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Search for complex organic molecules in space

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Search for complex organic molecules in space

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Abstract. It was 1969 when the first organic molecule in space, H₂CO, was discovered. Since then many organic molecules were discovered by using the NRAO 11 m (upgraded later to 12 m), Nobeyama 45 m, IRAM 30 m, and other highly sensitive radio telescopes as a result of close collaboration between radio astronomers and microwave spectroscopists. It is noteworthy that many famous organic molecules such as CH₃OH, C₂H₅OH, (CH₃)₂O and CH₃NH₂ were detected by 1975. Organic molecules were found in so-called hot cores where molecules were thought to form on cold dust surfaces and then to evaporate by the UV photons emitted from the central star. These days organic molecules are known to exist not only in hot cores but in hot corinos (a warm, compact molecular clump found in the inner envelope of a class 0 protostar) and even protoplanetary disks.

As was described above, major organic molecules were known since 1970s. It was very natural that astronomers considered a relationship between organic molecules in space and the origin of life. Several astronomers challenged to detect glycine and other prebiotic molecules without success. ALMA is expected to detect such important materials to further consider the exogenous delivery hypothesis.

In this paper I summarize the history in searching for complex organic molecules together with difficulties in observing very weak signals from larger species. The awfully long list of references at the end of this article may be the most useful part for readers who want to feel the exciting discovery stories.

1. Introduction

Molecules exist in a variety of physical conditions of the Universe. It was in 1940 when unidentified UV absorption lines were attributed to CH and CN in diffuse interstellar clouds [1]. This was the first report of molecules in space. In early 1930s radio astronomy opened new eyes to the Universe. In 1963 the OH molecule was discovered by a radio telescope [2]. As of December 2015 more than 190 molecules were detected or reported, primarily by means of radio astronomical observations, in interstellar clouds, circumstellar envelopes, and even external galaxies. The smallest and the lightest molecule is H₂. The longest and the heaviest molecule is HC₁₁N with its molecular weight of 147 [3]. A list of molecules in space may be found at, e.g., the Cologne Database for Molecular Spectroscopy (CDMS) [4].

Molecules in space may be classified into several categories: simple molecules, molecular ions, radicals, ring molecules and stable molecules. Simple molecules can be seen in a variety of sources. Among them, the most abundant molecule is H₂. Indeed around 99.99 % of molecules in space are H₂. The next abundant molecules are H₂O and CO whose relative abundances to H₂ are about 10⁻⁴. H₂O, CO and CO₂ are ubiquitous molecules in the solid phase; these molecules in dust mantles are often observed in absorption towards bright IR sources. Molecular ions and radicals are characteristic for molecules in space, since these are so-called “short-lifetime”



molecules. Under the terrestrial physical conditions where the mean free time is the order of milliseconds such “short-lifetime” molecules react and are converted into other species immediately they are formed. However, under the interstellar and circumstellar conditions where the mean free time is typically of the order of a year, such “short-lifetime” molecules can survive for a long time. It is now known that molecular ions play an important role in the gas-phase where “ion-molecule” reactions can successfully explain the formation of many major molecules in space.

Large organic molecules, the primary topics of this paper, belong to “Stable Molecules”. Many of large organic molecules are the closed-shell molecules, and many of them, such as CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, exist stably under the standard terrestrial conditions. Past studies have shown that many of large organic species are formed on cold, dust grains through the hydrogenation of small gas-phase molecules. For example, gas-phase CO is adsorbed onto dust grains. Since the hydrogen atoms on the dust surface can move quickly through the “tunneling effect”, CO is converted to H_2CO , and ultimately to CH_3OH . When a star is formed in the center of a molecular cloud core, the solid-phase CH_3OH molecules may be heated by the UV photons from the central star and evaporated back to the gas-phase.

From now I will summarize the detection history of such large organic molecules in space. In this paper organic molecules refer primarily to carbon-bearing species except for a few species (e.g., CO) which have been regarded “inorganic” traditionally.

2. Detection History: Between 1969 and 1979

Table 1. Organic Molecules Detected between 1969 and 1979.

