J2000 pointing position employed was $\alpha = 17^{\text{h}}47^{\text{m}}19^{\text{s}}.8$, $\delta = -28^\circ22'17''$, and a local standard of rest (LSR) source velocity (v_{LSR}) of $+64$ km s^{-1} was assumed. Data were taken in the OFF-ON position-switching mode, with the OFF position 60' east in azimuth with respect to the ON-source position. A single scan consisted of 2 minutes in the OFF-source position followed by 2 minutes in the ON-source position. Automatically updated dynamic pointing and focusing corrections were employed based on real-time temperature measurements of the structure input to a thermal model of the GBT; zero points were adjusted typically every 2 hr or less using the calibrators 1626–298 and/or 1733–130. The two polarization outputs from the spectrometer were averaged in the final data reduction process to improve the signal-to-noise ratio.

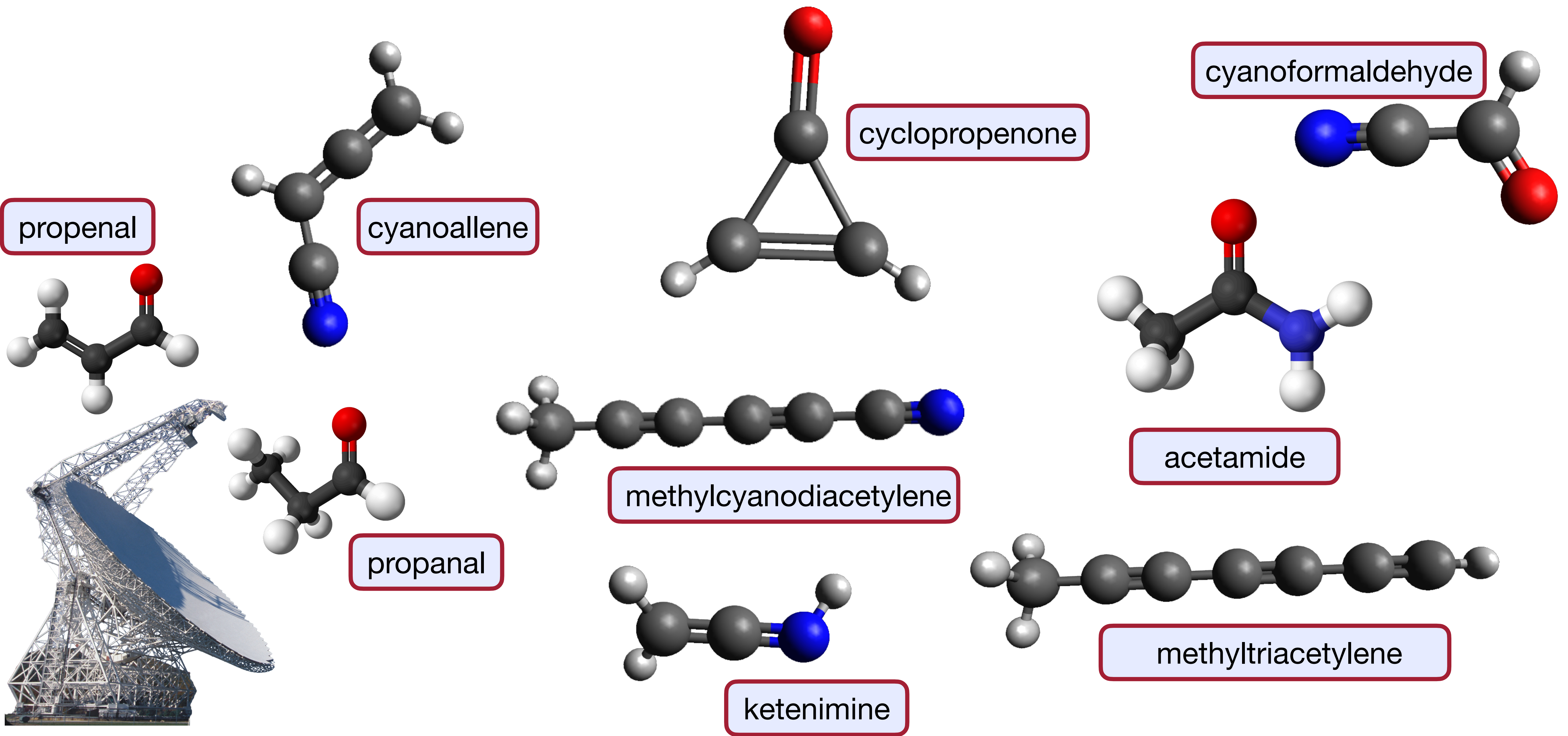
Observations of propynal, propenal, and propanal are summarized in Table 1, in which columns (6), (7), and (8) give measured intensities at LSR velocities of $+82$, $+74$, and $+64$ km s^{-1} .

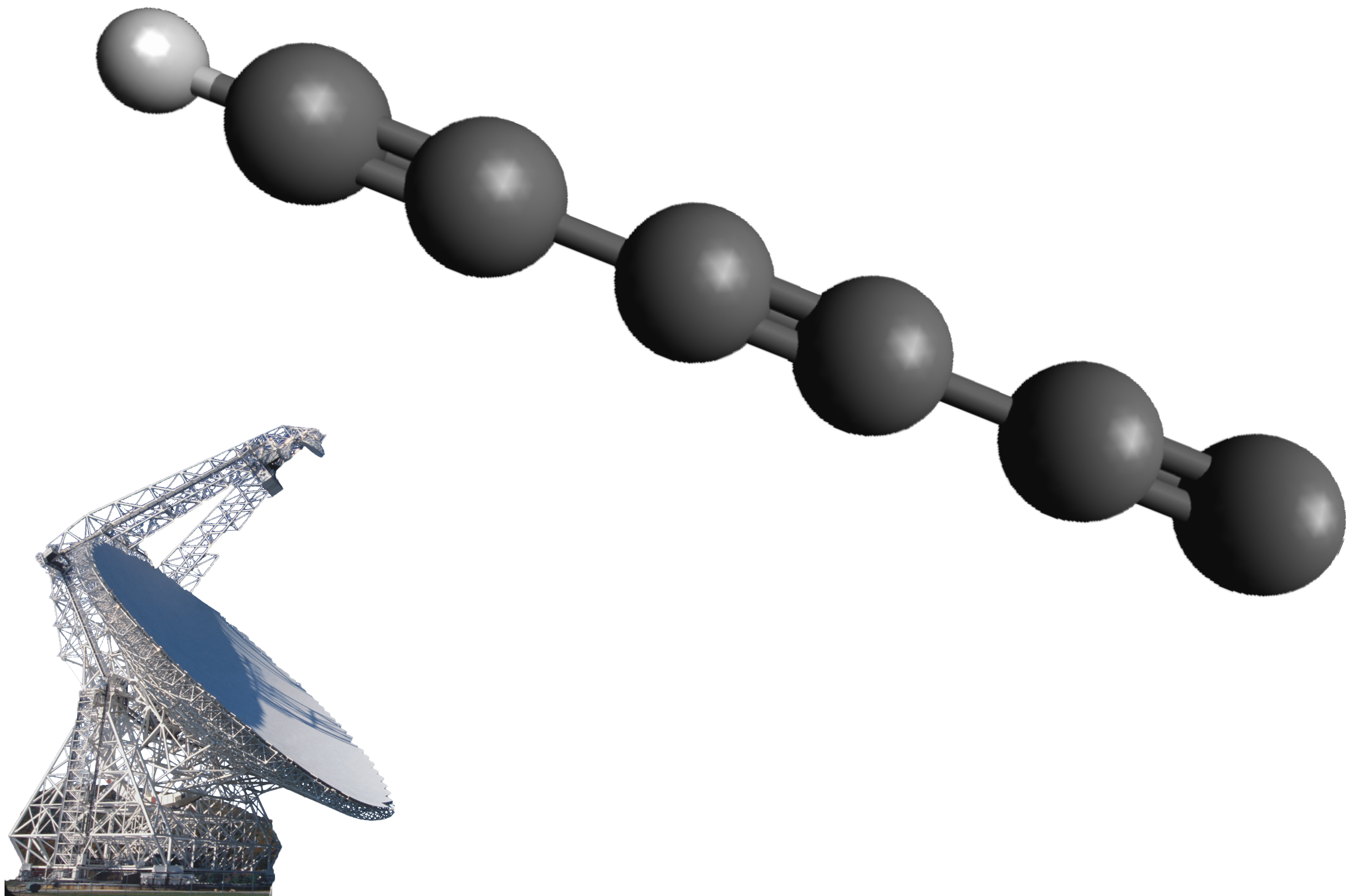
⁶ The National Radio Astronomy Observatory is a facility of the National Science Foundation, operated under cooperative agreement by Associated Universities, Inc.

L21

2006 - 2007: A MOLECULAR FIRESALE

Hollis et al. 2006 *ApJ* 642, 933
Hollis et al. 2006 *ApJ* 643, L25
Remijan et al. 2008 *ApJ* 675, L85
Lovas et al. 2006 *ApJ* 637, L37
Lovas et al. 2006 *ApJ* 645, L137
Remijan et al. 2006 *ApJ* 643, L37
Snyder et al. 2006 *ApJ* 647, 412
Hollis et al. 2004 *ApJ* 610, L21





THE ASTROPHYSICAL JOURNAL, 652: L141–L144, 2006 December 1
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LABORATORY AND ASTRONOMICAL IDENTIFICATION OF THE NEGATIVE MOLECULAR ION C₆H⁻

M. C. MCCARTHY,¹ C. A. GOTTLIEB,¹ H. GUPTA,^{1,2} AND P. THADDEUS¹

Received 2006 September 28; accepted 2006 October 17; published 2006 November 20

ABSTRACT

The negative molecular ion C₆H⁻ has been detected in the radio band in the laboratory and has been identified in the molecular envelope of IRC +10216 and in the dense molecular cloud TMC-1. The spectroscopic constants derived from laboratory measurements of 17 rotational lines between 8 and 187 GHz are identical to those derived from the astronomical data, establishing unambiguously that C₆H⁻ is the carrier of the series of lines with rotational constant 1377 MHz first observed by K. Kawaguchi et al. in IRC +10216. The column density of C₆H⁻ toward both sources is 1%–5% that of neutral C₆H. These surprisingly high abundances for a negative ion imply that if other molecular anions are similarly abundant with respect to their neutral counterparts, they may be detectable both in the laboratory at high resolution and in interstellar molecular clouds.

Subject headings: ISM: molecules — line: identification — molecular data — molecular processes — radio lines: ISM

The importance of negative ions (anions) in astronomy was demonstrated nearly 70 years ago by Wildt (1939a, 1939b), who showed that H⁻ is the major source of optical opacity in the solar atmosphere and therefore the material that one mainly sees when looking at the Sun and similar stars. It is remarkable that in the many years since, during which nearly 130 neutral molecules and 14 positive molecular ions have been found in astronomical sources, no molecular anion has been identified. More than 1000 molecular anions have now been studied in the laboratory at low resolution by photoelectron spectroscopy (Rienstra-Kiracofe et al. 2002), but almost none have been produced at sufficiently high density to study at the high spectral resolution required for an astronomical search (Hirota 1992; Owrutsky et al. 1987), and it is only for two, OH⁻ (Liu & Oka 1986; Liu et al. 1987; Matsushima et al. 2006) and SH⁻ (Civiš et al. 1998), that rotational spectra have been obtained. The purpose of this Letter is to report the laboratory detection in the radio band of the large carbon chain anion C₆H⁻, the measurement of its rotational spectrum to high accuracy, and its identification in two well-known astronomical sources: the molecular shell of the evolved carbon star IRC +10216 and the rich molecular cloud TMC-1 in the Taurus complex of dark nebulae. In IRC +10216, our identification solves the puzzle of the unidentified harmonic sequence of lines discovered over 11 years ago by Kawaguchi et al. (1995) and designated B1377 because it is apparently from a closed-shell linear molecule with a rotational constant *B* of 1377 MHz.

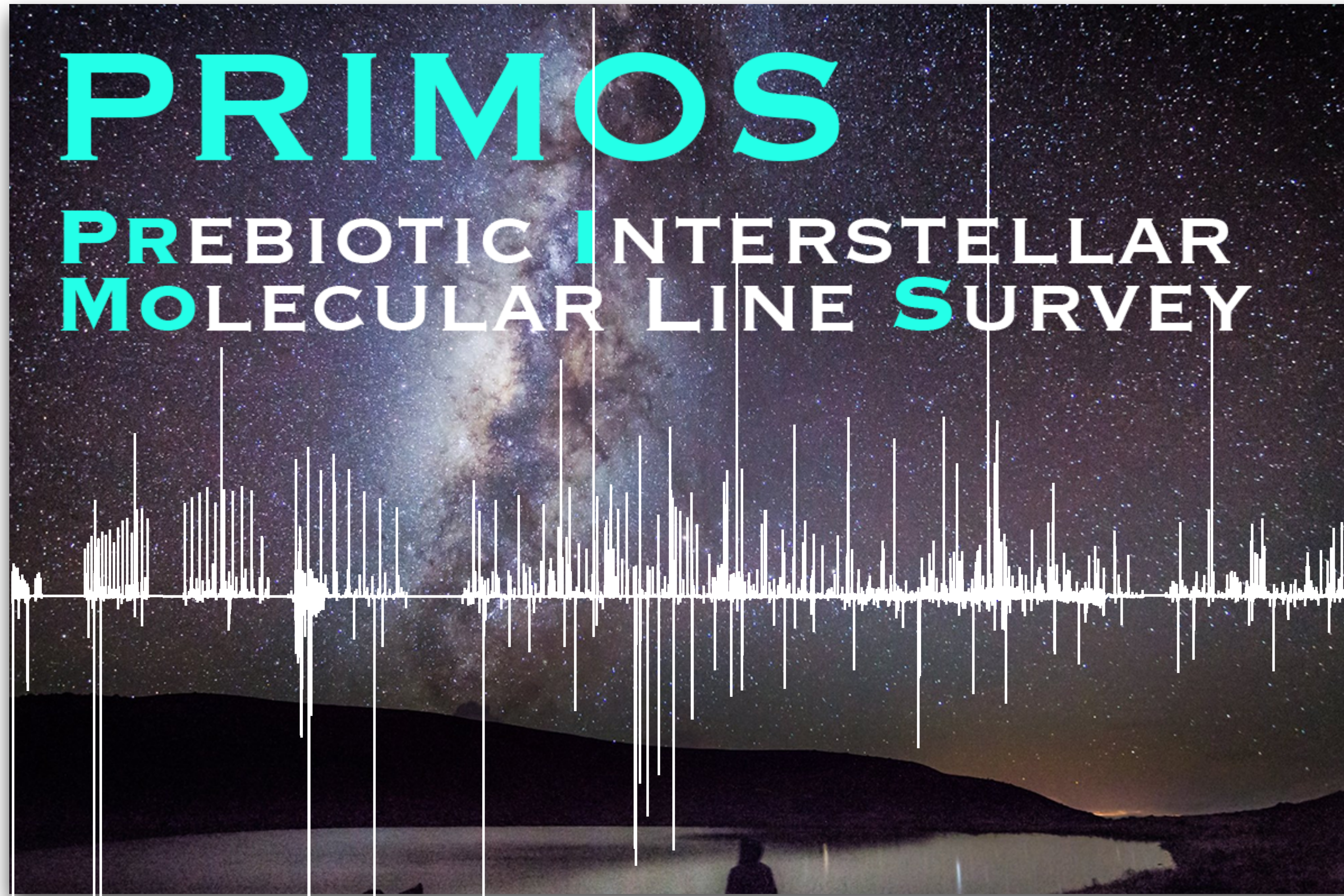
The rotational constant of the C₆H radical, one of the most abundant molecules in IRC +10216, is 1391 MHz (Pearson et al. 1988), only 1% larger than that of B1377, but this open-shell molecule with fine and hyperfine structure and lambda doubling is clearly not the carrier of B1377. Attachment of an electron to form the anion C₆H⁻, however, suppresses this structure and yields the required closed-shell ground state (Fehér & Maier 1994). Aoki (2000) has shown from a theoretical quantum calculation that the rotational constant of this anion is also within 1% of that observed—as might be expected because

electron attachment is a small perturbation on the geometrical structure of the molecule, generally resulting in a slight decrease in the rotational constant.

In the laboratory, we have now observed rotational lines of C₆H⁻ in both the centimeter-wave and millimeter-wave bands at frequencies in precise agreement with those measured in space. Those in the millimeter-wave band were observed first in absorption with a free-space spectrometer (Gottlieb et al. 2003) used previously to detect seven carbon-chain radicals, C₃H through C₆H, under conditions similar to those that produce strong lines of C₆H: a DC discharge through a flowing mixture of argon (15%) and acetylene (85%), a total pressure of ≤10 mtorr when the cell walls were cooled to 150 K, but with a somewhat lower discharge current (~150 mA) than that which produces the most intense lines of C₆H (~400 mA). Under these conditions, lines of C₆H⁻ are about 20 times less intense than those of C₆H, but these were still observed with a signal-to-noise ratio of 10 or more in 1 hr of integration, allowing line frequencies to be measured to about 40 kHz or better. The C₆H⁻ line frequencies are unaffected by ion drift because the millimeter-wave radiation makes two passes in opposite directions through the discharge cell. The concentration of C₆H⁻ in our discharge (7 × 10⁵ cm⁻³), corresponding to a mole fraction of about 10⁻⁹, is about 200 times less than that of C₆H.

