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INTERSTELLAR MOLECULES

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The first molecules in the interstellar medium were found during the 1930's starting with the diffuse bands discovered by Merrill. These rather broad lines in the optical spectrum have yet to be identified with a particular molecule, although there are now about 25 diffuse bands known. At about the same time that Merrill found these bands, Adams and Dunham discovered lines of CH, CH^+, and CN. The identification of these lines took several years and in the case of CH^+, Douglas and Herzberg undertook laboratory experiments to generate CH^+ and obtain its optical spectrum.

Spectral line observations in radio astronomy began with the detection of the 21 cm hydrogen emission line by Ewen and Purcell in 1951. The recombination lines of ionized hydrogen were observed both by Kardashev in Russia and by Mezger around 1964. The radical OH was found in 1963 by Weinreb, Barrett, Meeks, and Henry in absorption against Cas A. This followed many years of searching for OH and the detection was primarily due to a new type of autocorrelation receiver developed by Sandy Weinreb. In 1965 the anomalous OH emission was discovered simultaneously by a group at Berkeley (Weaver, Dieter, and Williams) and a group at Harvard (Gunderman and Lilley). These peculiar emission lines were originally called "mysterium" because of their narrow line widths, large intensities, and strange line ratios. It is now known that these lines are produced in interstellar masers but the exact pumping mechanism is still hotly debated.

The current surge of new molecular line discoveries began in 1968, when Lew Snyder and Dave Buhl became interested in searching for interstellar water vapor. At the same time Charles Townes and Jack Welch at Berkeley began developing a receiver for ammonia. The frequencies of the two molecular lines are very close and using the same receiver Townes and Welch detected NH_3 in November, 1968 and

H_2O in December, 1968. The ammonia line exhibited relatively normal emission on at least 2 lines with an excitation temperature of 23° K The excitation temperature is defined by the population distribution among the various energy levels. The water exhibited very anomalous excitation similar to the masering OH lines. Antenna temperatures as high as 4500° K have been measured on the 140-foot telescope and the angular sizes as determined from VLB experiments are less than 0.01"

The discovery of formaldehyde (H_2CO) in March, 1969 by Snyder, Buhl, Zuckerman and Palmer started numerous searches for other complex molecules. This molecule showed a normal absorption spectrum everywhere except in the dark clouds. In these dusty regions an absorption line was seen without a background source, thus indicating that the molecule was absorbing radiation from the 3° K microwave background. This situation is the reverse of the maser where the upper state of a molecule becomes over-populated. In this case the lower state is being over-populated, giving an excitation temperature of less than 1° K. This can be accomplished under rather special circumstances by collisional pumping (Townes and Cheung).

In April, 1970 Penzias, Wilson, and Jefferts found CO and CN using the 36-foot telescope in Tucson. The CO cloud in Orion was particularly interesting in that it was 30' of arc in diameter (approximately the same angular size as the Moon). The molecule has a small dipole moment which means weak radiation interaction. The antenna temperature of 40° K requires that the excitation temperature of the molecule be greater than 100° K over a distance of 5 pc. A similar situation occurs in the NH_3 cloud in the galactic center where an excitation temperature of 50° K is maintained in a cloud 30 pc in diameter. How these high temperatures are produced over such large distances is an interesting astrophysical problem.

Subsequently hydrogen cyanide (HCN) was detected in a number of galactic sources by Lew Snyder and Dave Buhl. This molecule is interesting because it is a by-product of reactions which produce complex amino acids out of H_2O, NH_3, and CH_4. Laboratory experiments demonstrating these reactions were originally done by Stanley Miller and followed up by Cyril Ponnamperuma at NASA Ames.

Another significant interstellar molecule was found by Barry Turner. This molecule, cyanoacetylene (HC_3N) is also important in organic synthesis. The present list now totals 22 interstellar molecules detected. Our present knowledge of the interstellar medium indicates that amino acids can be produced in interstellar clouds, and that complex organic chemistry may be an important part of the evolution of clouds into protostars and planets.

The pumping mechanisms for H_2CO, H_2O, and OH are not very well understood despite a large amount of theoretical work by Turner, Litvak, Solomon, Thaddeus, Townes, Cheung, Hills, and others. Among the dozen molecules already discovered, two are masering and one is refrigerating. These two processes are not completely independent of each other, since energy dumped into the molecule at one frequency must be radiated away at another frequency. The formaldehyde gives an example of how a molecule cloud is trying, albeit unsuccessfully, to cool off the Big Bang radiation.

The refrigerator works by pumping a molecule by collisions or radiation into a higher state. The molecule will spontaneously decay preferentially into the lower state of a transition. Absorption can then occur whenever the molecule encounters a photon or passing hydrogen atom. In the case of the hydrogen atom it is slowed down or cooled by the encounter.

Collisional pumping is another means of cooling the hydrogen by using it directly to pump the molecule. For example, if the H_2O molecule is pumped by collisions, the kinetic energy of the hydrogen atoms is absorbed and stored in the H_2O molecules by exciting them into the upper state. The masering transition then radiates away the kinetic energy which was provided by the hydrogen atoms.

Such an interstellar refrigerator is very useful in cooling clouds of hydrogen during the early stages of condensation into a protostar. It is interesting that the rate of energy released during the collapse of an average cloud is equal to the power being radiated by some of the strong H_2O masers. In addition, there are many transitions of these molecules in the infrared region of the spectrum which can only be observed from balloons, satellites, or high flying aircraft. It is likely that the formaldehyde molecule is radiating away in the infrared the energy absorbed at the 6 cm transition. Hence, interstellar refrigerators and masers may be a very common feature of the infrared spectrum.

