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ABSTRACT
        This booklet is part of an American Astronomical
Society curriculum project designed to provide teaching materials to
teachers of secondary school chemistry, physics, and earth science.
The following topics are covered: the physical conditions in
interstellar space in comparison with those of the earth,
particularly in regard to gas density, temperature, and radiation;
the concept of quantized molecular motion (electronic, vibrational,
rotational), and the corresponding energy ranges of radiation;
spectroscopic methods for identifying molecules in space; the organic
nature of interstellar chemistry; and application of our knowledge of
interstellar molecules to study the birth of stars, the structure and
movement of our galaxy, the history of interstellar matter, and the
origin of the universe and life. Each section is followed by
questions and answers, and an appendix contains suggested student
projects. Also included are a glossary of terms and suggested
reference materials. (MH)

Chemistry Between the Stars

ED133198

NASA
National Aeronautics and
Space Administration

2

CHEMISTRY BETWEEN THE STARS

A curriculum project of the American Astronomical Society

prepared with the cooperation of the

National Aeronautics and Space Administration and the National Science Foundation

by

Richard H. Gammon

National Radio Astronomy Observatory
Charlottesville, Virginia

National Aeronautics and Space Administration
Washington, DC 20546   September 1976

PREFACE

In the past half century astronomers have provided mankind with a new view of the universe, with glimpses of the nature of infinity and eternity that beggar the imagination. Particularly, in the past decade, NASA's orbiting spacecraft as well as ground-based astronomy have brought to man's attention heavenly bodies, sources of energy, stellar and galactic phenomena, about the nature of which the world's scientists can only surmise.

Esoteric as these new discoveries may be, astronomers look to the anticipated Space Telescope to provide improved understanding of these phenomena as well as of the new secrets of the cosmos which they expect it to unveil. This instrument, which can observe objects up to 30 to 100 times fainter than those accessible to the most powerful Earth-based telescopes using similar techniques, will extend the use of various astronomical methods to much greater distances. It is not impossible that observations with this telescope will provide glimpses of some of the earliest galaxies which were formed, and there is a remoter possibility that it will tell us something about the edge of the universe.

The researches of the past 10 years, plus the possibility of even more fundamental discoveries in the next decade, are fascinating laymen and firing the imagination of youth. NASA's inquiries into public interest in the space program show that a major source of such interest is stellar and galactic astronomy. NASA's enabling Act, the Space Act of 1958, lists a primary purpose of NASA, "the expansion of human knowledge of phenomena in the atmosphere and space"; the Act requires of NASA that "it provide for the widest practicable and appropriate dissemination of information concerning its activities and the results of those activities."

In the light of the above, NASA is publishing for science teachers, particularly teachers of secondary school chemistry, physics, and Earth science, the following four booklets prepared by the American Astronomical Society (AAS) with the cooperation of NASA:

The Supernova, A Stellar Spectacle, by Dr. W. C. Straka, Department of Physics, Jackson State University, Jackson, Mississippi.

Extragalactic Astronomy, The Universe Beyond our Galaxy by Dr. Kenneth C. Jacobs, Department of Astronomy, University of Virginia, Charlottesville, Virginia.

Chemistry Between the Stars, by Dr. Richard H. Gammon, National Radio Astronomy Observatory, Charlottesville, Virginia.

Atoms in Astronomy, by Dr. Paul A. Blanchard, Theoretical Studies Group, NASA Goddard Space Flight Center, Greenbelt, Maryland.

5

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TABLE OF CONTENTS

8

A NOTE TO THE TEACHER

This brochure is designed to present in a single unit a new field of astronomy, and is intended for the high school *teacher* of physics, chemistry, astronomy, or earth science courses. Some of the concepts and language may be unfamiliar; the final translation of this material to the appropriate student level is left to you, the teacher. Probably only your best students will be able to read this unit without your interpretation. To aid you in explaining this material to your students, make use of the comprehension questions following sections III through VIII, respectively, the supplemental material at the end of the unit, and especially the section of demonstrations and projects. Many of the ideas for things to do were generated at a teacher-astronomer workshop, sponsored by the National Science Foundation and held in Richmond, Virginia, in June 1974. (Special thanks to Jeanne Bishop and Ed DeJulio for their help in putting these ideas together.) Teachers wishing to contact the author may write him at his present address: Battelle Pacific Northwest Laboratories, Batelle Boulevard, Richland, Washington 99352.