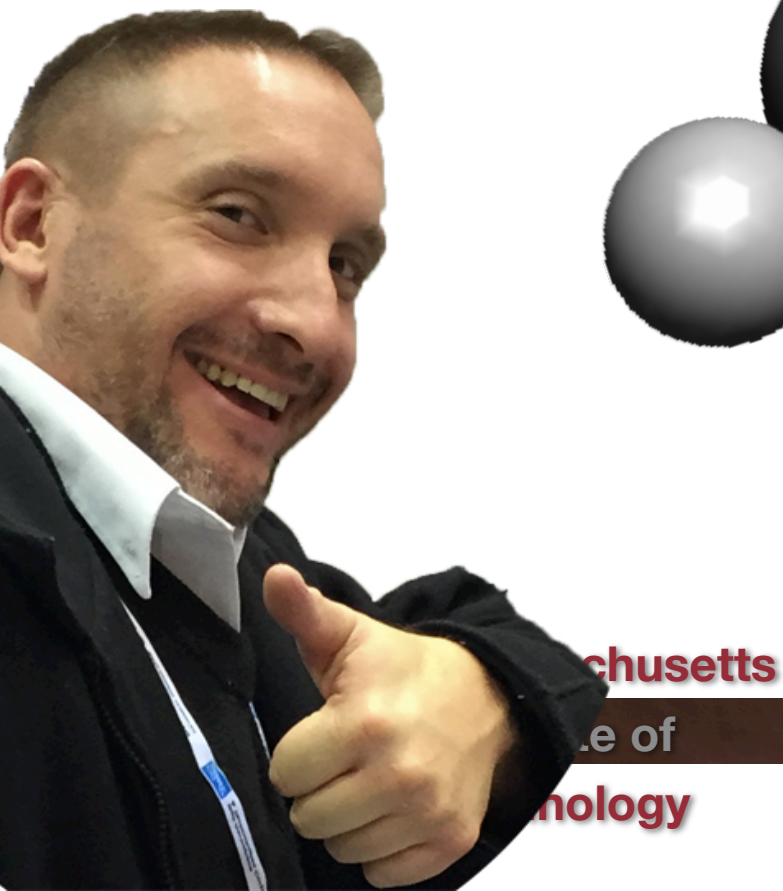
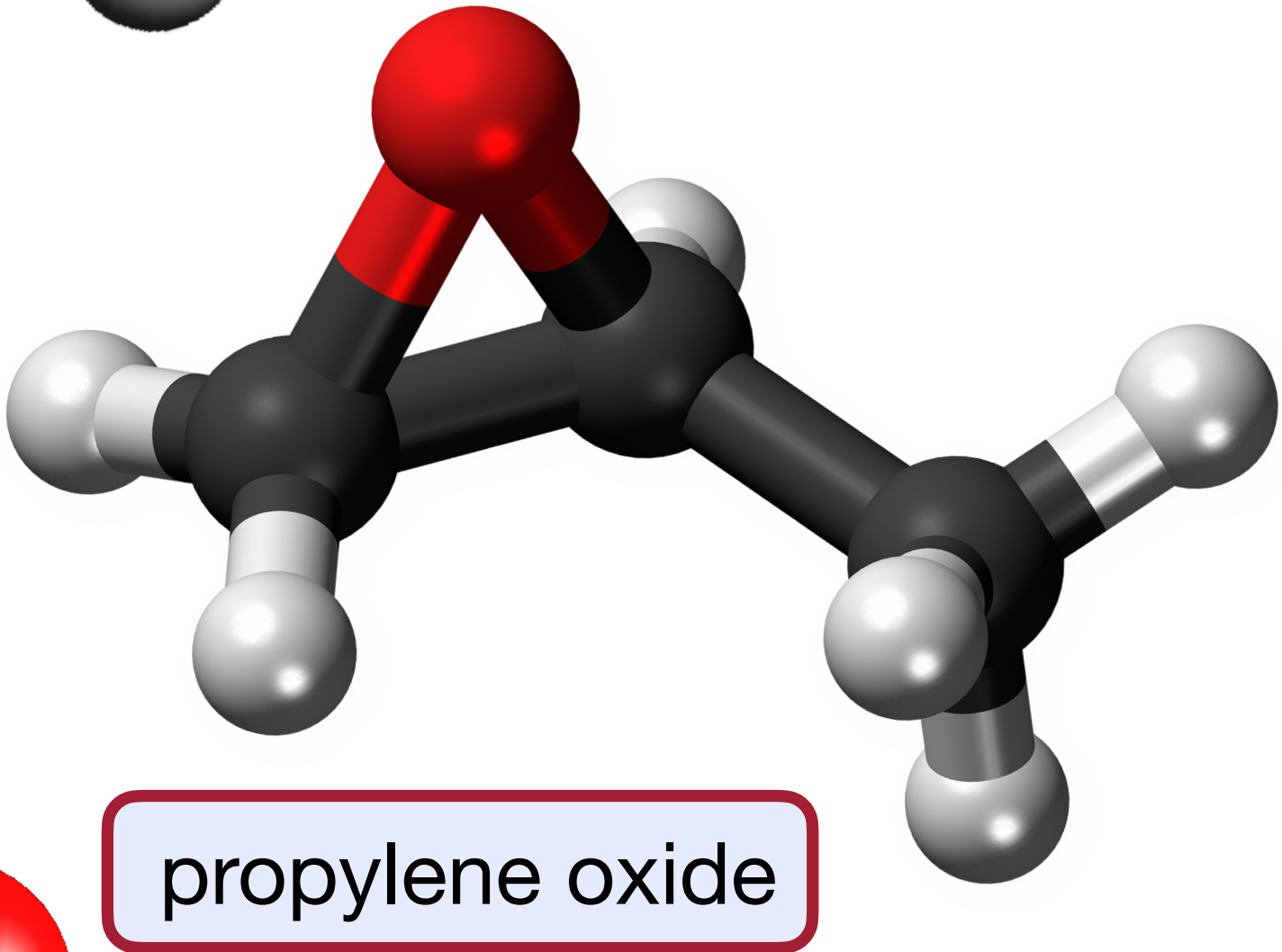
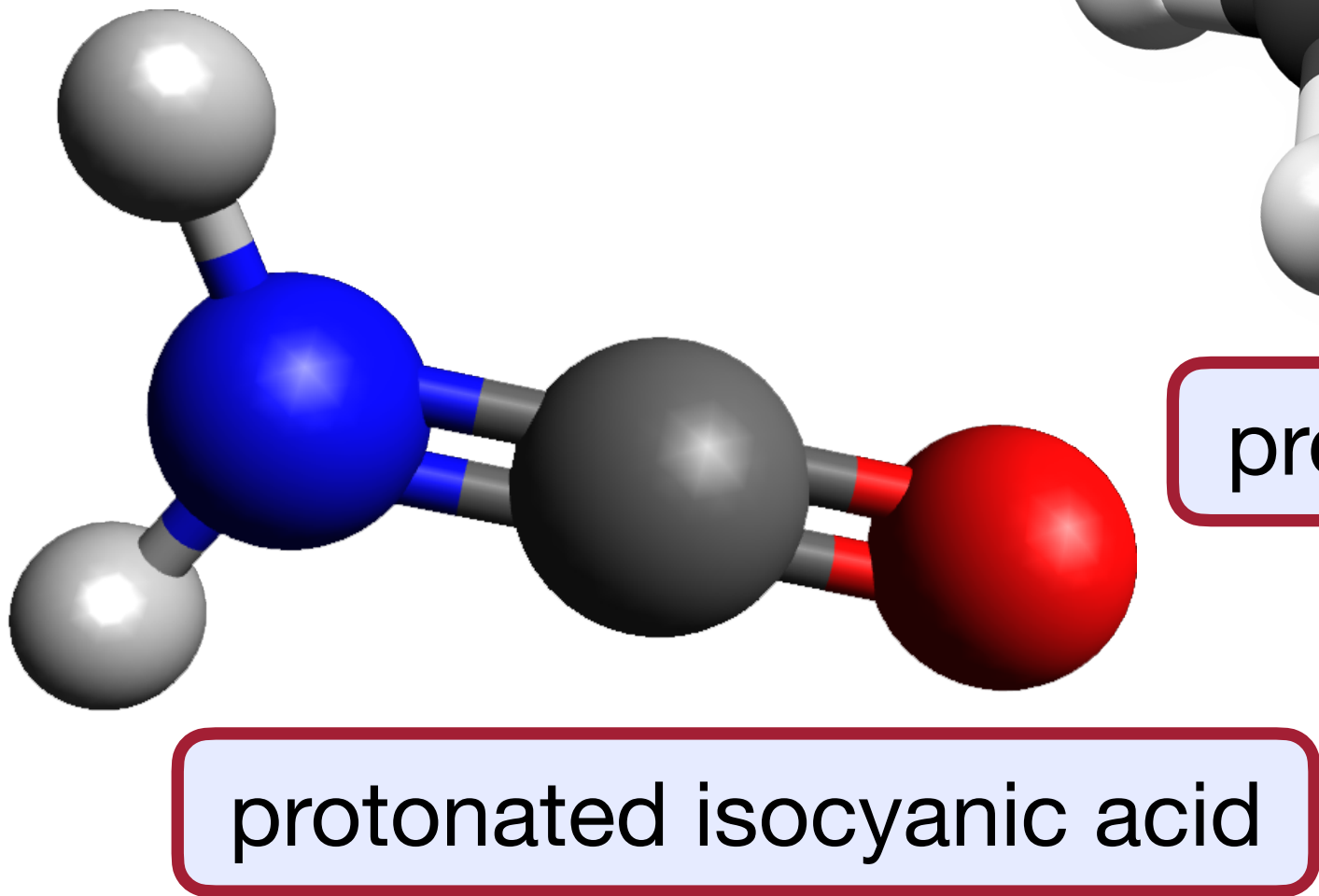
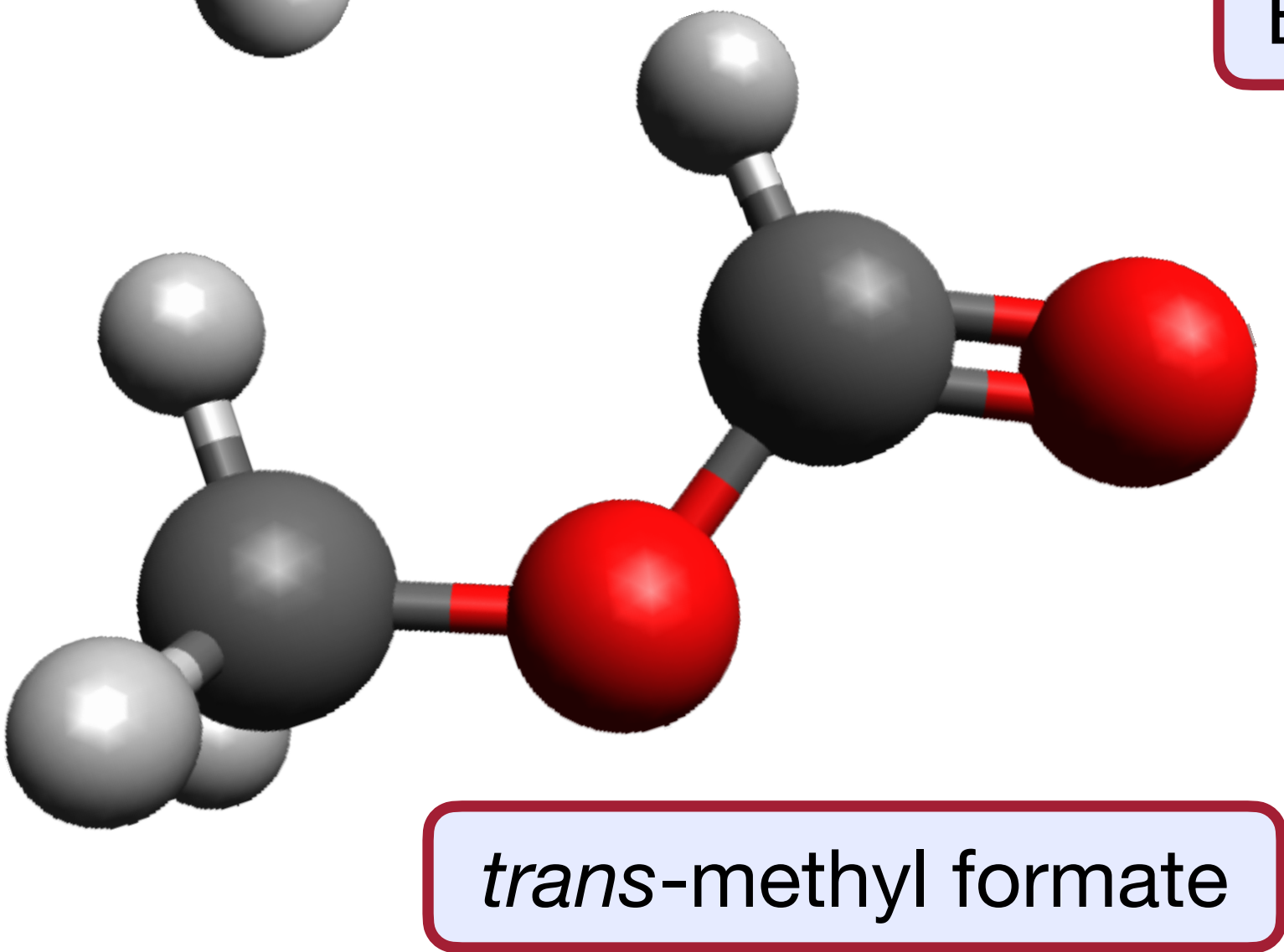
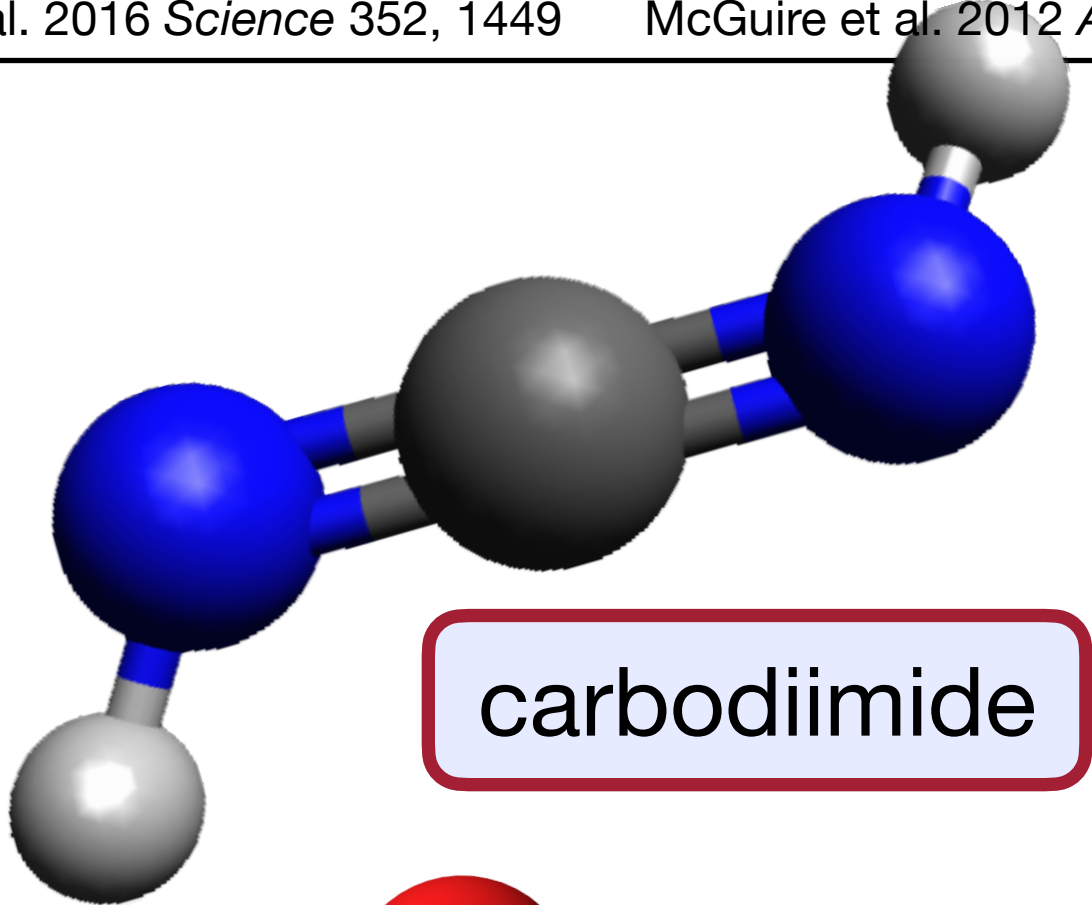
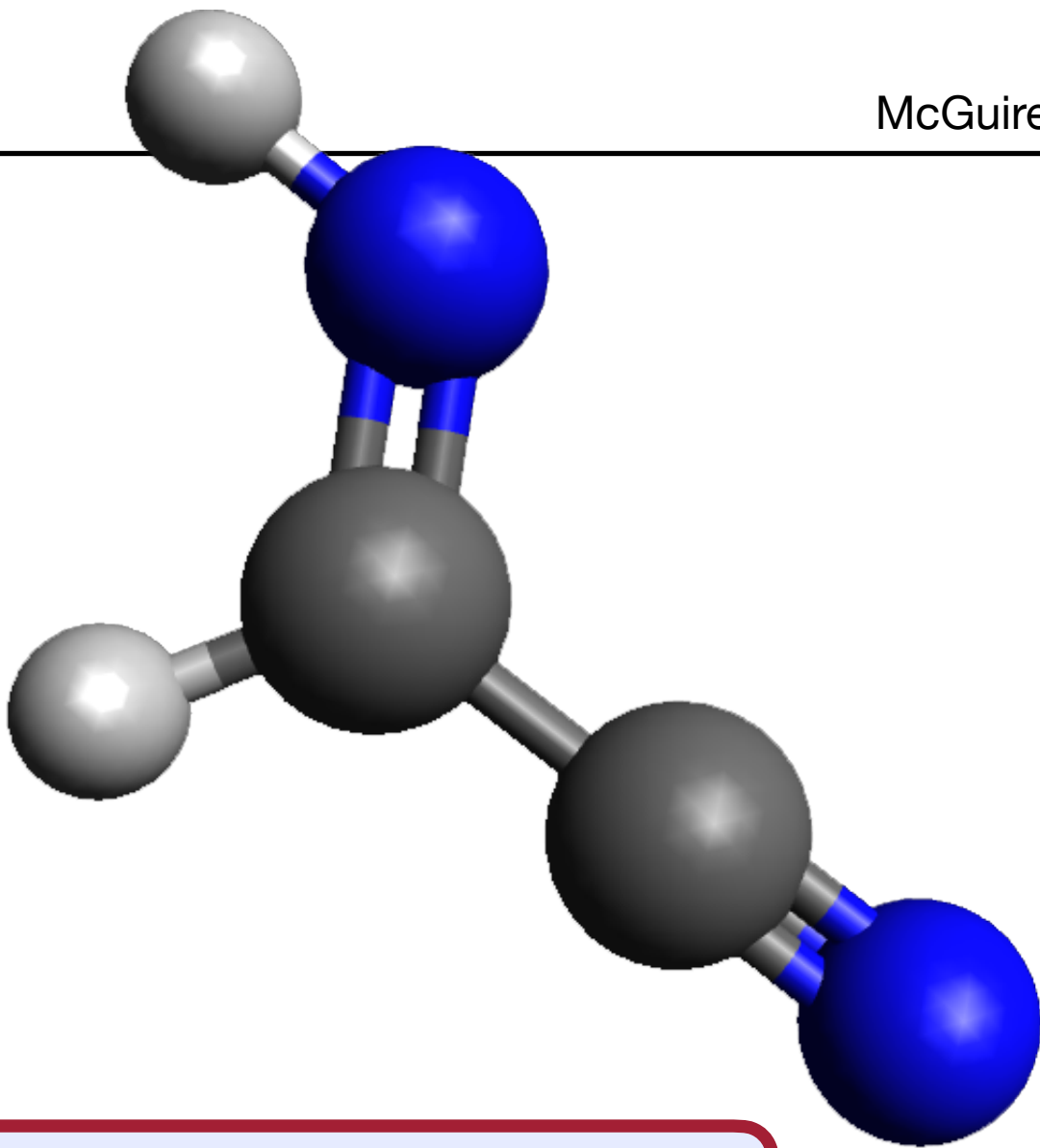
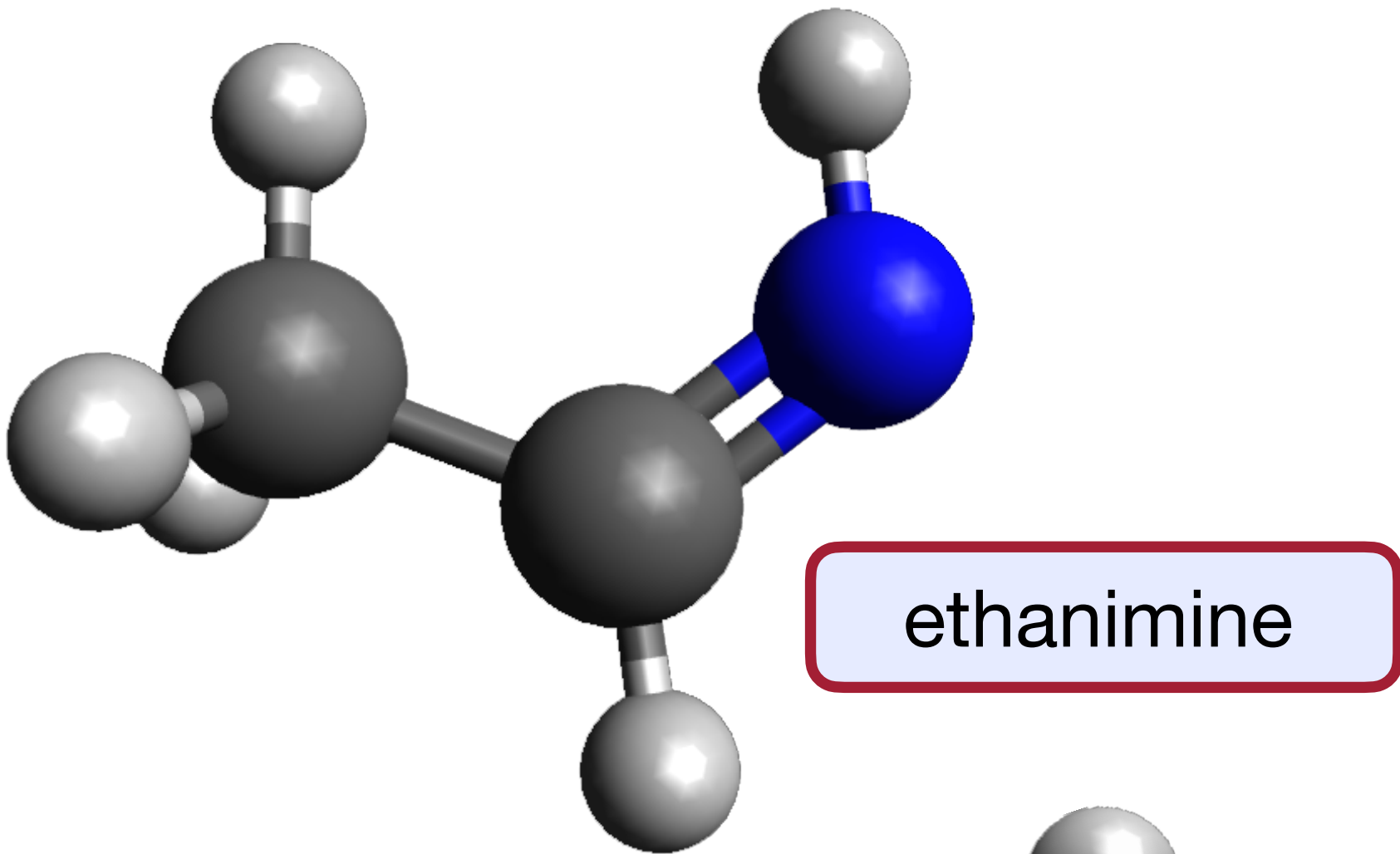
Rotational lines of C₆H⁻ have also been observed in the centimeter band by Fourier transform microwave spectroscopy of a supersonic molecular beam, using a spectrometer (McCarthy et al. 2000) in which the cavity mirrors and first-stage amplifier are cooled to 77 K. The anion was produced by a 600 V low-current (~20 mA) gas discharge synchronized with a gas pulse 330 μs long (yielding a flow of 25 cm³ minute⁻¹ at standard temperature and pressure), the gas sample consisting of either acetylene or diacetylene (0.10%) heavily diluted with Ne at a stagnation pressure of 2.5 ktorr behind the pulsed valve of the nozzle. Diacetylene produces the stronger lines, but because DCCD was readily available, that was the precursor used for C₆D⁻. The optimum discharge voltage for both C₆H⁻ and C₆D⁻ is considerably lower than that which produces the strongest lines of the neutral (1000 V), and the polarity of the discharge is reversed with respect to the neutral as well, but these conditions are nearly identical to those used to measure the photoelectron spectrum of C₆H⁻ using a similar discharge