The number densities of the molecules which have been found over the past three years are much larger than anyone expected. This has upset many established concepts of the interstellar medium, particularly the notion that nothing more complicated than diatomic molecules could exist because cosmic rays, stellar UV, and high energy particles would dissociate them immediately. What is becoming increasingly apparent is that exactly the opposite occurs. Rather than being under-abundant, the large heavy molecules are actually over-abundant compared with expected abundances based on the simpler diatomics. Whether this is because they exist in regions protected by dust grains or just simply due to a high rate of formation is not yet known. In some cases reasonable molecules such as ketene (H_2C_2O) and NO and SO and SH have been searched for without success. This either means that these molecules don't exist or, more likely, that the molecules are there but the excitation conditions are such that the line doesn't appear in either emission or absorption. The presence or absence of certain types of molecules may be clues to the direction in which the chemical evolution is going. This is very important in discerning the pattern which nature chooses to form complex organic molecules. Such patterns may eventually provide an understanding of the origin of life on the Earth and possibly on other planets within the Galaxy.

Table II lists the molecules found up till now, including some recent heavy organics which have not been published yet. The similarity to products obtained in organic synthesis of amino acids and other important prebiological molecules is quite striking. It suggests that there is a fundamental direction in these chemical reactions which dominates the chemistry even under the severe conditions of interstellar space. Some of the heaviest molecules are found only in the direction of the galactic center, probably a consequence of the higher density and longer path length in this region.

For most of these large molecules we are working at the limit of sensitivity for present telescopes and receivers. Improvements in radiometer sensitivity, particularly at wavelengths less than 1 cm will provide the best chance for detecting molecules such as amino acids, long chain sugars, nitriles and other prebiotic molecules. Short wavelength radio receivers have a potential increase in sensitivity of between 10 and 100. In addition, the millimeter wave transitions of large molecules with quantum numbers up to and probably beyond J = 10 are much stronger than lower lying centimeter wave transitions. This is related to three factors: the increasing strength of the transitions with frequency, the better spatial resolution of millimeter telescopes, and the peculiar excitation conditions of the interstellar medium which appear to preferentially excite millimeter wave transitions. The next few years should see an enormous increase in the list of interstellar molecules, particularly the millimeter wave lines. The most important problem is to answer the very intriguing questions raised by these new molecular line discoveries, namely: What is the dominant chemistry and physics of the cool interstellar clouds?

Molecular Abundances

Molecule	Observed	Expected
CO	1000	1/3,000
OH	1	1
NH_3	1	1/10
CN	1	1/30,000
H_2CO	1/10	1/3,000
HCN	1/30	1/30,000

Cosmic Atomic Abundances

O/H	7×10^{-4}
N/H	9×10^{-5}
C/H	3×10^{-4}

Table II

MOLECULES FOUND IN THE INTERSTELLAR MEDIUM

Year	Molecule	Symbol	Wavelength	Telescope	Reference
1937		CH	4300 Å	Mt. Wilson 100 in	Dunham
1940	Cyanogen	CN	3875 Å	Mt. Wilson 100 in	Adams
1941		CH^+	3745-4233 Å	Mt. Wilson 100 in	Adams
1963	Hydroxyl	OH	18, 6.3, 5.0, and 2.2 cm	Lincoln Lab 84 ft	Weinreb et al., 1963
1968	Ammonia	NH_3	1.3 cm	Hat Creek 20 ft	Cheung et al., 1968
1968	Water	H_2O	1.4 cm	Hat Creek 20 ft	Cheung et al., 1969
1969	Formaldehyde	H_2CO	6.2, 2.1, 1 cm 2.1, 2.0 mm	NRAO 140 ft	Snyder et al., 1969
1970	Carbon Monoxide	CO	2.6 mm	NRAO 36 ft	Wilson et al., 1970
1970	Cyanogen	CN	2.6 mm	NRAO 36 ft	Jefferts et al., 1970
1970	Hydrogen	H_2	1100 Å	UV Rocket Camera	Carruthers, 1970
1970	Hydrogen Cyanide	HCN	3.4 mm	NRAO 36 ft	Snyder and Buhl, 1971
1970	X-ogen	?	3.4 mm	NRAO 36 ft	Buhl and Snyder, 1970
1970	Cyano-acetylene	HC_3N	3.3 cm	NRAO 140 ft	Turner, 1970
1970	Methyl Alcohol	CH_3OH	36 cm	NRAO 140 ft	Ball et al., 1970
1970	Formic Acid	CHOOH	18 cm	NRAO 140 ft	Zuckerman et al., 1971
1971	Carbon Mono-Sulphide	CS	2.0 mm	NRAO 36 ft	Bell Lab
1971	Formamide	NH_2CHO	6.5 cm	NRAO 140 ft	U. of Illinois
1971	Silicon Oxide	SiO	2.3 mm	NRAO 36 ft	Bell Lab
1971		OCS	2.5 mm	NRAO 36 ft	Bell Lab
1971	Acetonitrile	CH_3CN	2.7 mm	NRAO 36 ft	Bell Lab
1971	Isocyanic Acid	HNCO	3.4 mm, 1.4 cm	NRAO 36 ft	U Va/NRAO
1971	Hydrogen Iso-Cyanide	HNC	3.3 mm	NRAO 36 ft	U Va/NRAO
1971	Methyl-acetylene	CH_3C_2H	3.5 mm	NRAO 36 ft	U Va/NRAO

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