Richard H. Gammon

CHAPTER I

CONCEPTUAL GOALS OF THIS UNIT

To achieve the conceptual goals of this unit, the student should attain a general understanding of the following:

A. The physical conditions in interstellar space in comparison with those of the Earth, particularly in regard to gas density, temperature, and radiation.

B. The concept of quantized molecular motion (electronic, vibrational, rotational); the corresponding energy ranges of radiation (ultraviolet, visible, infrared, radio); the windows of atmospheric transparency.

C. Methods for identifying molecules in space; definition of a spectrum and the information it can give about the chemistry and physical conditions in interstellar dust clouds.

D. The "organic" nature of interstellar chemistry; the kinds of molecules found; some possible ways these molecules are made and destroyed in space, including the role of the interstellar dust grains.

E. Application of our knowledge of interstellar molecules to study the birth of stars, the structure and movement of our galaxy, the history of interstellar matter, and the origin of the universe and of life.

10

CHAPTER II

REVIEW OF BASIC CONCEPTS

Matter may be separated into the simplest substances, called *elements*. Each element is made up of atoms of only one kind. Atoms of different elements may combine chemically to form a *compound*. Any chemical combination of two or more atoms is called a *molecule*. A *mixture* is a combination of different substances that can be separated only by physical means; a compound can be separated into its constituent elements only by chemical means.

The simplest element is hydrogen. Every atom of hydrogen has one (positively charged) *proton* in the nucleus, around which orbits one (negatively charged) *electron*. Atoms of the heavier elements have more protons in the nucleus, as well as a number of neutral particles, called *neutrons*, and a correspondingly greater number of orbiting electrons. The number of protons, the *atomic number*, determines the elemental nature of an atom. Atoms of the same element which have different numbers of neutrons are called *isotopes*. Isotopes are distinguished by *atomic weight*, the sum of the weights of all the individual protons and neutrons in the nucleus.

Energy is the ability to do work. Energy can be classified as *potential* or *kinetic*. Potential energy is, for example, the stored and ready energy of a battery, or a mousetrap. Kinetic energy is the energy of an object in motion — for example, a speeding car. The average kinetic energy of the random motions of molecules in a gas is measured as the gas *temperature*. Except in nuclear reactions, energy is conserved. Energy may be transmitted through empty space in the form of waves of *electromagnetic radiation*. Not only visible light, but also X-rays and radio waves are examples of electromagnetic radiation.

The *frequency* (f) of a wave is the number of wavecrests passing by each second. The *wavelength* (λ) is the distance between consecutive wavecrests. The frequency and wavelength of electromagnetic waves are related through the *speed of light* ($c = 3 \times 10^{10}$ cm per second).

$$\lambda f = c$$

Electromagnetic waves are not continuous but rather are divided (quantized) into small definite amounts of energy called *photons*. The energy (E) of a single photon depends upon the frequency (f) of the radiation as

$$E = hf$$

where h is a fundamental constant of quantum physics called Planck's constant (6.6×10^{-34} joule-sec).

All matter emits a type of electromagnetic radiation called *thermal radiation* since the intensity and wavelength emitted depend upon the temperature of the matter. Hot stars and light bulbs emit white light; cooler stars and toasters emit red light; our bodies send out infrared radiation; and cold gas clouds in space emit radio waves. The cooler the matter, the longer the wavelength of the emitted thermal radiation.

3

Since scientists need to express very large and very small quantities, they use *scientific notation*, expressing numbers in powers of ten; for example, $29\ 700 = 2.97 \times 10^{+4}$, $0.0015 = 1.5 \times 10^{-3}$.

12

4

CHAPTER III

THE NATURE OF INTERSTELLAR SPACE

Our Sun is a typical star, similar to many of the estimated hundred billion stars that together form our galaxy, the *Milky Way*. Viewed from extragalactic space, the Milky Way would look much like the spiral galaxy Andromeda (figure 1), one of our closest neighboring galaxies. Like Andromeda, the Milky Way is a disk-shaped collection of stars, gas, and dust — a galactic phonograph record about 10^5 light years (ly) across, but less than 10^3 ly thick. [One light year is the distance light travels in one year, or about six trillion miles (6,000,000,000,000)!]