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² Also at Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

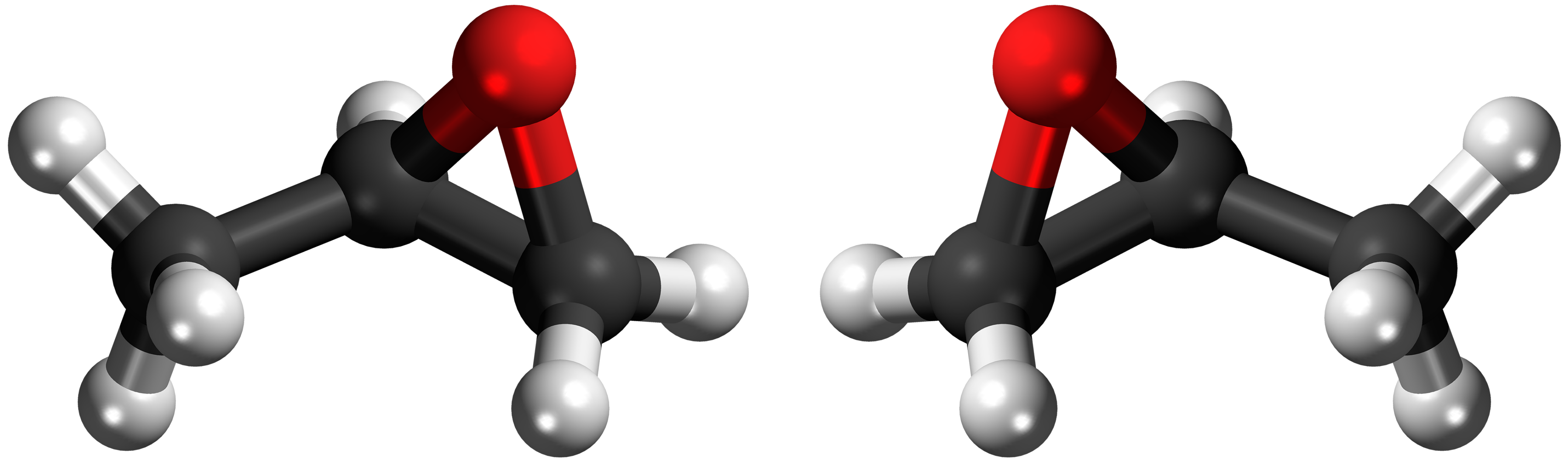


WHERE WINGS TAKE DREAM

Gupta et al. 2013 *ApJ* 778, L1
Neill et al. 2012 *ApJ* 755, 153
McGuire & Carroll et al. 2016 *Science* 352, 1449
Loomis et al. 2013 *ApJL* 765, L9
Zaleski et al. 2013 *ApJL* 765, L10
McGuire et al. 2012 *ApJL* 758, L33

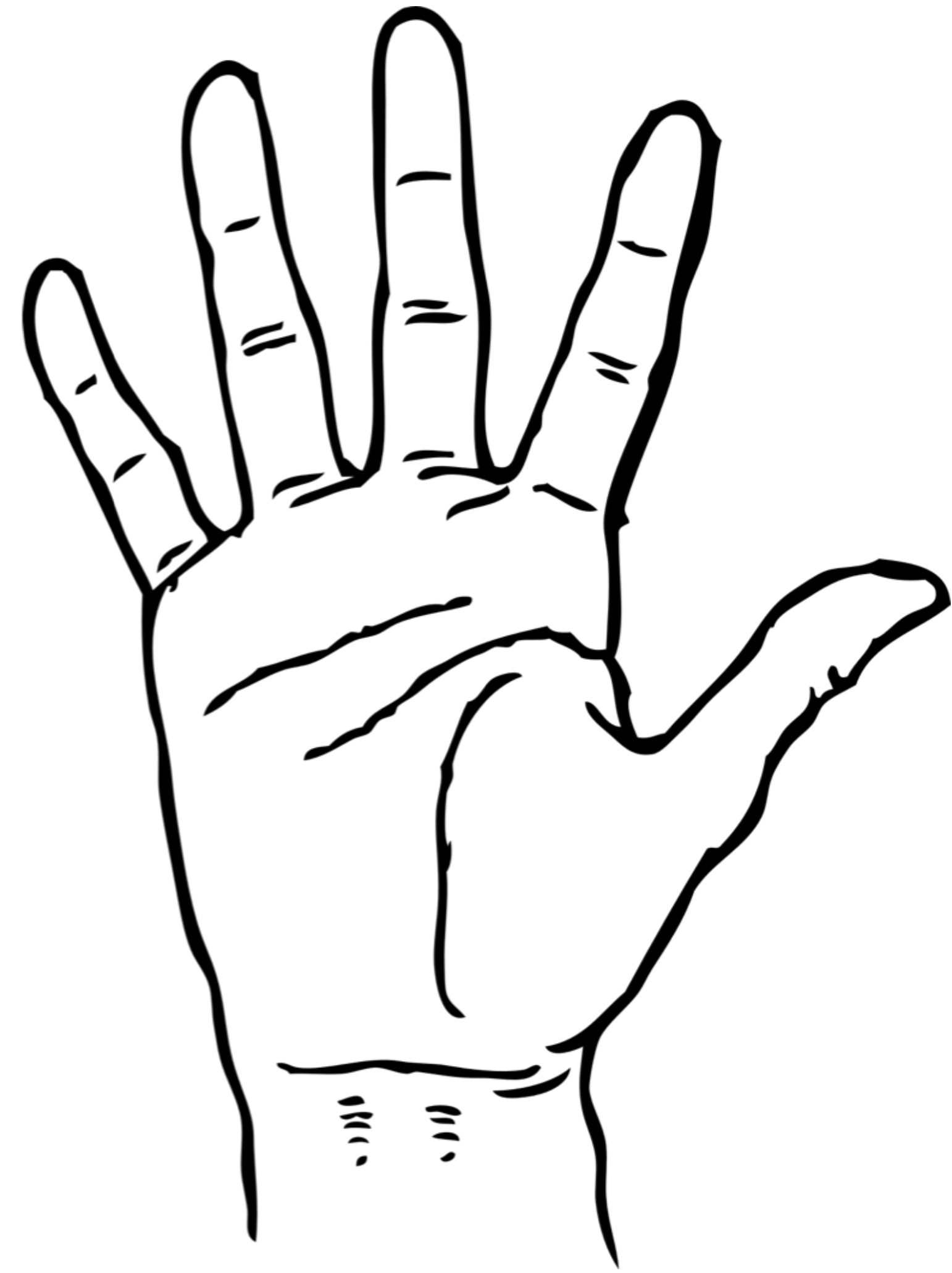
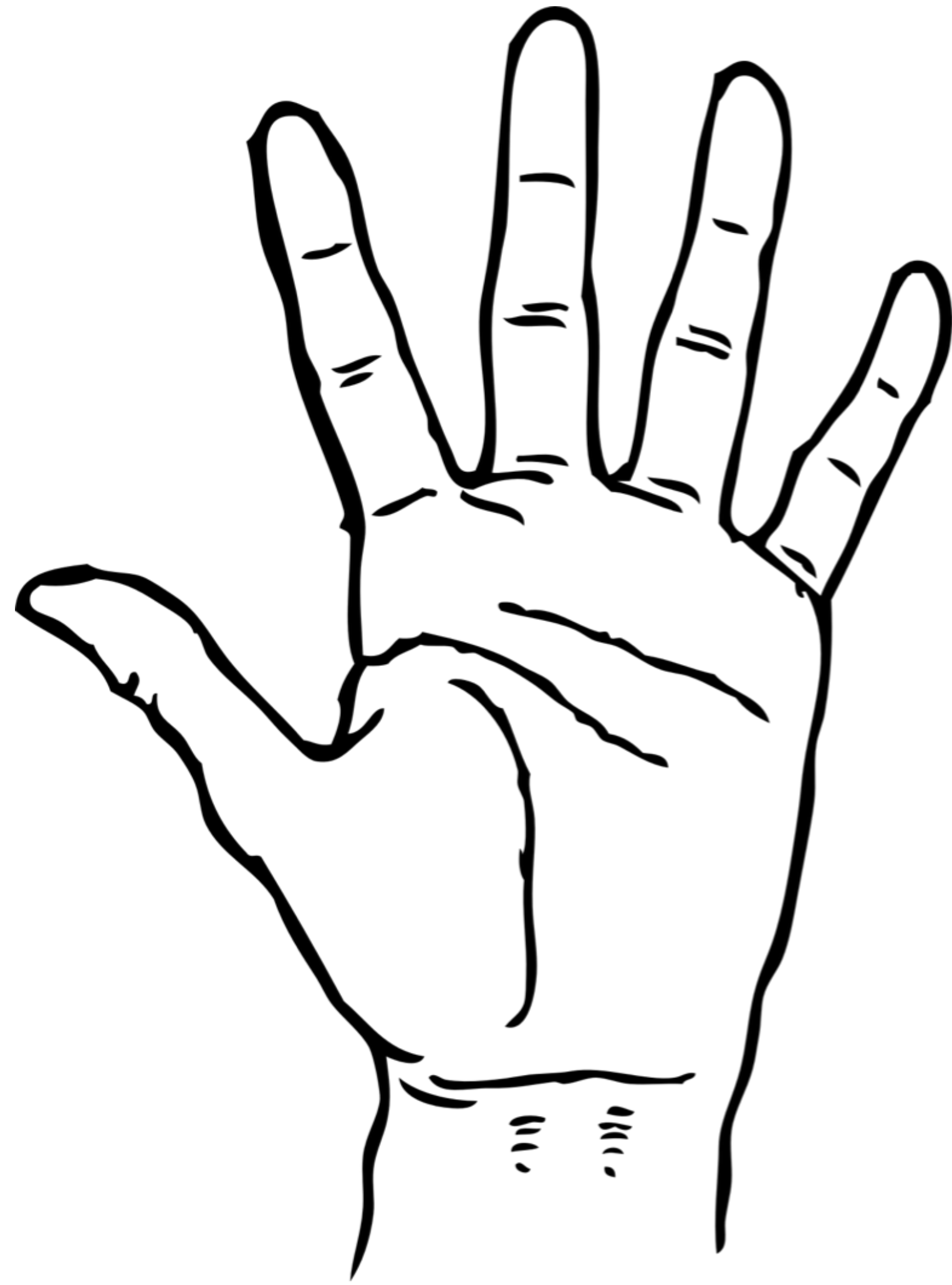


A CHIRAL MOLECULE



Propylene Oxide

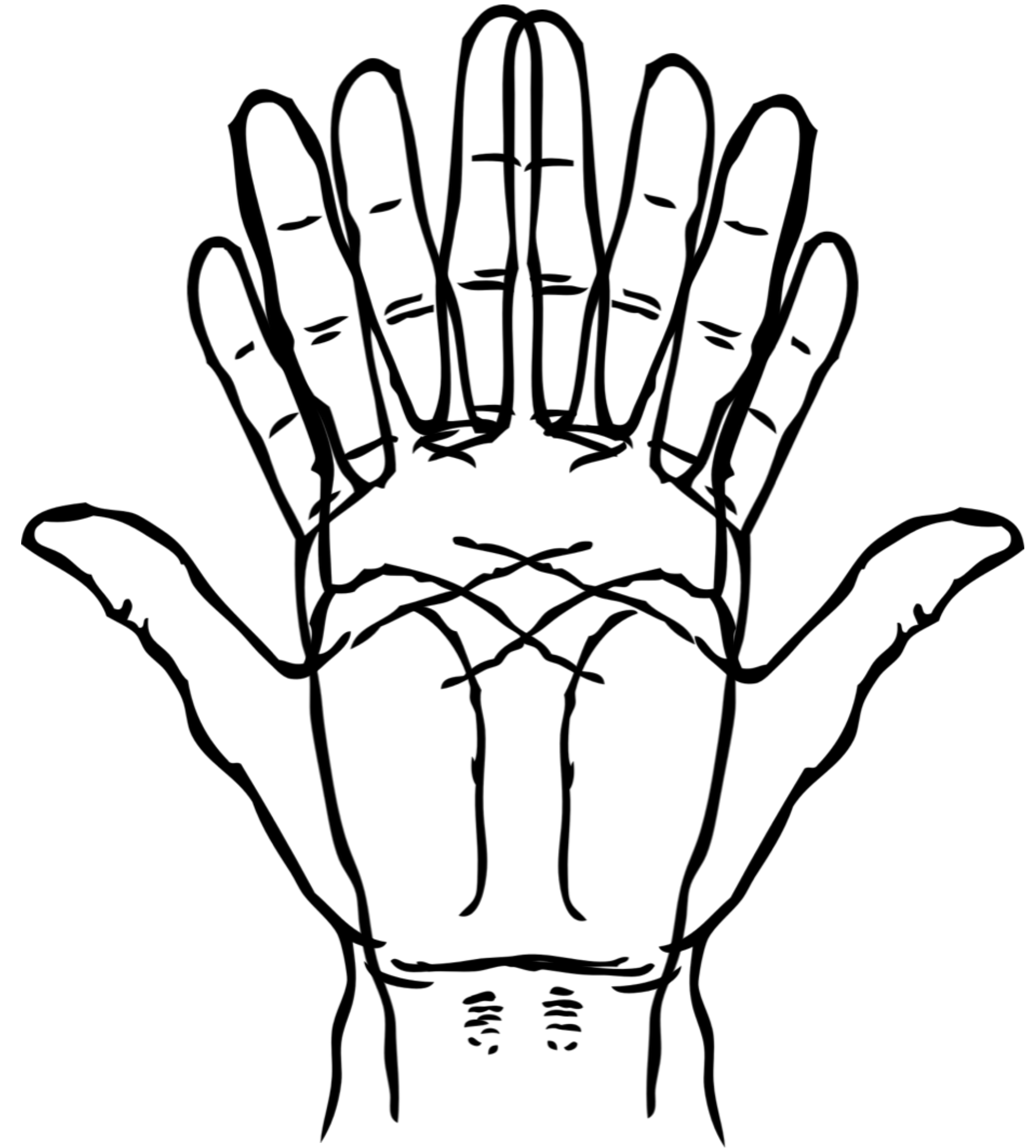
THE SAME, BUT DIFFERENT



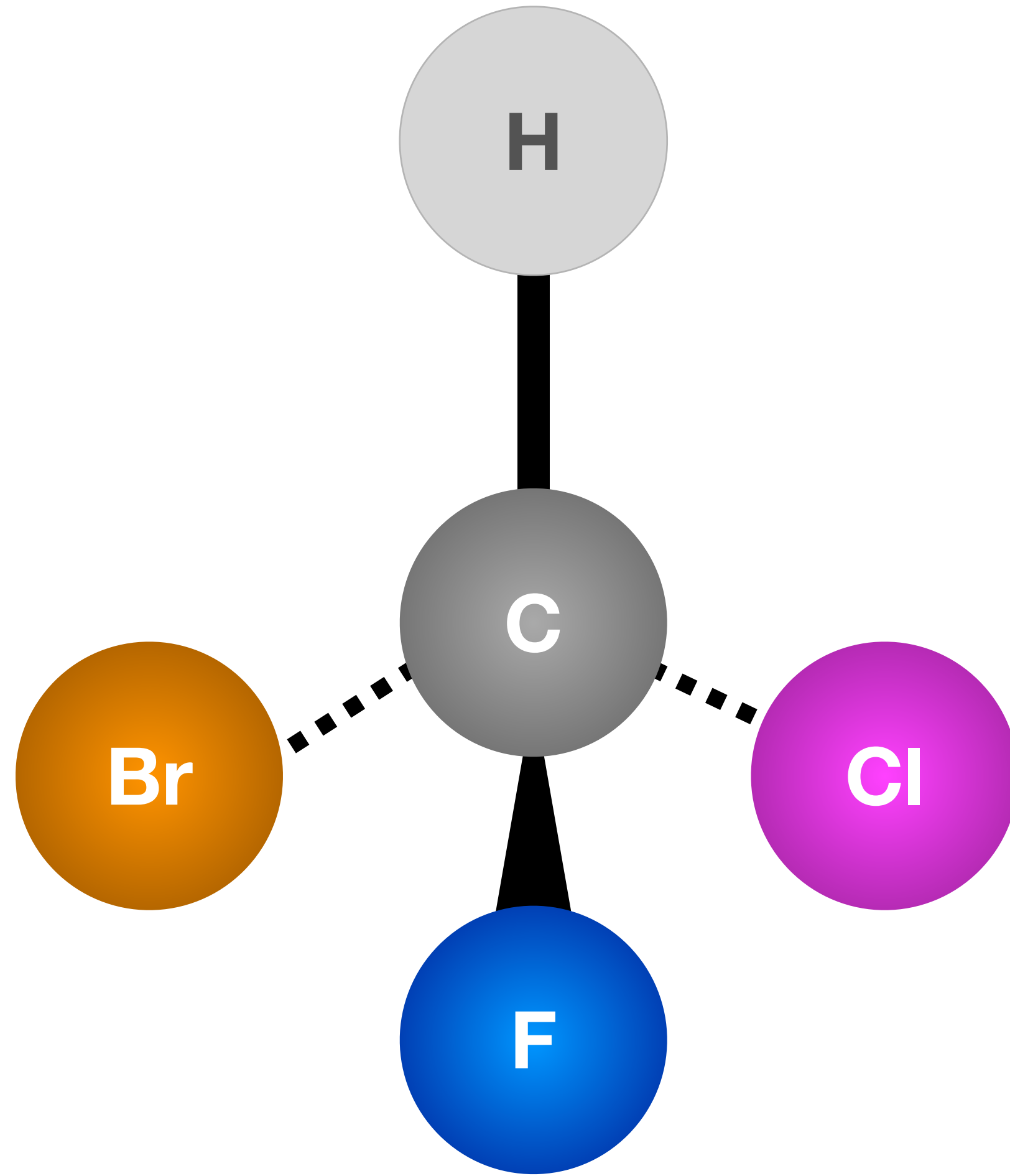
Chirality

kai'rælitɪ

χείρ (kheir) - 'hand'