Year Reported	Species					
1969	H_2CO [5]					
1970	CH_3OH [6]					
1971	CH_3CN [7]	HC_3N [8]	HCOOH [9]	NH_2CHO [10]	HCN [11]	
1972	HNCO [12]					
1973	CH_3CHO [13]	H_2CS [14]	CH_2NH [15]			
1974	$(\text{CH}_3)_2\text{O}$ [16]	CH_3NH_2 [17]	C_2H [18]			
1975	CH_2CHCN [19]	$\text{C}_2\text{H}_5\text{OH}$ [20]	HCOOCH_3 [21]	NH_2CN [22]		
1976	HC_5N [23]	C_2H_2 [24]				
1977	$\text{C}_2\text{H}_5\text{CN}$ [25]	H_2CCO [26]	C_3N [27]			
1978	HC_7N [28]	HC_9N [29]				
1979	CH_3SH [30]	HNCS [31]				

Table 1 shows a list of molecules reported detected between 1969 and 1979. 1969 is the year when the first organic polyatomic molecule, H_2CO , was detected [5] towards many galactic and extragalactic sources. Prior to the detection of H_2CO , the first “large” millimeter-wave telescope, the 11 m radio telescope of the National Radio Astronomy Observatory (NRAO), started its operation in 1968. The NRAO 11 m radio telescope was one of pioneering telescopes; it discovered CO [32], CH_3CN [7], HCN [11], HNCO [12], $(\text{CH}_3)_2\text{O}$ [16], C_2H [18], $\text{C}_2\text{H}_5\text{OH}$ [20], NH_2CN [22], $\text{C}_2\text{H}_5\text{CN}$ [25], H_2CCO [26], C_3N [27], and HNCS [31] in the 1970s. It was in the 1970s when other countries joined the “molecular hunting”. Australia used the Parkes 64 m radio telescope in detecting H_2CS [14], CH_2NH [15], CH_2CHCN [19] and HCOOCH_3 [21]. Canada succeeded in detecting “long carbon-chain molecules” such as HC_5N [23], HC_7N [28],

and HC₉N [29]. Japan constructed the 6 m millimeter-wave telescope, and succeeded to discover CH₃NH₂ [17].

It should be stressed that many organic molecules were already detected in the 1970s. It is well known that CH₃OH is widespread in a variety of sources; CH₃OH masers are commonly observed towards young, star forming regions. Large organic molecules, such as CH₃CN, CH₃CHO, (CH₃)₂O, NH₂CHO, are usually observed towards dense and hot regions, *i.e.*, hot cores and/or hot corinos.

There was an important reason why such successful results were obtained in the early days of radio astronomy – interdisciplinary collaboration between radio astronomy and microwave spectroscopy. In the reference list at the bottom of this paper, we can find many famous microwave spectroscopists: Gottlieb, Thaddeus, Brown, Godfrey, Lovas, Winnewisser, Kroto and Oka. Oka made a great contribution in predicting transition frequencies for HC₉N and HC₁₁N [33]. Immediately after the discovery of HC₇N, Oka extrapolated the molecular constants of HCN, HC₃N, HC₅N and HC₇N toward predicting molecular constants of longer cyanopolyynes HC₉N and HC₁₁N. HC₉N was successfully discovered based on the prediction! [29] Such a prediction was not possible without detailed knowledge on the microwave spectroscopy, and it was an epoch-making proof that close interdisciplinary collaboration was so fruitful not only for radio astronomy but microwave spectroscopy. For microwave spectroscopists, the extreme condition of the interstellar space is ideal in studying very unstable “short-lifetime” molecules, such as molecular ions and radicals. It was possible for microwave spectroscopists to measure, for example, very small hyperfine splittings, to study very detailed intra-molecular interactions that were not possible in the laboratories.

3. Detection History: 1980s

Table 2. Organic Molecules Detected in the 1980s.

Year Reported	Species			
1980	none			
1981	C ₂ H ₄ [34]	C ₄ H [35]	CH ₃ C ₂ H [35]	HOCO ⁺ [36]
1982	none			
1983	none			
1984	CH ₃ C ₃ N [37]	CH ₃ C ₄ H [38, 39]		
1985	C ₃ O [40]	<i>c</i> -C ₃ H ₂ [41]	<i>l</i> -C ₃ H [42]	
1986	C ₅ H [43]	C ₆ H [44]	HCNH ⁺ [45]	
1987	(CH ₃) ₂ CO [46]	CCS [47]	C ₃ S [48]	<i>c</i> -C ₃ H [49]
1988	C ₃ [50]	CH ₃ NC [51]	HCCCHO [52]	CH ₂ CN [53]
1989	C ₅ [54]	C ₄ Si [55]		