The space between the stars is almost empty, each cubic centimeter containing on the average only one hydrogen atom ($n_H \approx 1$ per cm^3). For comparison, the density of the Earth's atmosphere is about 10^{19} molecules cm^{-3}. The galactic gas and dust are not evenly spread throughout space but are collected into patterns of denser material called "spiral arms." In spiral galaxies like our own and Andromeda (figure 1), these arms, clearly traced by bright young stars and lanes of dust, appear to uncoil outward from the center. Our Sun is located in one of these arms at a distance of 30,000 light years from the center. For us, the center of the Milky Way lies in the direction of the constellation Sagittarius (figure 2). The entire, vast collection of stars, gas, and dust pinwheels slowly about its center at such a rate that we complete the galactic merry-go-round once every two hundred million years. (We've gone around once since the age of dinosaurs!)

Keeping in mind this larger view of the Milky Way and our place within it, let's take a closer look at *interstellar space*, the nearly empty space between the stars from which we came. Most of the observed matter in our galaxy has condensed into individual stars, spaced light years apart. To visualize the distance between stars, shrink our Sun to the size of a ping-pong ball, and place it in New York City; then the ping-pong balls representing our neighboring stars would be placed in Colorado!

Stars make up roughly 90 percent of the mass of the Milky Way. The remaining 10 percent of galactic matter not now in the form of stars is scattered unevenly throughout the vast reaches of interstellar space. This stuff between the stars, called *interstellar matter*, collects in great ragged patches of gas and dust called *interstellar clouds*. These clouds fill about 10 percent of interstellar space and range in size from small blobs with a diameter less than 0.1 light year up to enormous blankets of gas stretching across 50 light years or more. Within these clouds, the number density of hydrogen atoms varies from 10 per cm^3 in "thin" clouds to more than 1000 per cm^3 in the denser, darker clouds. Though much more dense than the galactic average of one atom per cm^3, these clouds still represent a nearly perfect vacuum by earthly standards. The temperature within interstellar clouds is very low, less than $100°$ Kelvin, or more than $280°$ below zero Fahrenheit. The 90 percent of interstellar space between the dust clouds is much hotter ($T > 10^3$ K) and emptier ($n_H < 0.1$ per cm^3).

13

Figure 1 Andromeda (M31), a nearby spiral galaxy. Viewed from the perspective of extragalactic space, our own galaxy, the Milky Way, might look something like this, and the Sun would be located about two-thirds of the way out from the center. (Hale Observatory photograph)

15

14

Figure 2 – View of stars and dust clouds toward the galactic center, located in the constellation Sagittarius. (Hale Observatory photograph)

In appearance, interstellar space looks like the sky on a stormy day. The interstellar clouds resemble turbulent storm clouds, swirling streamers and ragged clumps continually evaporating, condensing, and colliding with each other every million years or so. Within these clouds, long known as the birthplace of new stars, a great variety of organic molecules have recently been discovered. To understand how such a rich chemistry might take place in space, we need first to know what kinds of atoms make up the gas and dust in clouds. The cosmic abundances of the most common elements (table I) have been determined from chemical analysis of the Earth's crust, moon rocks, meteorites, and the light reaching us from the Sun and other stars.

Table I
Cosmic Abundances of the Most Common Elements

Element	Symbol	Atomic Weight	Abundance (number of atoms relative to hydrogen)
Hydrogen	H	1	1.0
Helium	He	4	0.1
Carbon	C	12	0.0003
Nitrogen	N	14	0.0001
Oxygen	O	16	0.0007
Neon	Ne	20	0.0003
Magnesium	Mg	24	0.00003
Silicon	Si	28	0.00003
Sulfur	S	32	0.000004
Iron	Fe	56	0.00001
⋮	⋮	⋮	⋮
Uranium	U	238	$\sim 10^{-12}$

The interstellar matter exists in gaseous and solid forms. The gas consists almost entirely of hydrogen (90 percent) and helium (10 percent) in relative amounts that have changed little since the beginning of the universe. The cosmic abundance of elements heavier than helium is constantly increasing as these elements are produced in stars by nuclear fusion reactions at temperatures of more than a million degrees Kelvin. All of the elements heavier than helium together constitute only ~ 0.2 percent of the hydrogen abundance by number of atoms, or about 1 percent by mass. The most abundant of these "heavy" elements are carbon, nitrogen, and oxygen. These three elements are found in the gas, in the elemental atomic form, and also in molecular combination with each other and with hydrogen.