THE SAME, BUT DIFFERENT



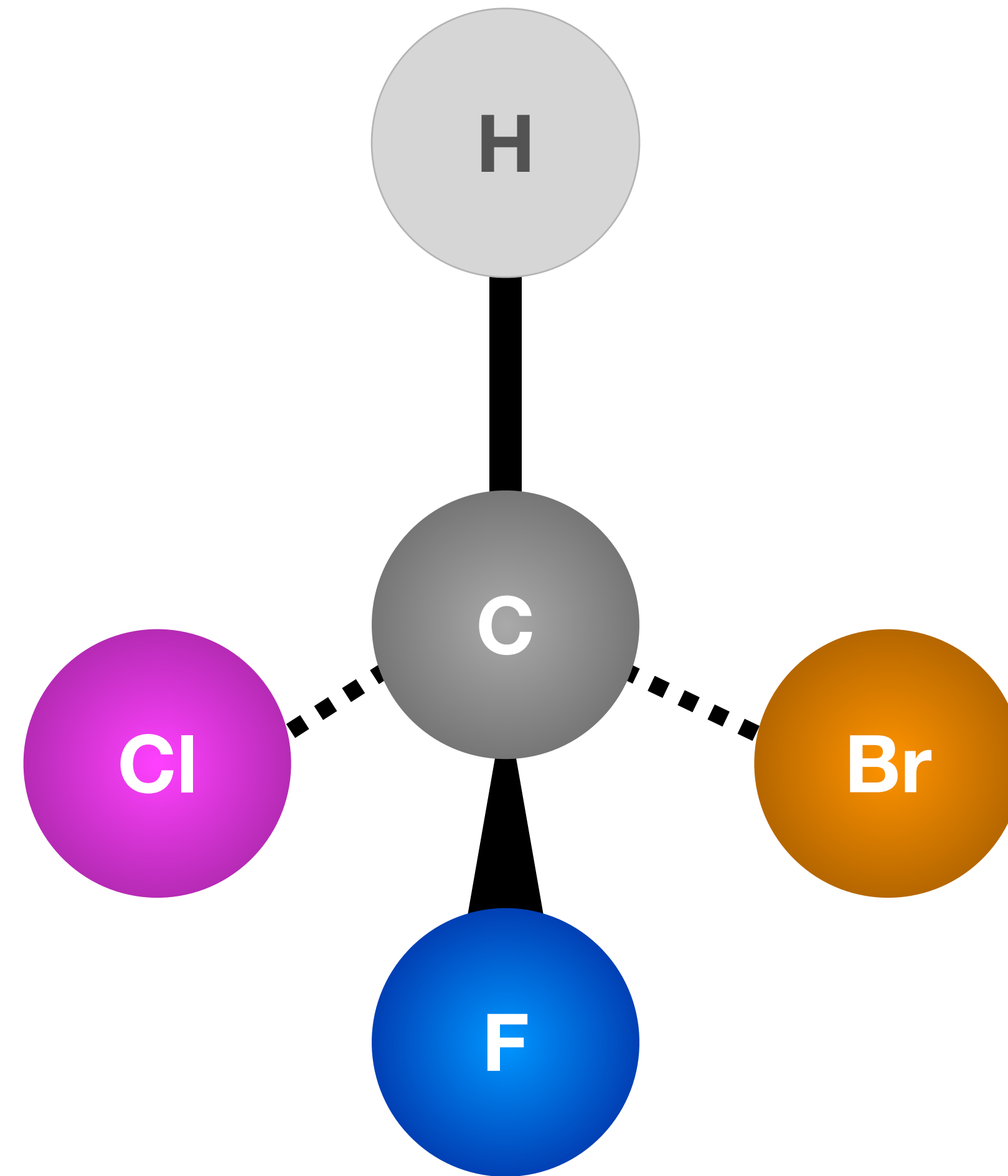
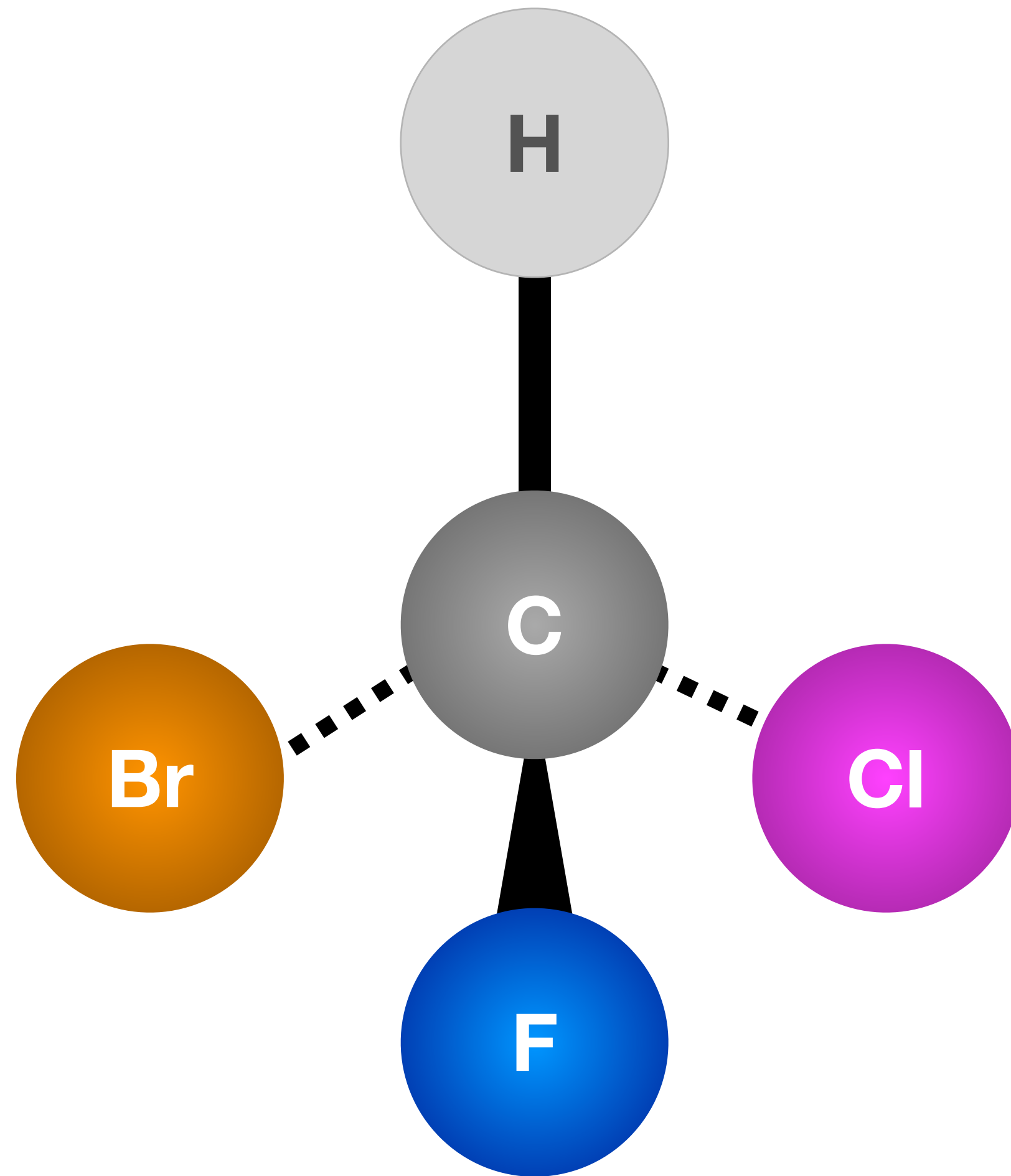
Bromochlorofluoromethane

From Wikipedia, the free encyclopedia

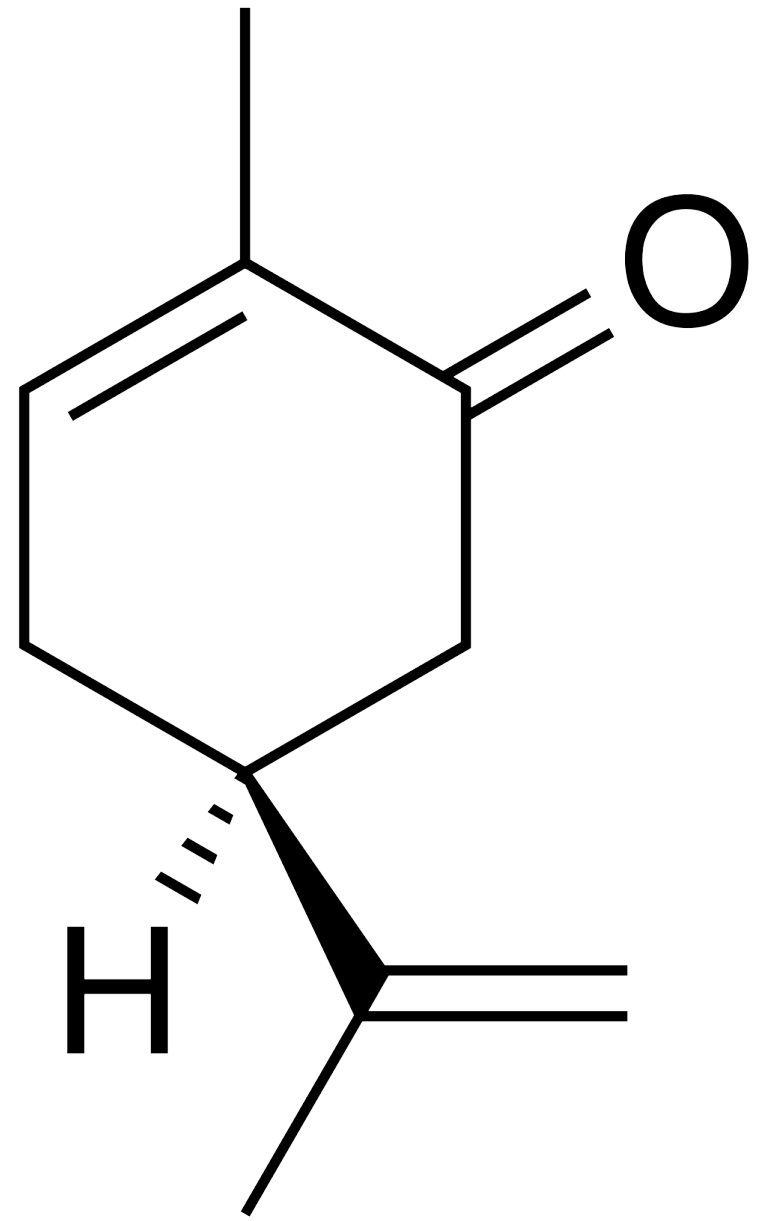
Bromochlorofluoromethane or **fluorochlorobromomethane**, is a chemical compound and [trihalomethane](#) derivative with the chemical formula [CHBrClF](#). As one of the simplest possible stable [chiral](#) compounds, it is useful for fundamental research into this area of chemistry.^[1] However its relative instability to [hydrolysis](#),^[2] and lack of suitable [functional groups](#), made separation of the [enantiomers](#) of bromochlorofluoromethane especially challenging,^[3] and this was not accomplished until almost a century after it was first synthesised, in March 2005, though it has now been done by a variety of methods.^{[4][5][6][7][8]} More recent research using bromochlorofluoromethane has focused on its potential use for experimental measurement of [parity violation](#), a major unsolved problem in [quantum physics](#).^{[9][10][11]}

▲ = out of the plane ■■■ = into the plane

THE SAME, BUT DIFFERENT



▲ = out of the plane ■■■ = into the plane

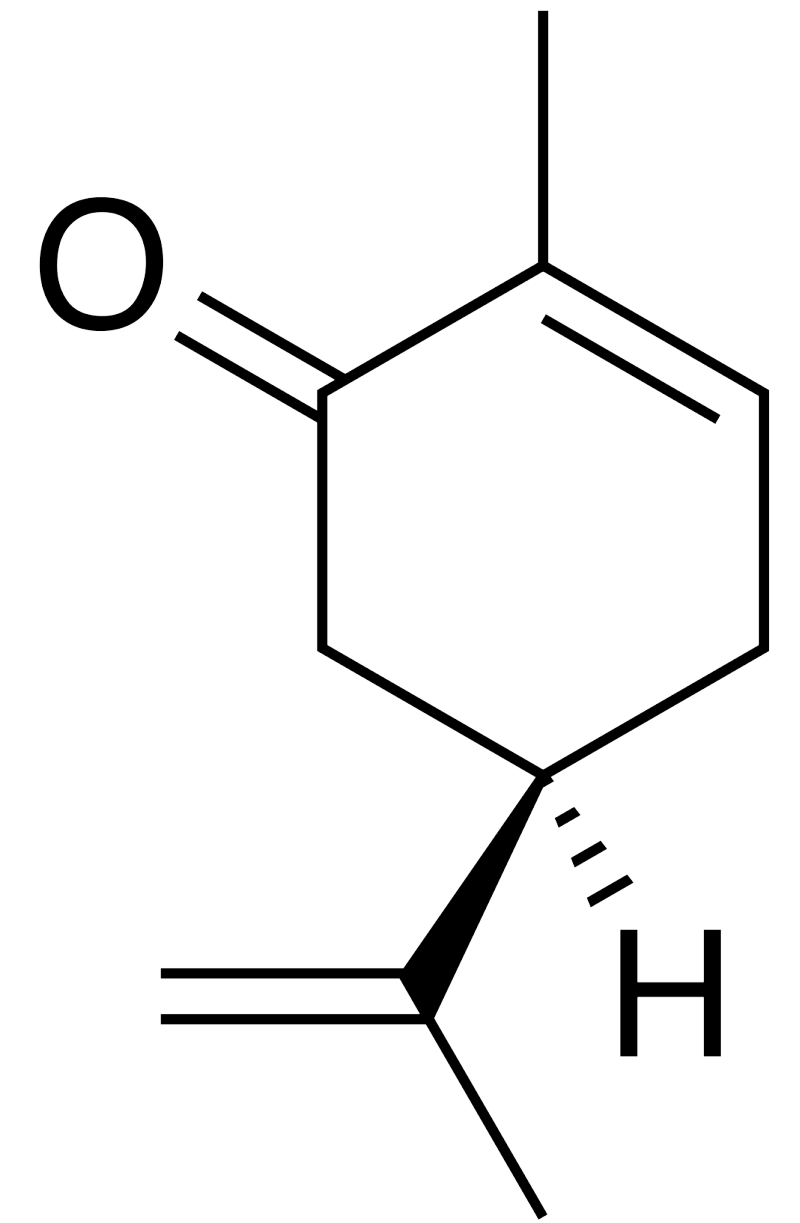


(S)

Caraway



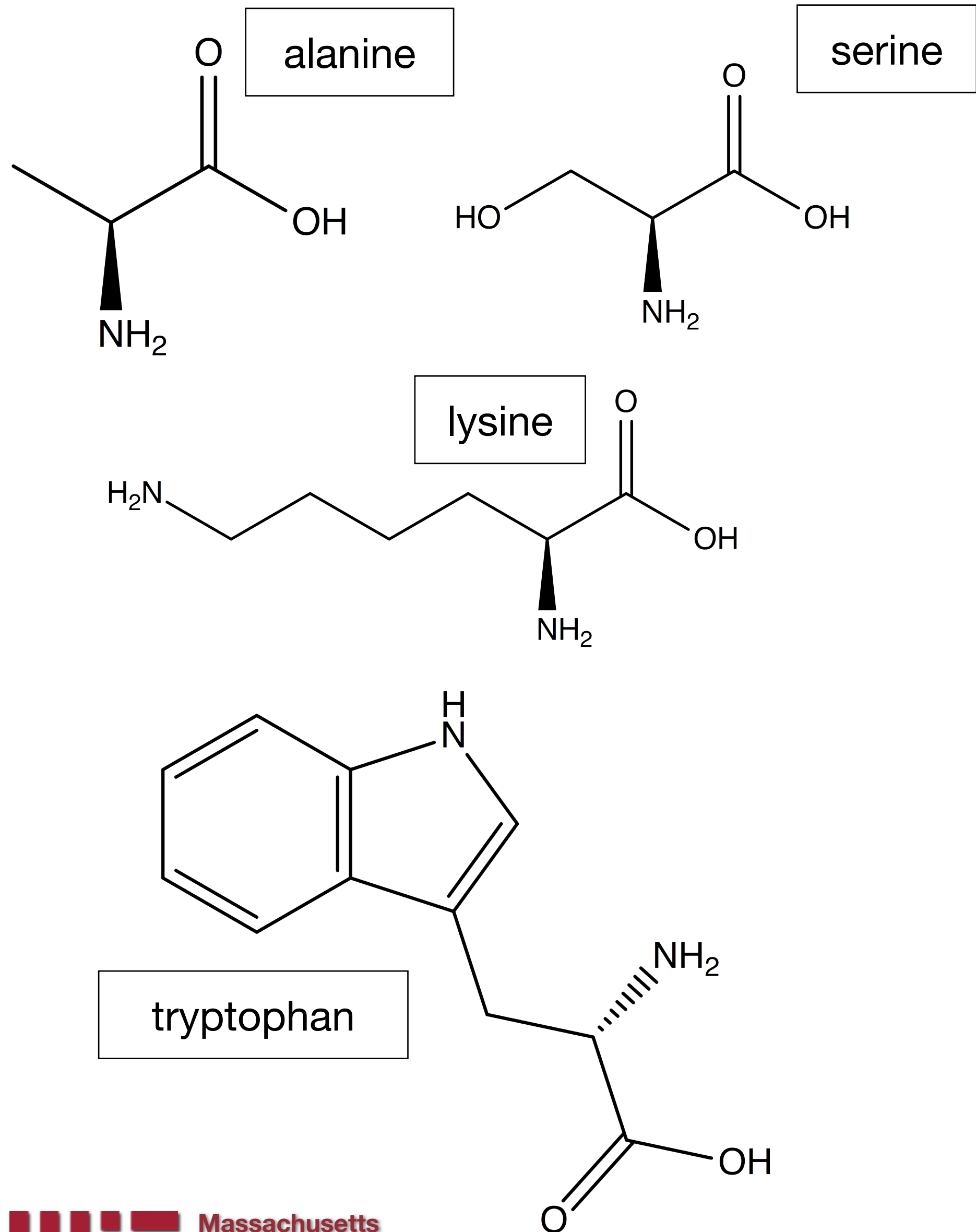
Carvone



(R)