Table 2 shows a list of molecules reported detected between 1980 and 1989. As is seen in this table, fewer molecules were detected for a few years in the early 80s. Comparing with the exciting ten years in the 70s, some people rumored that no more new molecules would be detected. Such the situation was changed after the three very large millimeter-wave telescope started to operate: the Onsala 20 m telescope in Sweden, the Nobeyama 45 m telescope in Japan and the IRAM 30 m telescope in Spain. The Onsala group made the first extensive “spectral line surveys” towards Orion KL and IRC+2016 between 72.2 and 91.1 GHz [56], which reported approximately 170 lines from 24 known molecules towards Orion KL and 45 lines from 12 molecules towards IRC+10216.

Followed by the successful spectral line survey project at the Onsala Space Observatory, the Nobeyama and the IRAM groups started their wide-band line survey projects. The Nobeyama 45 m telescope covered very wide frequency ranges between 1.4 GHz and 116 GHz. However the Nobeyama group concentrated their spectral line surveys between 8.8 and 116 GHz. Especially the 7 mm range was covered only by the 45 m telescope. Further the telescope was equipped with the 16 000 channel radiospectrometers with frequency resolutions of 37 kHz (high-resolution) and 250 kHz (wide-band). Thus it was possible for the 45 m telescope to observe cold, dark clouds, such as TMC-1 where the typical line width was around 0.5 km s^{-1} . The spectral line survey results towards TMC-1, that covered between 8.8 and 50 GHz, contained 414 lines from 38 species including 11 new interstellar molecules [57]. The Nobeyama group was successful in detecting many new interstellar molecules: C_3O [40], C_6H [44], CCS [47], C_3S [48], $c\text{-C}_3\text{H}$ [49], HCCCHO [52], CH_2CN [53] and C_4Si [55] only in the 80s.

The IRAM 30 m telescope group made the extensive spectral line survey between 1 and 3 mm ranges towards IRC+10216. In the 80s they discovered C_5H [43], $(\text{CH}_3)_2\text{CO}$ [46], CH_3NC [51] as well as several metal halides (NaCl , AlCl , KCl and AlF) [58]. Many unidentified lines observed by the IRAM 30 m telescope were later identified to be $c\text{-SiC}_2$ [59]. $c\text{-SiC}_2$ was the first molecular ring. It was curious to see that some microwave spectroscopists resisted to accept the identification since three-membered ring molecules were thought to have much higher energy than their linear forms. It was demonstrated that the ring form of the SiC_2 molecule has much lower energy than its linear form; it is the lowest energy isomer.

As is easily seen many molecules discovered by the Nobeyama 45 m and the IRAM 30 m telescopes are linear carbon-chain species. It was established in the 80s that linear carbon-chain molecules are important constituents in the interstellar and circumstellar environment.

4. Detection History: 1990s

Table 3. Organic Molecules Detected in the 1990s.

Year Reported	Species					
1990	none					
1991	C ₂ O [60]	<i>l</i> -C ₃ H ₂ [61]	<i>l</i> -C ₄ H ₂ [62]	HCCN [63]		
1992	HCCNC [64]	HNCCC [65]				
1993	none					
1994	C ₆₀ ⁺ [66]	H ₂ CN [67]	HC ₃ NH ⁺ [68]			
1995	CH ₂ [69]					
1996	C ₈ H [70]	H ₂ COH ⁺ [71]				
1997	<i>l</i> -C ₆ H ₂ [72]	C ₇ H [73]	<i>c</i> -C ₂ H ₄ O [74]	CH ₃ COOH [75]	HC ₁₁ N [3]	
1998	C ₅ N [76]					
1999	none					

Table 3 shows a list of molecules reported detected between 1990 and 1999. Many new molecules were discovered primarily by using the Nobeyama 45 m and the IRAM 30 m telescopes. Researchers were able to detect less abundant species since these telescopes equipped with very sensitive Superconductor-Insulator-Superconductor (SIS) receivers since late 1980s. In the late 90s several complex organic molecules were detected as well as linear carbon-chain molecules. In some cases such complex organic molecules are higher energy isomers of already known species. For example, $c\text{-C}_2\text{H}_4\text{O}$ [74] is a higher energy isomer to $\text{C}_2\text{H}_5\text{OH}$ and CH_3COOH [75] is an higher

energy isomer to HCOOCH_3 . Further the detection of HCCNC [64] and HNCCC [65], which are isomers to HC_3N , prompted detailed studies regarding the formation of these carbon-chain species.