Most of the elements heavier than oxygen are largely missing from the interstellar gas, having frozen out of the gas as small specks of dust called *interstellar grains*. The interstellar matter is gradually being enriched in the heavy elements which make up these grains as new

8

stars form out of the interstellar gas, convert hydrogen to heavier elements, and eventually return this reprocessed matter to interstellar space, sometimes in the violent manner of a stellar explosion (see the unit on supernovae). In this cycle, which takes about 10^8 years, the interstellar dust grains accumulate as a kind of stellar debris or star dust. What are these grains like? Rocky? Ash? Though still not certain, there is good evidence that the interstellar dust grains are a fine grit of mixed sandy and sooty particles of irregular shapes and assorted sizes. These grains are very effective in blocking out starlight, so that to us the clouds of interstellar gas and dust appear as dark silhouettes against the background of surrounding stars (figure 2). For this reason, the astronomer Herschel spoke of the interstellar dust clouds two hundred years ago as "holes in the sky." From the way in which the dust scatters the starlight, astronomers have determined that the dust grains have an average size of ~ 0.1 micron. (One micron is one millionth of a meter; therefore, one centimeter = 10^4 microns.) Although the dust grains are very scarce compared to the hydrogen atoms, one dust grain for every 10^{12} hydrogen atoms, these grains play a very important role in making and destroying molecules in dust clouds.

In order to understand how molecules form in dust clouds, we need to know not only the kinds and amounts of atoms but also the physical conditions (table II). In particular, what are the forms of energy available to heat the clouds, to help make and break the molecules found there? In comparison to conditions on Earth or near a star, the interior of an interstellar cloud is quite a cold and dark place, with temperatures not far above absolute zero. Even at such low temperatures, there is kinetic energy in the random motion of the gas and dust. There is also potential energy in the gravitational attraction of each part of the cloud for the matter in the rest of the cloud. If this gravitational self-attraction is much greater than the kinetic energy, then the cloud will certainly contract to form a new star. If the kinetic energy is greater, then the cloud will evaporate and disappear as its matter spreads out with time, much like smoke or a drop of ink in a glass of water.

Table II
A Typical Interstellar Cloud

Within the cloud:

        Gas temperature ~ 20 K
        Gas density ~ 10 hydrogen atoms per cm^3
        Dust density $\sim 10^{-13}$ dust grains per cm^3

The cloud itself:

        Size ~ 10 light years[1]
        Mass ~ 50 solar masses[2]
        Lifetime ~ 10 million years

Speed with respect to other clouds ~ 10 km s^{-1}
Distance between clouds ~ 100 light years
Distance of nearest dust clouds to Earth ~ 400 light years

NOTES: (1) One light year is $\sim 10^{18}$ cm.
        (2) The Sun has one solar mass or $\sim 2 \times 10^{33}$ grams.

9

In addition to kinetic and potential energy, the cloud receives energy in the form of radiation from the surrounding interstellar space. Electromagnetic radiation (microwave, IR, VIS, UV, XR, gamma) and high-energy cosmic ray particles constantly strike the clouds from all sides. The cloud is bathed in the diffuse light of all the surrounding stars within a few thousand light years. This starlight is the average of stars of different temperatures (colors) but is strongest in the ultraviolet range (near the wavelength $\lambda \sim 1000$ Å). These UV rays have enough energy to start most chemical reactions, by breaking chemical bonds. This starlight is effectively blocked by the interstellar dust grains and can therefore penetrate only the outermost layers of a dense dust cloud. Molecules deep within a dust cloud are protected by the dust from this destructive ultraviolet radiation, much as the Earth's atmosphere protects us from most of the Sun's harmful UV rays. More energetic radiation, such as gamma rays and cosmic ray particles with energies greater than one hundred million *electron volts*, can pass completely through even the densest dust clouds. (One electron volt is the energy an electron receives in being accelerated across an electrical potential of one volt.)

Radiation of longer wavelength than visible light (for example, infrared, microwave, radio) is better able to "bend around" the dust particles and thus to penetrate deeper into interstellar clouds. In particular, all space (including the dust clouds) is evenly filled with the cosmic microwave radiation. This radiation, discovered in 1965 by scientists at Bell Telephone, is thermal in nature, equivalent to the radiation emitted by an object at a temperature of 3 K. Astronomers think this radiation is the remnant of the fireball at the explosive origin of our universe (see the unit on extragalactic astronomy).