Spearmint



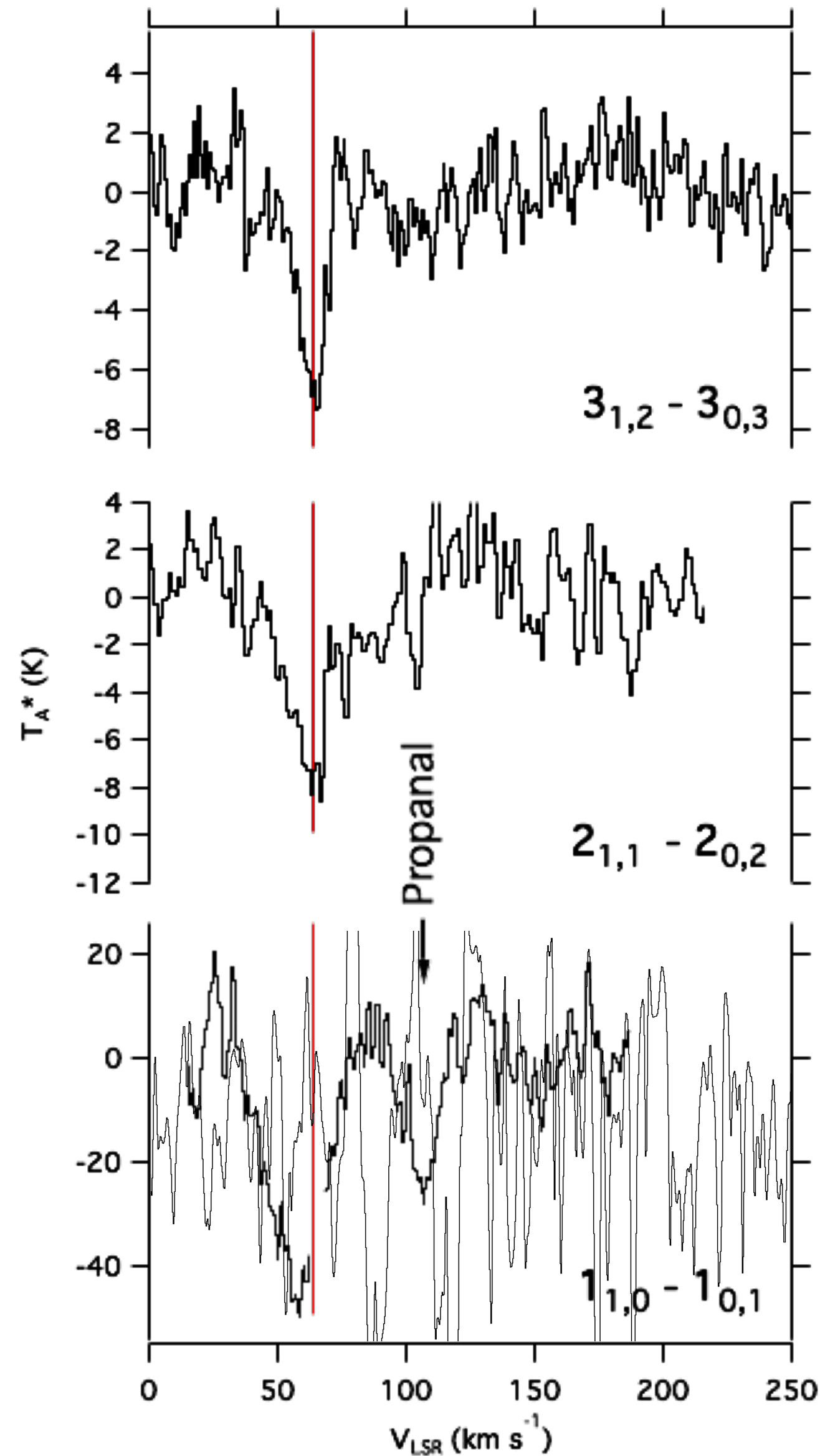


Homochirality

All life on Earth uses only a single enantiomer of amino acids, sugars, and other biomolecules

IN SEARCH OF A CHIRAL MOLECULE

McGuire & Carroll et al. 2016 *Science* 352, 1449



TMC-1 ○



~1 in 3 molecules is
detected for the first
time in space in TMC-1.

GBT OBSERVATIONS OF TMC-1: HUNTING AROMATIC MOLECULES

Actual
 C_6H_5CN Data!

GTHAM

PI/Founder:
Brett McGuire (MIT)*

**** Trainee**
*** Early career**



GOTHAM

Observations

PI: Andrew Burkhardt*
(Worcester State U.)

- Ryan Loomis (NRAO) *
- Mark Siebert (U. Virginia)**
- Tony Remijan (NRAO)
- Maddy Sita (U. Virginia)**
- Sergei Kalenskii (LPI)

Laboratory

PI: Ilsa Cooke*
(U. British Columbia)

- Kelvin Lee (Intel)*
- Tim Barnum (Union College)*
- Mike McCarthy (Harvard)
- Bryan Changala (Harvard)*
- Haley Scolati (U. Virginia)**
- Stefanie Milam (NASA)
- Katarina Yocum (NASA)*

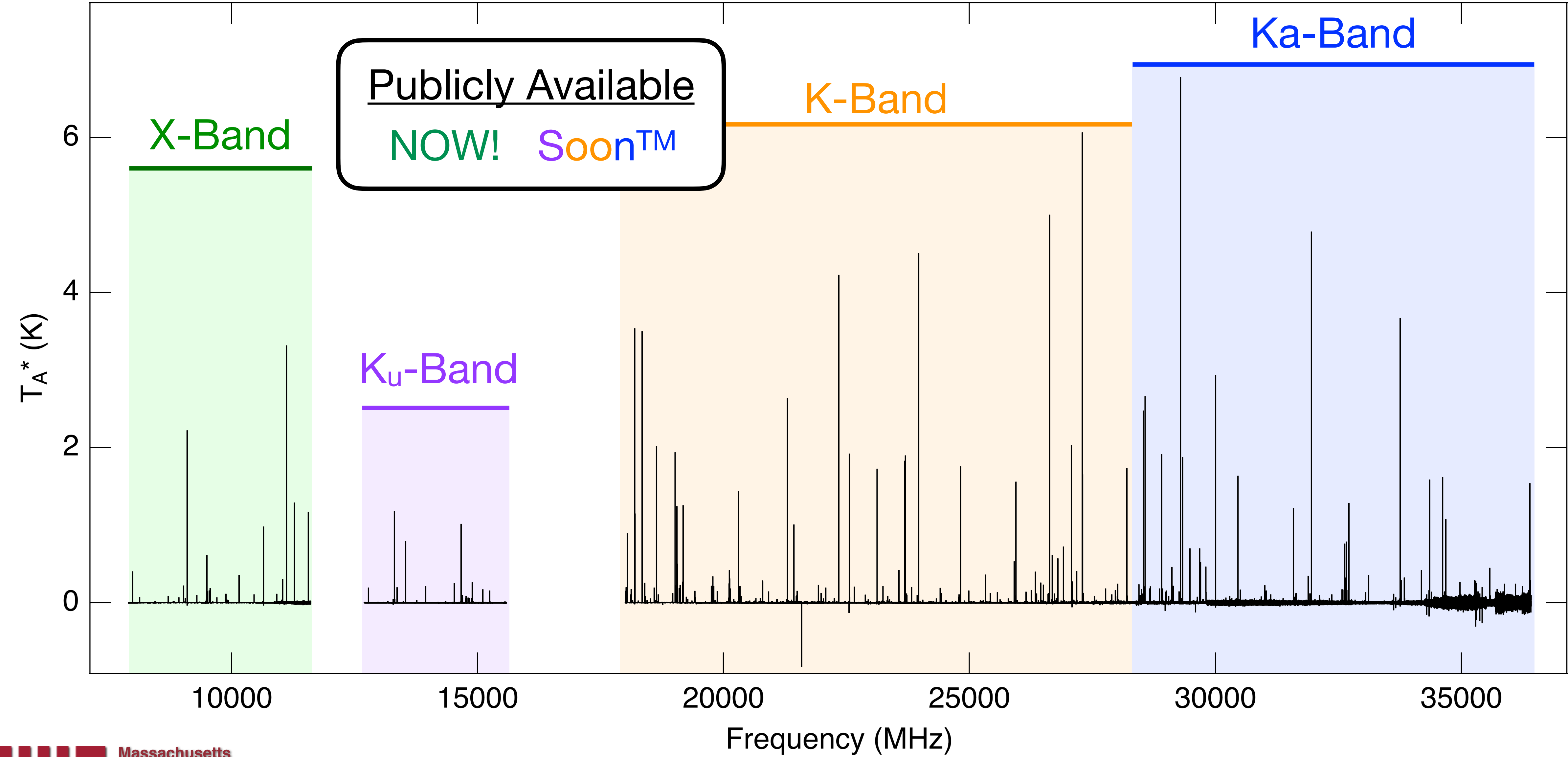
Modeling

PI: Ci Xue*
(MIT)

- Chris Shingledecker (Benedictine)*
- Eric Herbst (U. Virginia)
- Martin Cordiner (NASA)
- Steve Charnley (NASA)
- Thanja Lamberts (Leiden)*

GOTHAM: PLEASE USE OUR DATA!

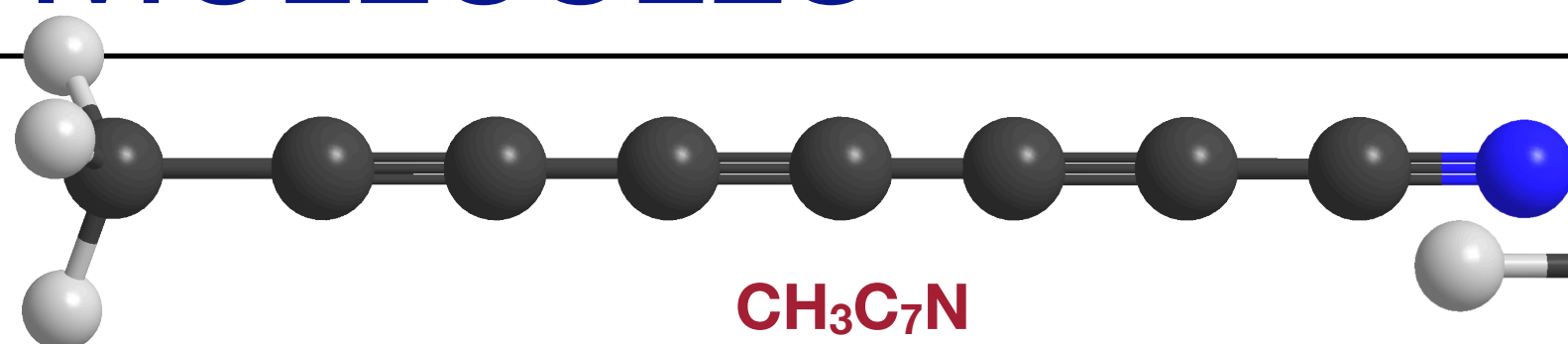
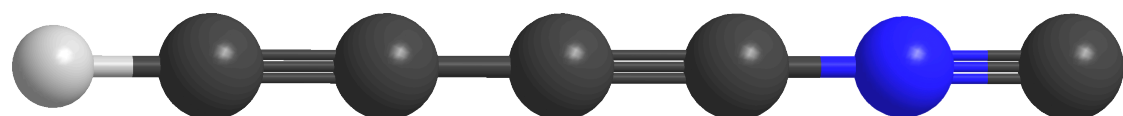
McGuire et al. 2020 *ApJL* 900, L10



GOTHAM: NEW MOLECULES

HC₄NC

Xue et al. 2020 ApJL 900, L9

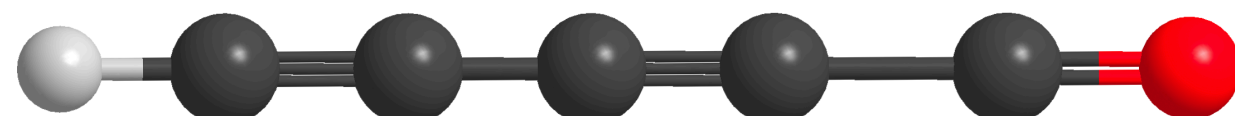


HC₁₁N

Loomis et al. 2021 Nat. Ast. 5, 188

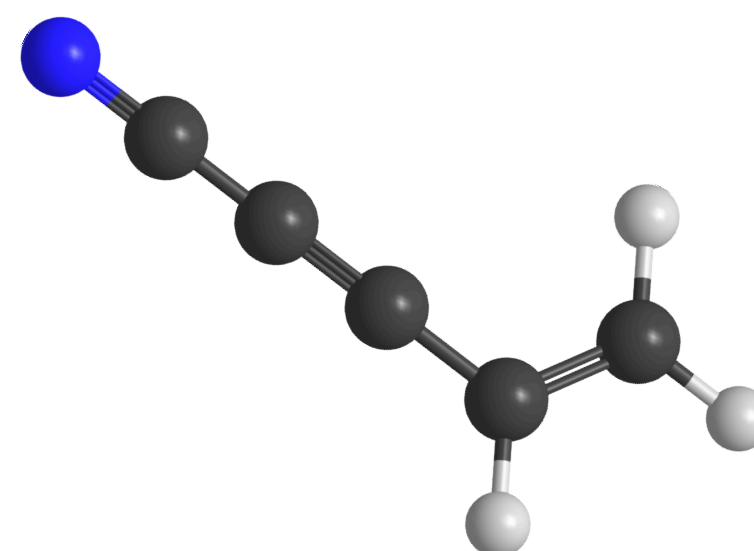
HC₅O

McGuire et al. 2017 ApJL 843, L28



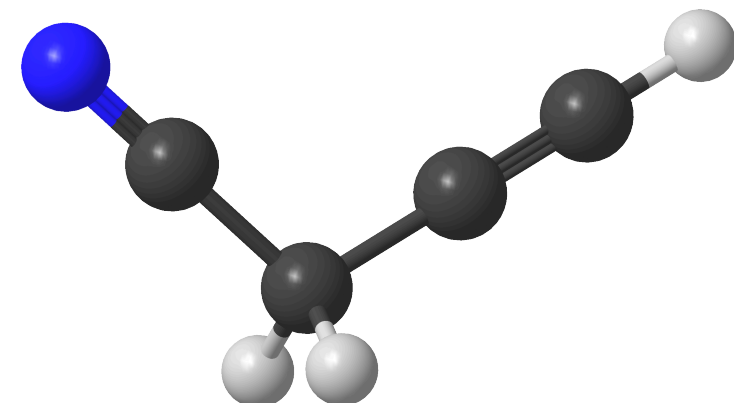
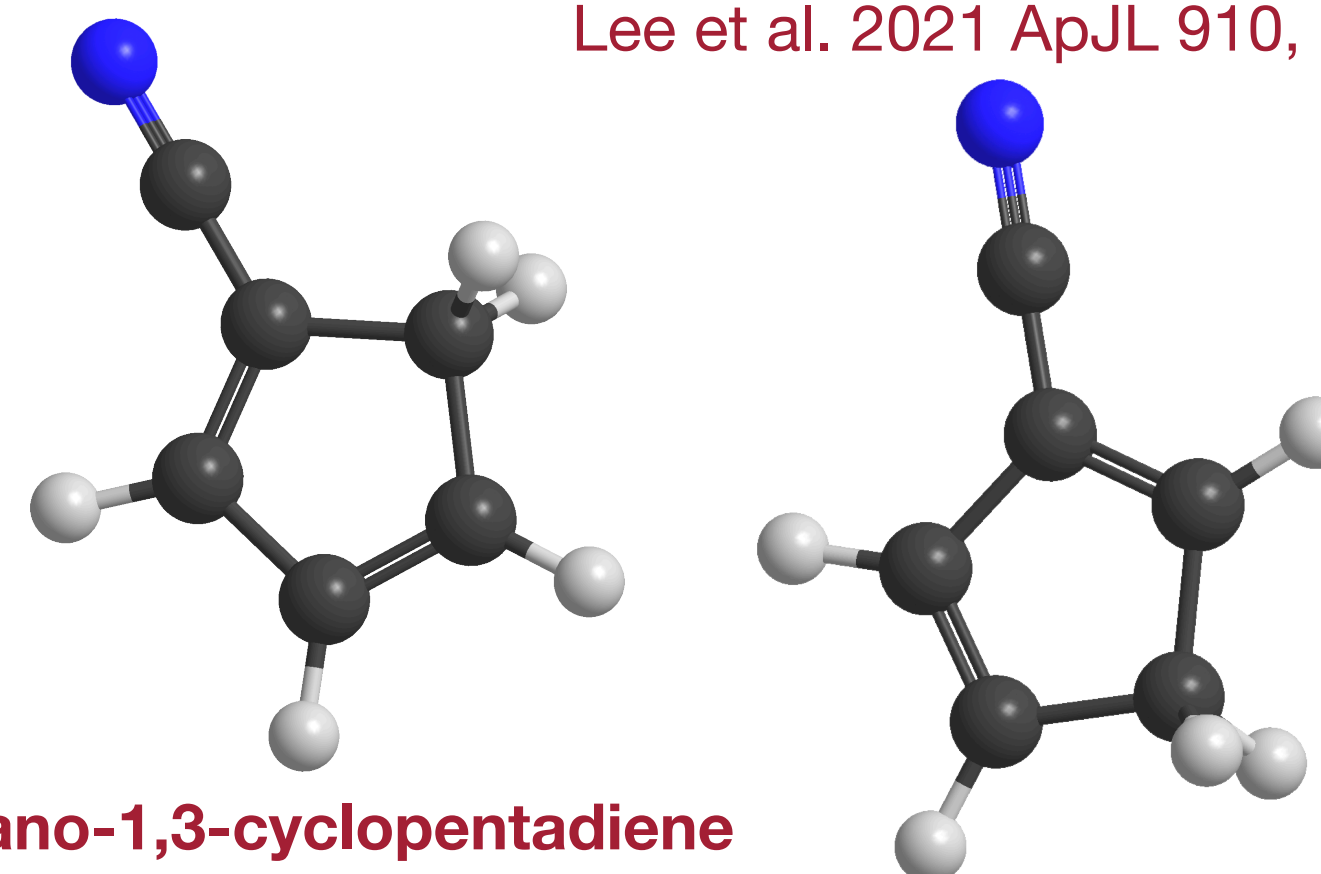
CH₃C₇N