5. Detection History: Between 2000 and 2015

Table 4. Organic Molecules Detected between 2000 and 2015.

Year Reported	Species			
2000	CH_2OHCHO [77]	CH_3 [78]		
2001	<i>c</i> - C_6H_6 [79]	CH_2CHOH [80]	<i>l</i> - HC_4H [79]	<i>l</i> - HC_6H [79]
2002	$(\text{CH}_2\text{OH})_2$ [81]			
2003	none			
2004	CH_2CHCHO ? [82]	$\text{CH}_3\text{CH}_2\text{CHO}$ [82]	<i>l</i> - HC_4N [83]	
2005	$\text{C}_2\text{H}_5\text{OCH}_3$? [84]			
2006	<i>c</i> - $\text{H}_2\text{C}_3\text{O}$ [85]	CH_2CCHCN [86]	CH_2CNH ? [87]	$\text{CH}_3\text{C}_5\text{N}$ [88]
	CH_3CONH_2 [89]	C_6H^- [90]		
2007	C_4H^- [91]	C_8H^- [92]	CH_2CHCH_3 [93]	
2008	HCOCN [94]	$\text{NH}_2\text{CH}_2\text{CN}$ [95]		
2009	$\text{C}_2\text{H}_5\text{OCHO}$ [96]	HCNO [97]	HOCN [98]	HSCN [99]
	<i>n</i> - $\text{C}_3\text{H}_7\text{CN}$ [96]			
2010	C_{60} [100]	C_{70} [100]		
2011	none			
2012	CH_3O [101]	HNCNH [102]		
2013	CH_3CHNH [103]	$\text{CH}_3\text{COOCH}_3$ [104]	H_2CNO^+ ? [105]	HNCHCN [106]
2014	C_2N [107]	$\text{CH}_3\text{CH}_2\text{SH}$? [108]	<i>i</i> - $\text{C}_3\text{H}_7\text{CN}$ [109]	
2015	CH_3NCO [110]	HCCO [111]	NCCNH^+ [112]	

Table 4 shows a list of molecules reported detected between 2000 and 2015. Note that a question mark (?) in this Table denotes that the detection was claimed but not yet confirmed. It is readily seen that many very complex organic molecules are detected since the Green Bank Telescope (GBT) started its operation in 2000. Further IRAM 30 m telescope has been very active in the “molecular hunting”; it has detected many new molecules even after its 30th anniversary

An epoch-making event was the discovery of glycolaldehyde (CH_2OHCHO) in 2000 [77]. According to the detection report [77], the generic form of sugar can be expressed as $(\text{H}_2\text{CO})_n$ ($n \geq 2$). Because glycolaldehyde has the form of $(\text{H}_2\text{CO})_2$, it was regarded as the simplest sugar in space. Thus this discovery had led astronomers to seriously search for other “prebiotic molecules” in space. It was unfortunate that the correct generic form of sugar is $(\text{H}_2\text{CO})_n$ ($n \geq 3$), not 2 !, *i.e.*, glycolaldehyde is not a sugar.

A large complex organic molecule generally shows very weak line intensities due to its very large rotational partition function. Thus the sensitivity of a telescope is crucial in searching for such weak lines. Further it is required to detect as many lines in a wide frequency range as possible to enable reliable excitation analysis prior to claiming secure detection. In this regard the GBT group has conducted the PRIMOS project [113], which has resulted in detecting many large complex organic molecules.

6. Search for Prebiotic Molecules

Nonetheless many astronomers have been searching for prebiotic molecules based on a hypothesis that simple bio-molecules are formed in the interstellar space, which would then be delivered to early Earth (planets) by comets and/or meteorites (“exogenous delivery”). Indeed the StarDust mission successfully detected the simplest amino acid, glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), in the ejecta from Comet Wild 2 [114].

Unfortunately astronomical searches for interstellar glycine and other prebiotic molecules have not yet been successful as of today. Since we already know that proposed precursors to glycine (*e.g.*, $\text{NH}_2\text{CH}_2\text{CN}$ and CH_3NH_2) exist in the interstellar space, it is expected to detect amino acids, precursors to nucleobases, and other prebiotic molecules by means of the collecting power by the ALMA telescope.

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