Siebert et al. 2022 ApJ 942, 221



2-cyano-1,3-cyclopentadiene

Lee et al. 2021 ApJL 910, L2

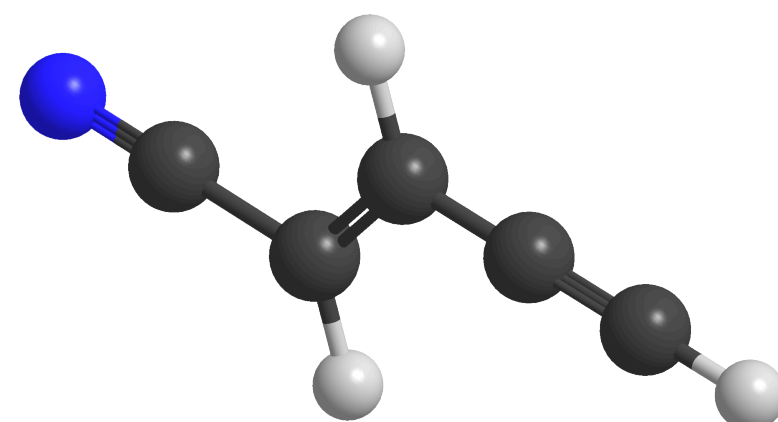


Propargyl Cyanide

McGuire et al. 2020 ApJL 900, L10

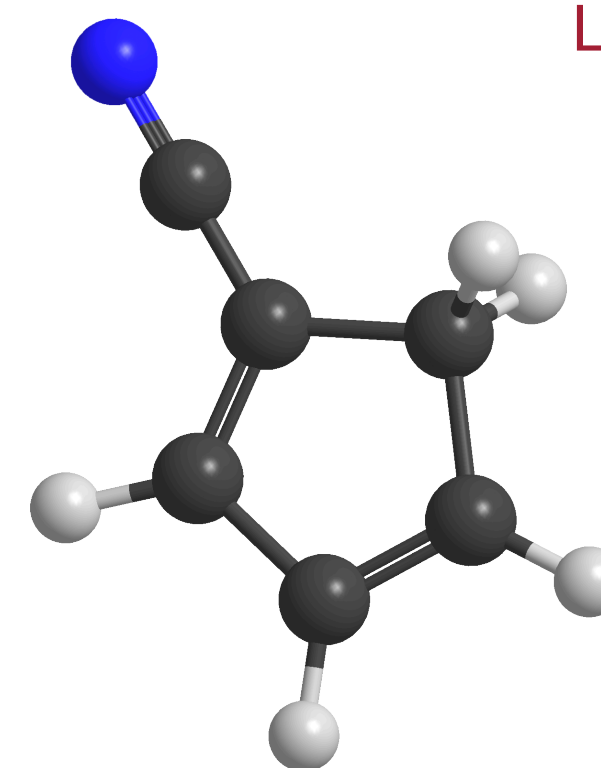
Cyanovinylacetylene

Lee et al. 2021 ApJL 908, L11



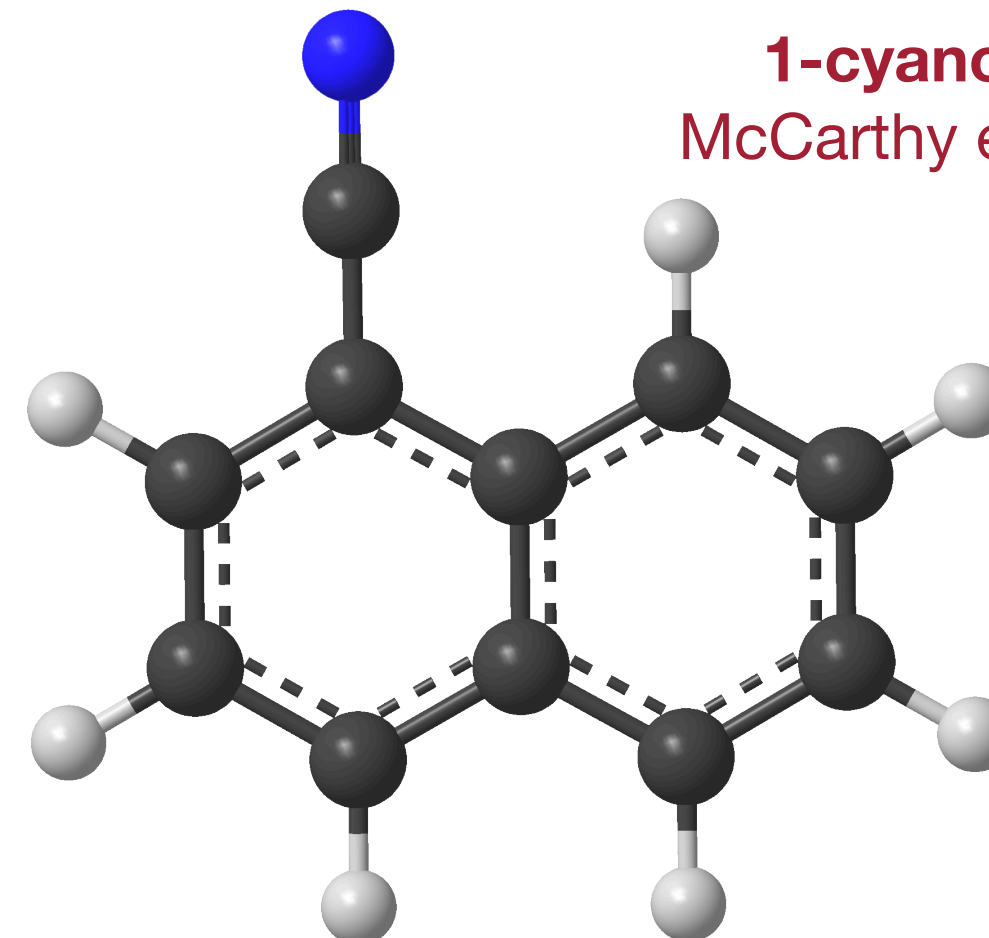
Vinylcyanoacetylene

Lee et al. 2021 ApJL 908, L11



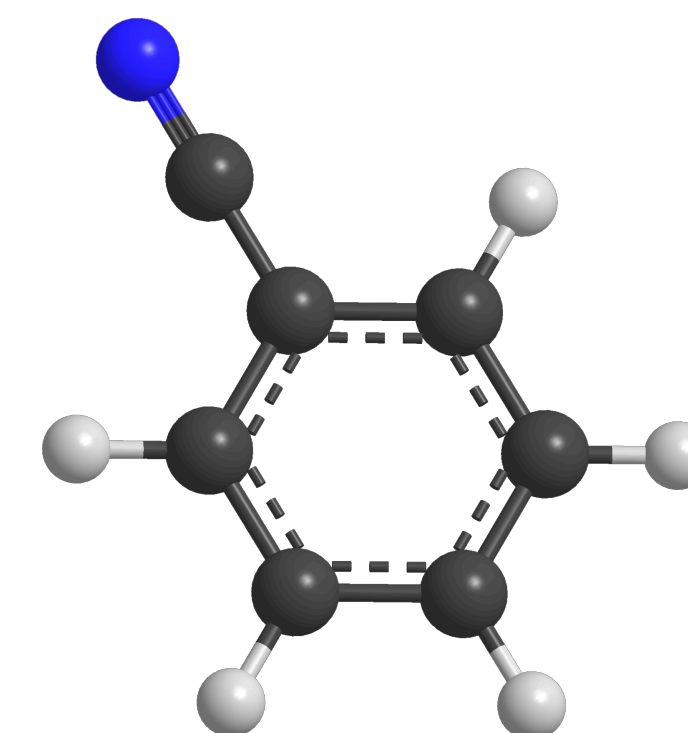
1-cyano-1,3-cyclopentadiene

McCarthy et al. 2021 Nat. Ast. 5, 176



Benzonitrile

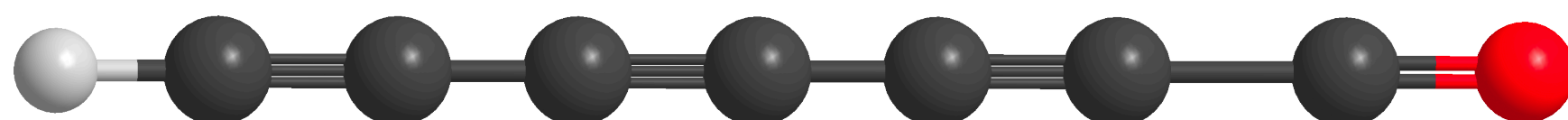
McGuire et al. 2018 Science 359, 202



HC₇O

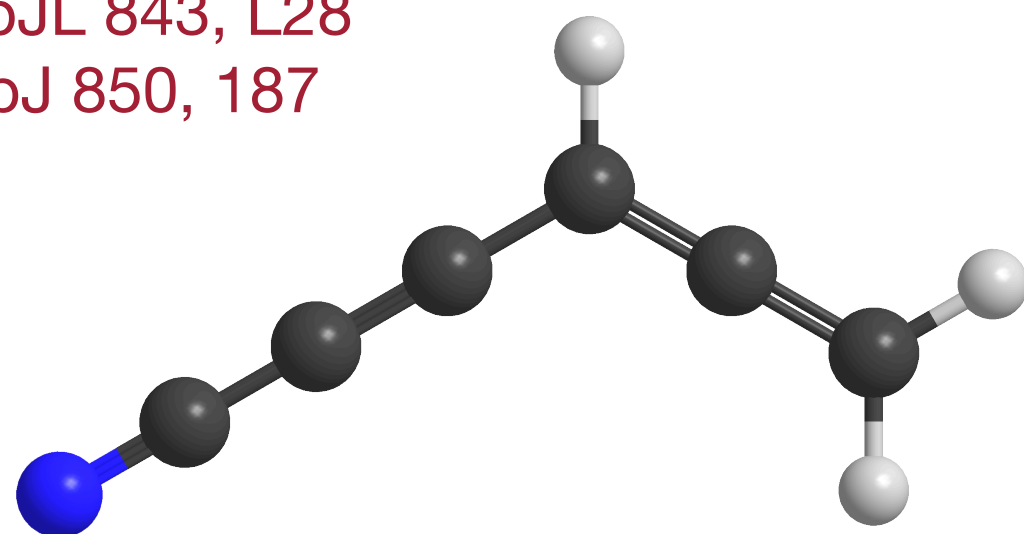
McGuire et al. 2017 ApJL 843, L28

Cordiner et al. 2017 ApJ 850, 187



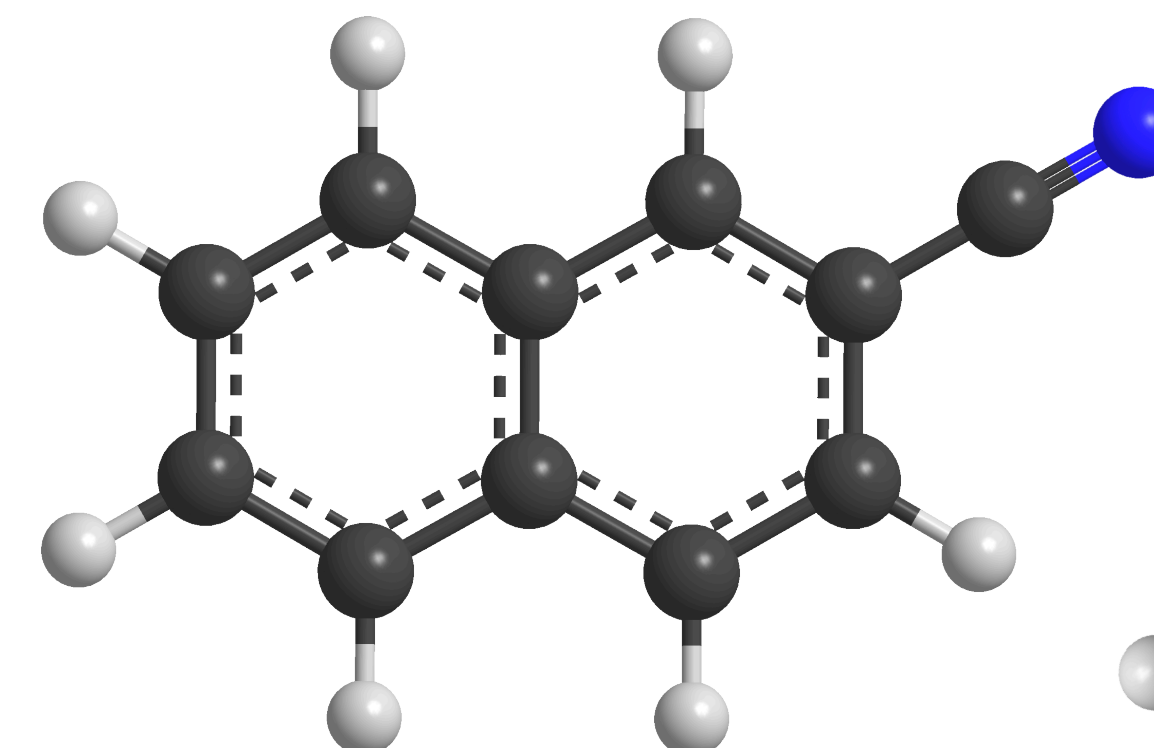
Cyanoacetyleneallene

Shingledecker et al. 2021 A&AL, 652, L12



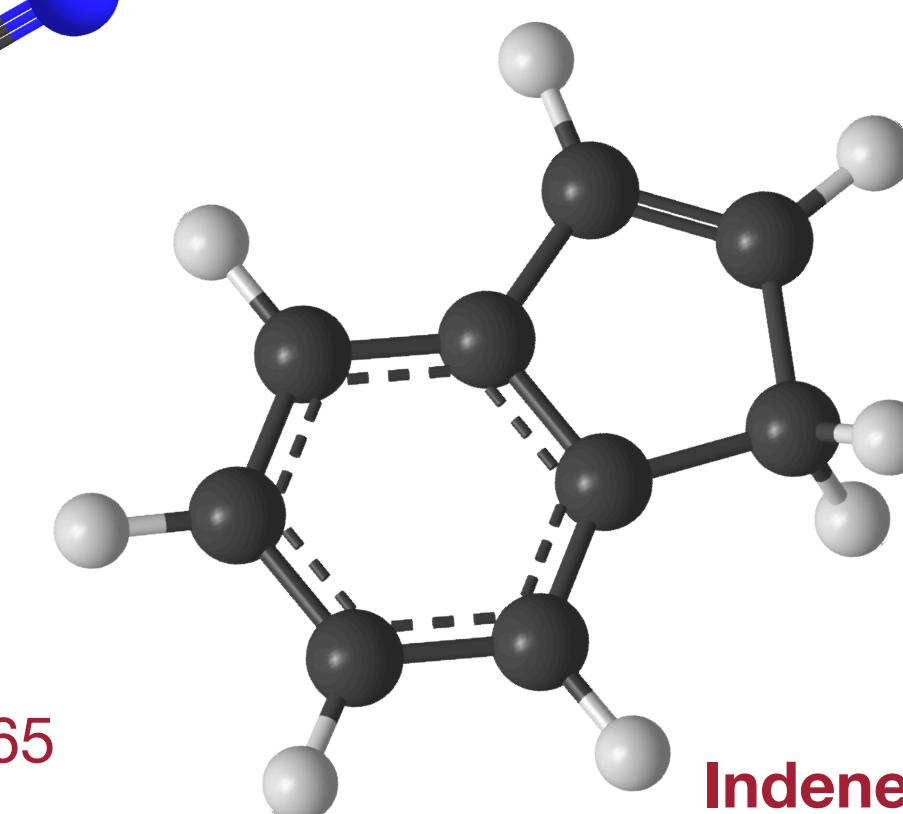
1-cyanonaphthalene

McGuire et al. 2021 Science 371, 1265



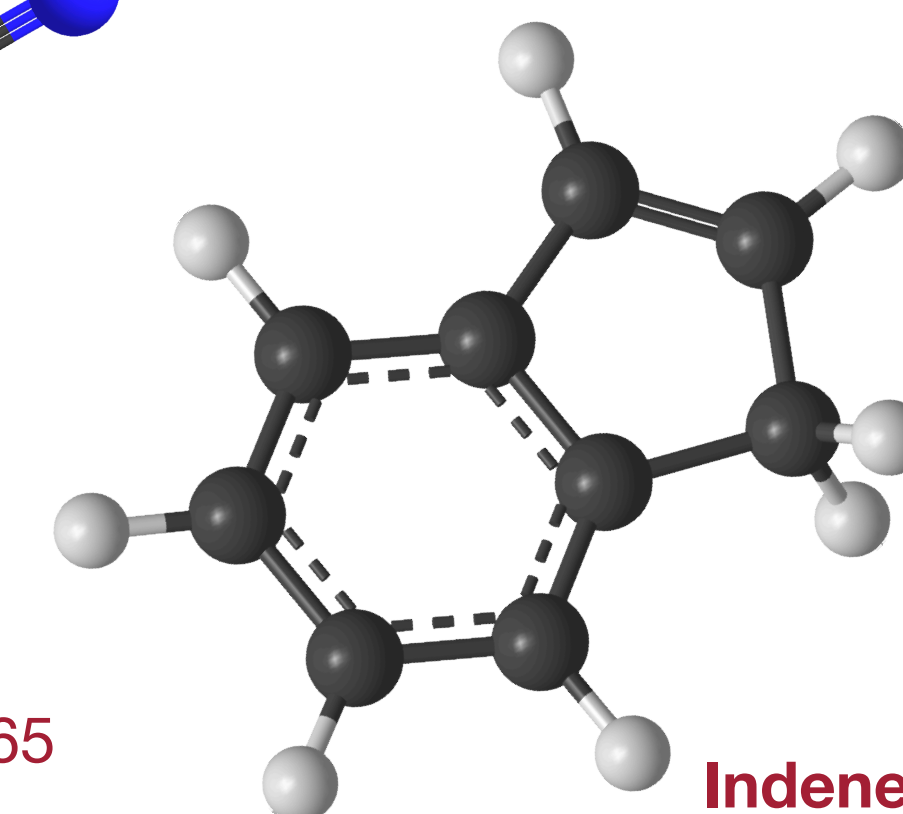
2-cyanonaphthalene

McGuire et al. 2021 Science 371, 1265



Indene

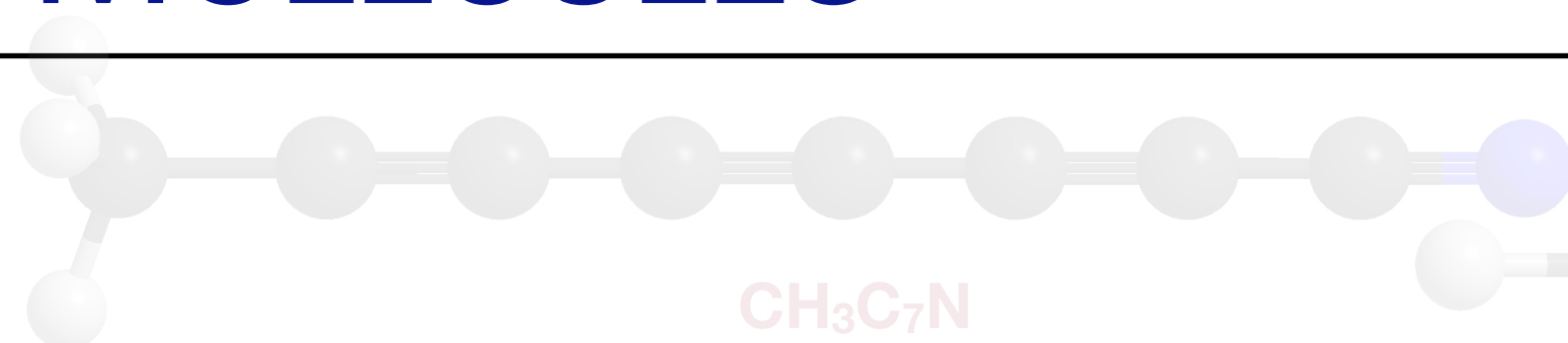
Burkhardt et al. 2021 ApJL 913, L18



GOTHAM: NEW MOLECULES

HC₄NC

Xue et al. 2020 ApJL 900, L9



HC₁₁N

Loomis et al. 2021 Nat. Ast. 5, 188

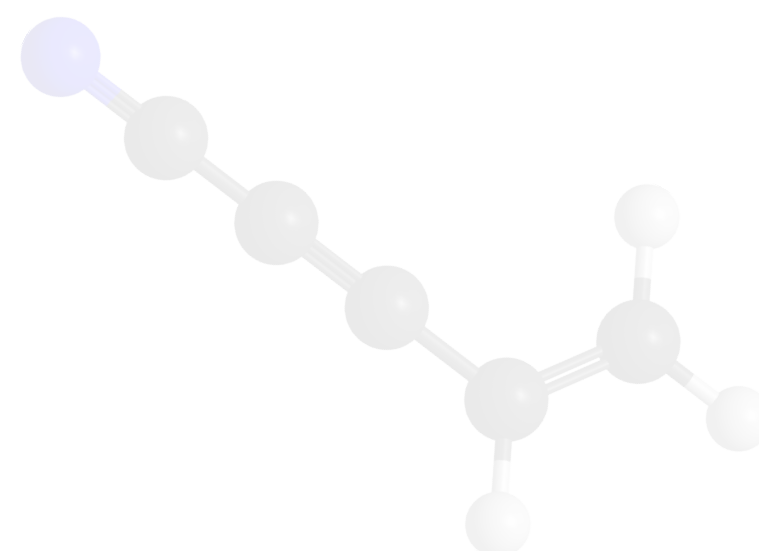
HC₅O

McGuire et al. 2017 ApJL 843, L28



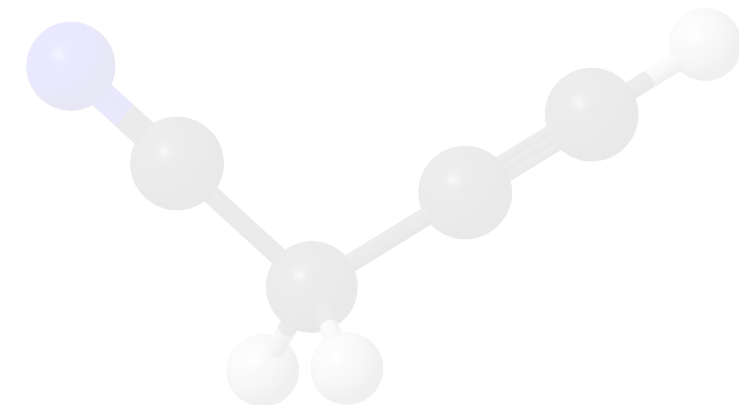
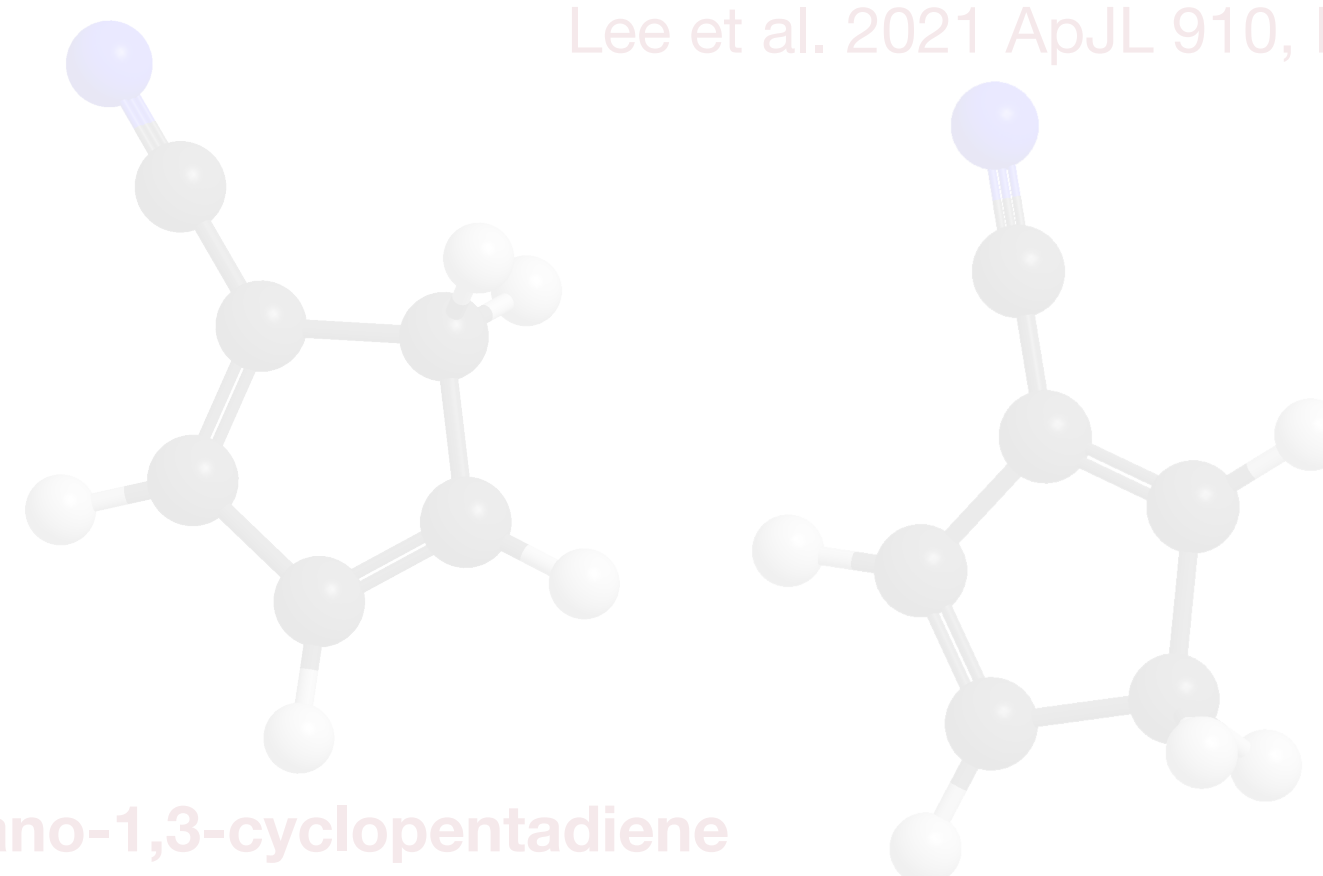
CH₃C₇N

Siebert et al. 2022 ApJ 942, 221



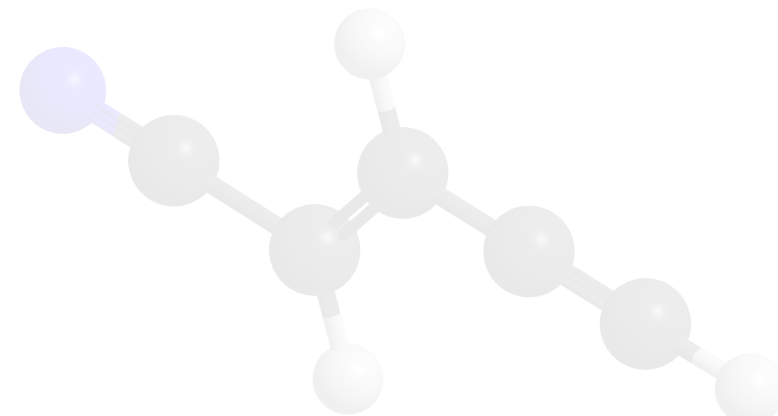
2-cyano-1,3-cyclopentadiene

Lee et al. 2021 ApJL 910, L2



Propargyl Cyanide

McGuire et al. 2020 ApJL 900, L10



Cyanovinylacetylene

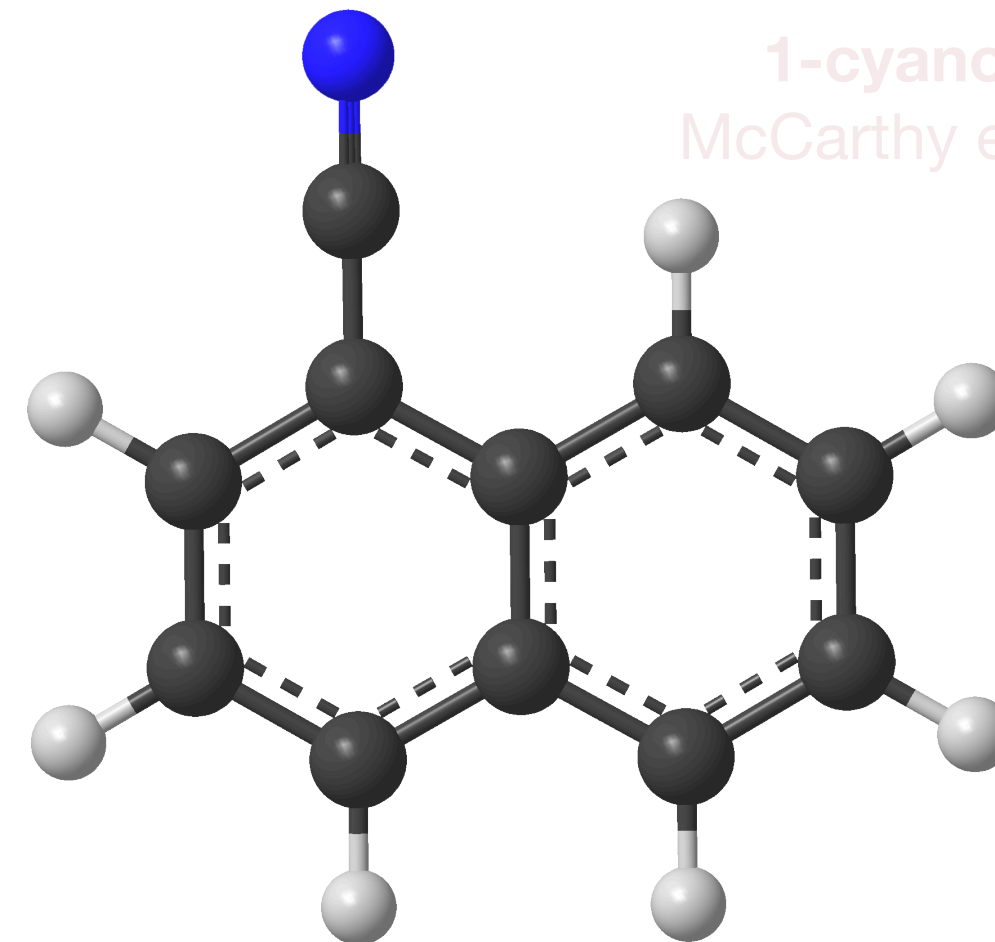
Lee et al. 2021 ApJL 908, L11

Vinylcyanoacetylene

Lee et al. 2021 ApJL 908, L11

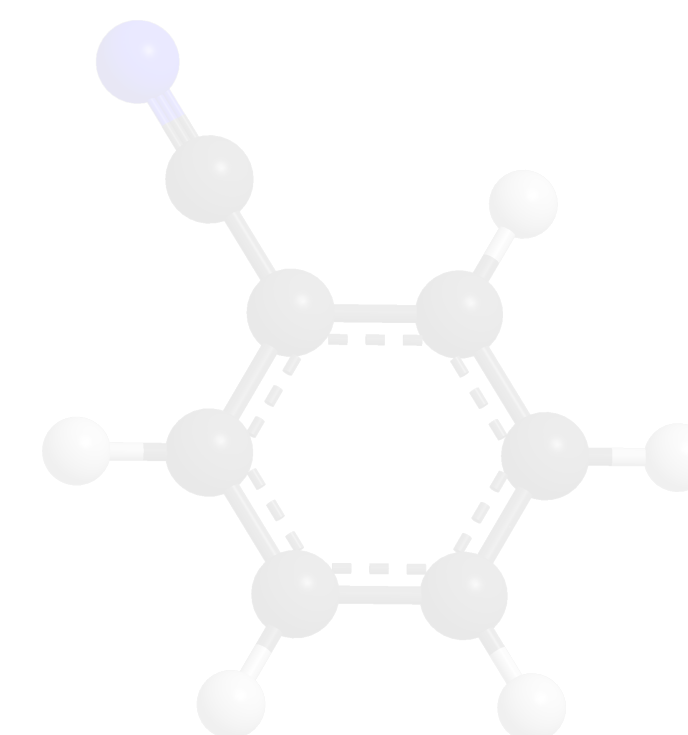
1-cyano-1,3-cyclopentadiene

McCarthy et al. 2021 Nat. Ast. 5, 176



Benzonitrile

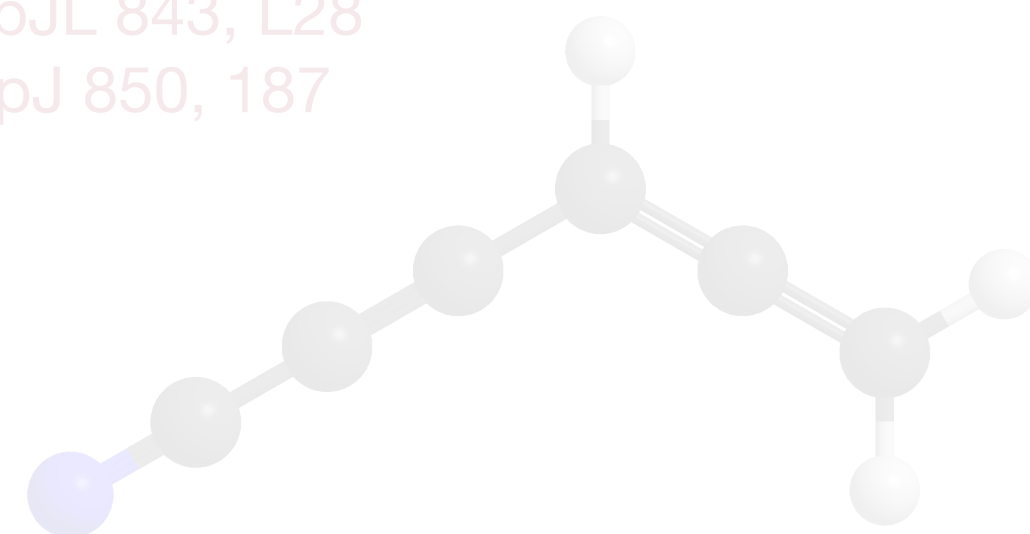
McGuire et al. 2018 Science 359, 202



HC₇O

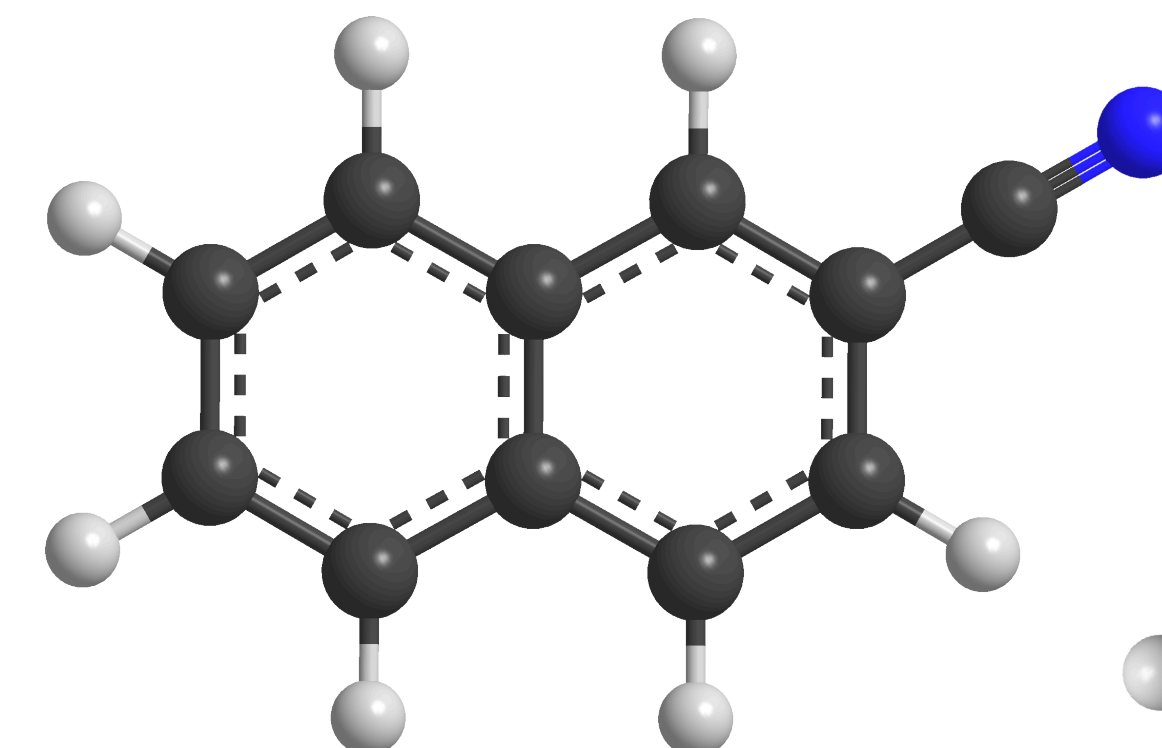
McGuire et al. 2017 ApJL 843, L28

Cordiner et al. 2017 ApJ 850, 187



Cyanoacetyleneallene

Shingledecker et al. 2021 A&AL, 652, L12

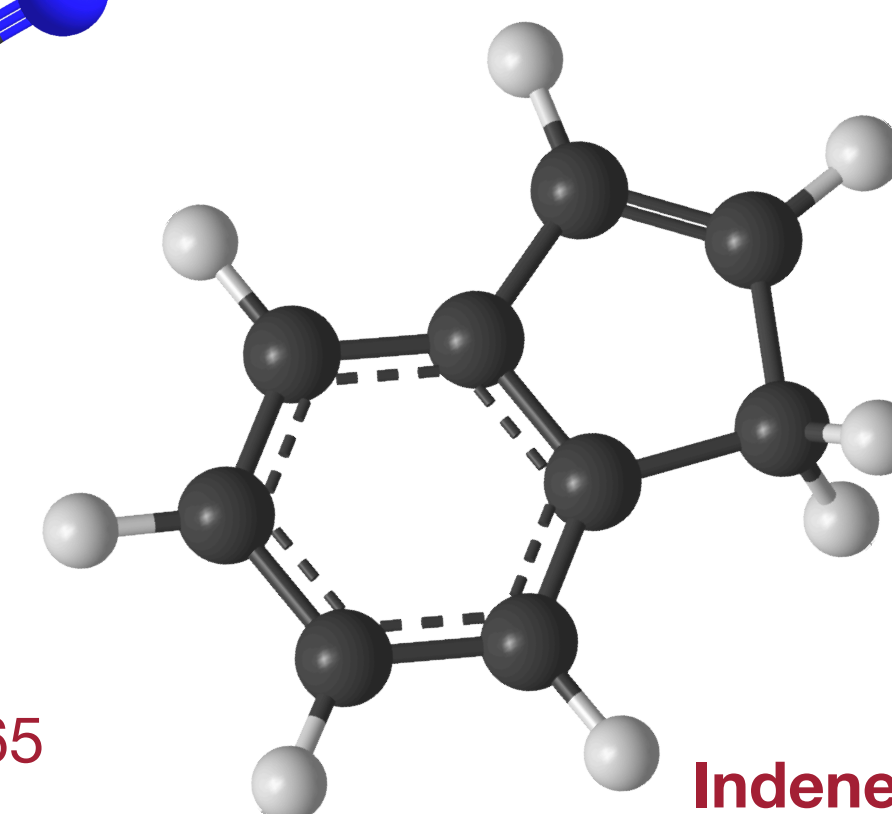


2-cyanonaphthalene

McGuire et al. 2021 Science 371, 1265

1-cyanonaphthalene

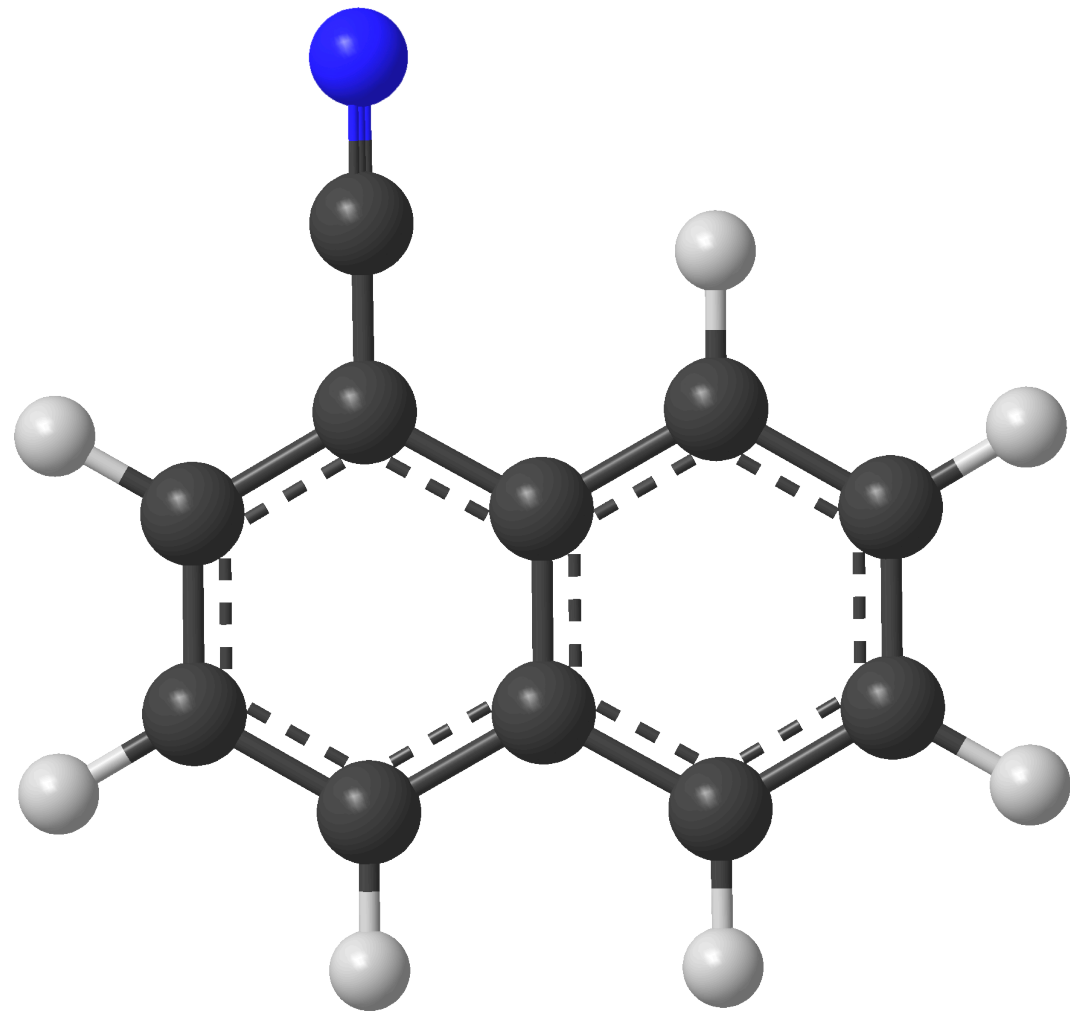
McGuire et al. 2021 Science 371, 1265



Indene

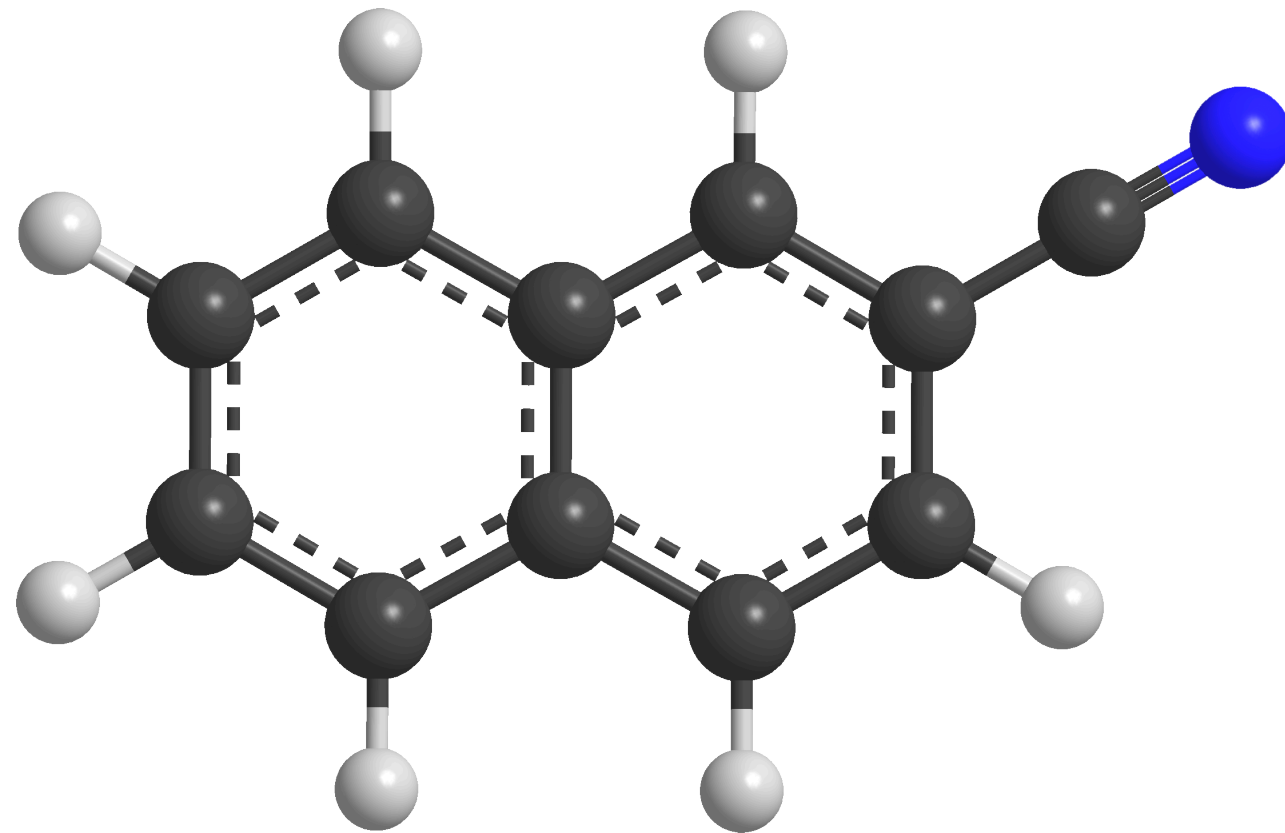
Burkhardt et al. 2021 ApJL 913, L18

GOTHAM: NEW MOLECULES



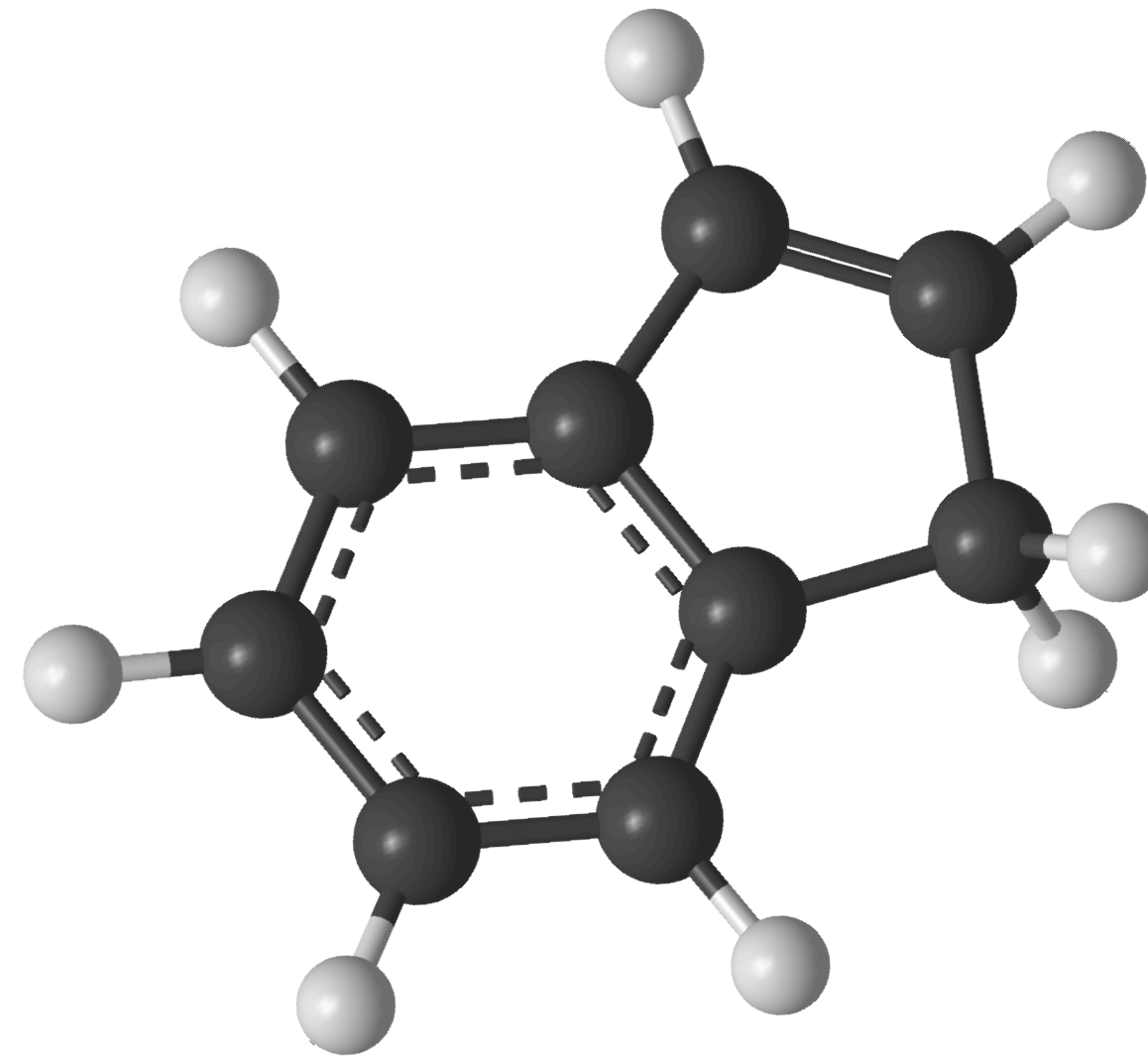
1-cyanonaphthalene

McGuire et al. 2021 Science 371, 1265



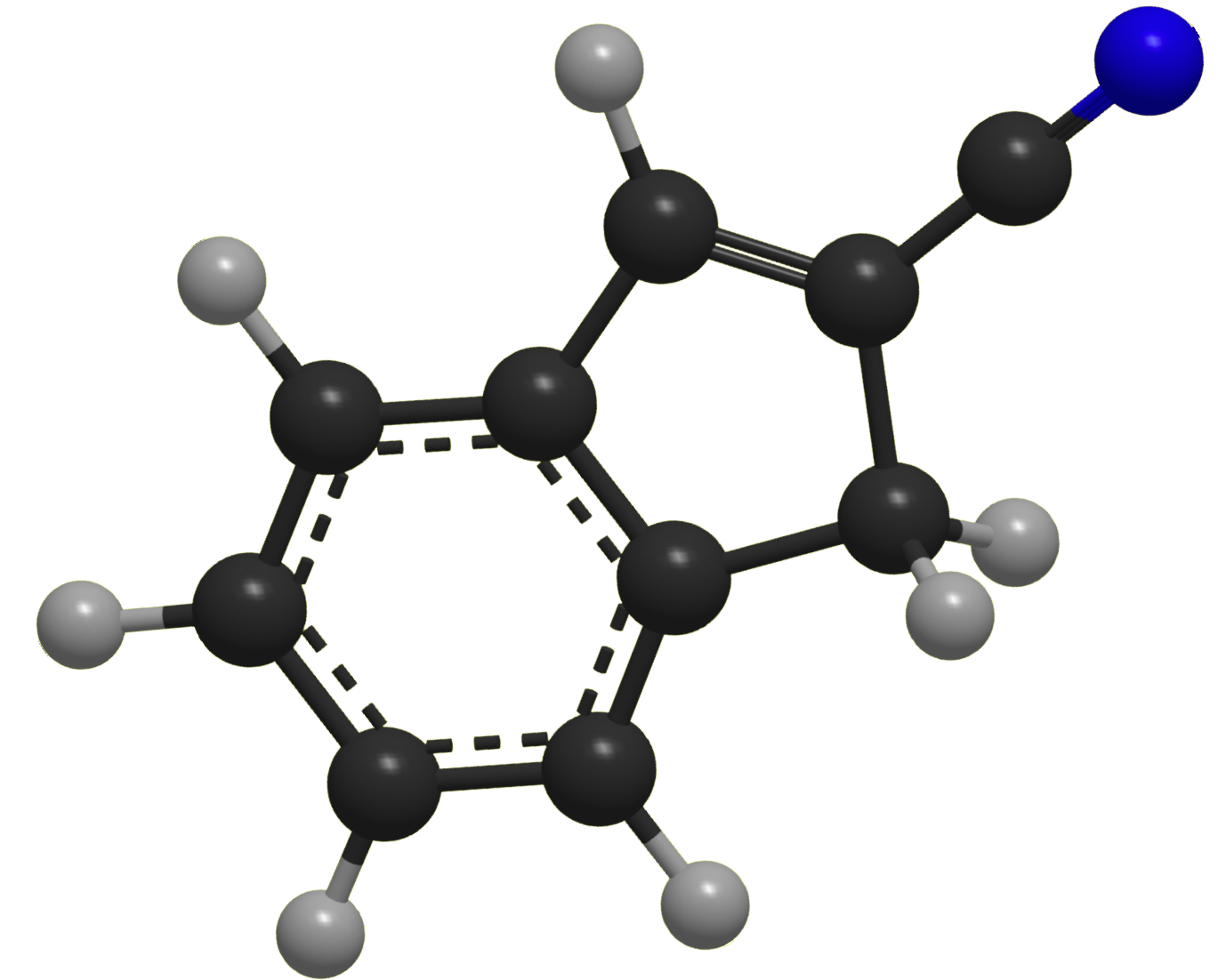
2-cyanonaphthalene

McGuire et al. 2021 Science 371, 1265



Indene

Burkhardt et al. 2021 ApJL 913, L18



2-cyanoindene

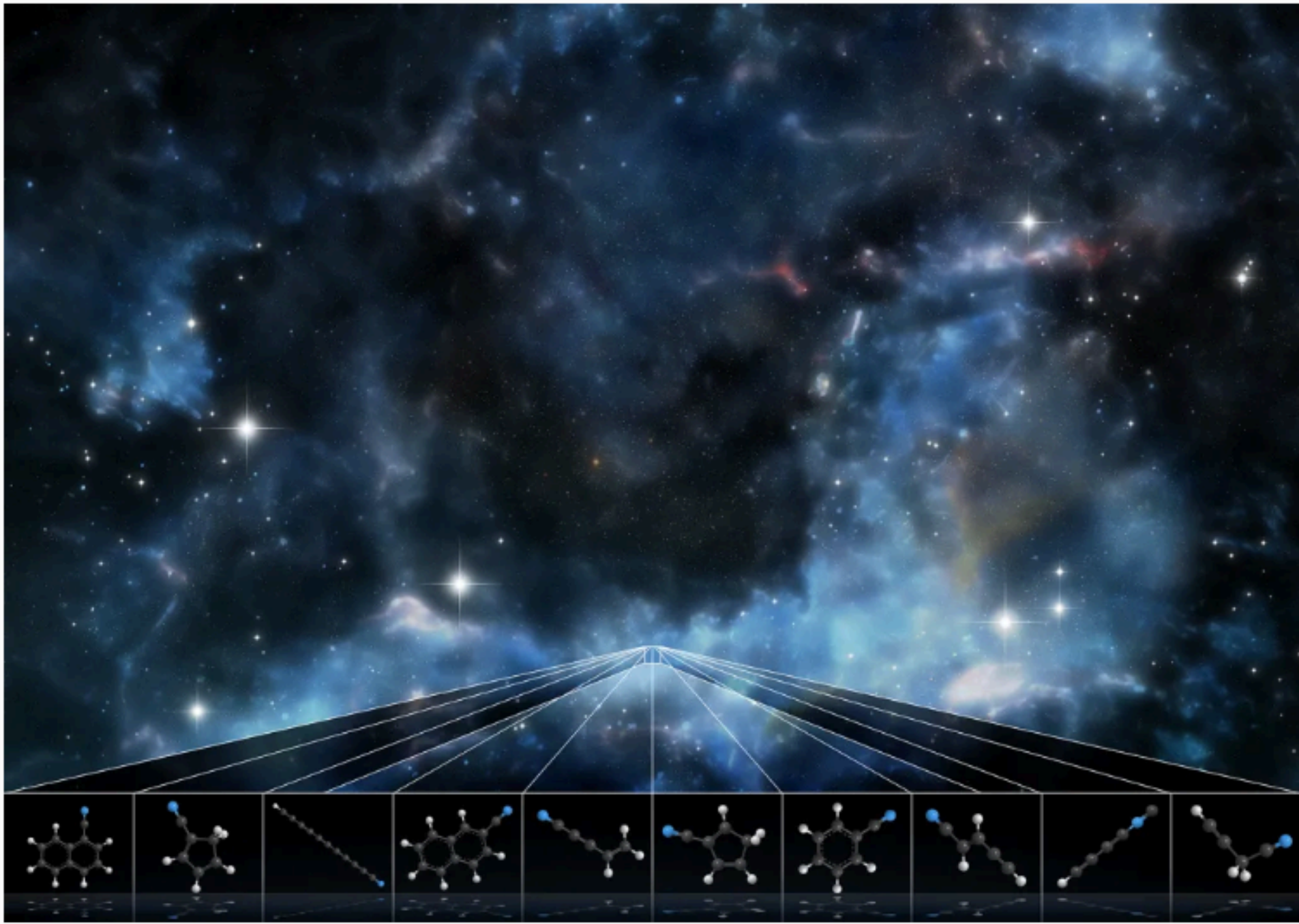
Sita & Changala et al. 2022 ApJ, accepted

WHAT A USELESS STAR

Scientists uncover warehouse-full of complex molecules never before seen in space

Posted on 2021-03-18 at 2:00 pm.
Written by [Jill Malusky](#)

Radio observations of a cold, dense cloud of molecular gas reveal more than a dozen unexpected molecules



Within the place the place we discovered them, there is no such thing as a star, so both they're being constructed up in place or they're the leftovers of a useless star
- Brett (Apparently)

The researchers then used the *Inexperienced Financial Institution Telescope*
(Green) (Bank)

The analysis staff additionally contains scientists from a number of different establishments, together with the

*College of Virginia
Nationwide Radio Astronomy Observatory
NASA's Goddard House Flight Middle.*
(Space) (Center)

Science Scales Linearly With Bandwidth

Broadband capabilities at
high spectral resolution turn
Large Programs into **small proposals**

Boston Sunday Globe November 15, 1970

Secrets of creation hunted

Radio scopes listen on rim of universe

Radio telescopes can see more than 10 times farther into space than optical telescopes. They were developed as an offshoot of radar equipment used during World War II, and were received by scientists with all the glee of a child confronted by a fascinating new toy.

Radio astronomy is essentially the same science as regular astronomy — the study of celestial bodies. But it is so much more sophisticated than astronomy that the interrelationship is like that between calculus and arithmetic. For radio astronomy's prime tool, the radio telescope, is to a regular optical telescope as an optical telescope is to a magnifying glass.

McGuire Group

Alex Byrne
Zach Fried
Hannah Shay
Dr. Gabi Wenzel (Soon!)
Dr. Ci Xue