The interstellar clouds also possess the kinetic energy associated with the swirling streams and flows of gas within clouds, and with the collisions between different clouds at supersonic speeds (~ 10 km s^{-1} or 20 000 mph). Within the denser interstellar clouds — those contracting to form new stars — the most important energy source is the conversion of gravitational potential energy into kinetic energy as the cloud shrinks. [A familiar example of the conversion of potential to kinetic energy would be an apple falling from a tree. Before it falls, the apple has the gravitational potential energy of its position high in the tree. As it falls to the ground, this potential energy becomes energy of motion (kinetic). When the apple hits the ground and stops, it is warmed (slightly) as the kinetic energy is converted to heat.] In the case of the collapsing molecular cloud, the gas and dust, heated as the cloud contracts, cools again by releasing this energy in the form of infrared and microwave radiation.

Energy is also contained in the magnetic fields in interstellar clouds. These fields, although about 10^5 times weaker than the Earth's magnetic field, have an important effect on the shape and stability of the clouds.

And finally, there is the energy released by spontaneous chemical reactions within the clouds. The most important of these reactions, $H + H \rightarrow H_2 + 4$ eV, converts hydrogen from atomic to molecular form. In equilibrium each of these energy sources has about the same amount of energy.

The unique nature of interstellar space results in a unique chemistry. As shown in table III, the interstellar clouds are much colder and much less dense than is the atmosphere of

10

the Earth or of a typical star. Most stars are simply too hot to allow atoms to stay bound together as molecules. The strength of the chemical bond between atoms, a few electron volts, allows molecules to survive only near stars like the Sun (T ~ 6000 K) or cooler. Molecules can't exist in very hot places (T ~ 10^4 K), like the regions of ionized hydrogen surrounding bright young stars, or in most of interstellar space outside of the dust clouds.

Table III
Comparison of Physical Conditions

Place	Temperature (degrees Kelvin)	Gas Density (atoms, molecules per cm^3)	Chemistry?
Earth's Atmosphere	300	10^{19}	Yes
Interstellar Cloud	30	10^3	Yes
Star's Atmosphere[1]	10,000	10^{15}	No
NOTE: (1) Star of type A, somewhat hotter and more massive than the Sun.			

What kind of chemistry is possible in dust clouds where temperatures are much lower? At the density typical of interstellar clouds, the molecules in the gas collide with each other only about once a year on the average, after traveling a collision-free distance from here to the Sun (1 AU). A chemical reaction can take place only when the reacting atoms or molecules collide. The chance of collision is obviously decreased by decreasing the number density of particles. Lowering the temperature also decreases the collision rate by reducing the speed of the colliding particles.

Not every collision leads to a chemical reaction. Most reactions between stable molecules require excess initial energy (*activation energy*), even if the final products are more stable than the starting reactants. The most important effect of the low temperature in dust clouds is that less energy is available at the moment of collision for overcoming this activation barrier.

The two effects of decreased temperature and density combine to make chemical reactions in space much slower than on Earth. Compared to conditions on Earth, collisions between molecules in interstellar clouds are rare indeed, and those infrequent collisions which do occur are much less likely to lead to a chemical reaction.

A consideration of these slow reaction rates, as well as the harsh radiation in space, led most chemists and astronomers to the conclusion that only very simple molecules would form in interstellar space. They were astonished in the late 1960s when large organic molecules were first discovered in dust clouds. How were these molecules detected and identified? To answer this question, we must first have a brief introduction to molecular spectroscopy, which is the study of molecules by means of their characteristic radiations or "spectral fingerprints."

11

COMPREHENSION QUESTIONS

Q: Compare the density (atoms/cm^3) and temperature (degrees Kelvin) in (a) a typical interstellar cloud, (b) the space between the interstellar clouds, and (c) the Earth's atmosphere.

A: (a) 10-10^3 cm^{-3}, 10-100 K; (b) $\leqslant 0.1$ cm^{-3}, 10^4 K; (c) 10^{19} cm^{-3}, 300 K.

Q: Name the five most abundant elements in the universe. What is the relative abundance of each compared with that of hydrogen? Origin of each?

A: H, He, C, N, and O (see table I). Hydrogen and helium have been present since the beginning; others are made in stars.

Q: What are interstellar grains made of? How are they formed?

A: Fine sandy and sooty particles, formed from matter ejected from stars.

Q: What are the main energy sources in interstellar clouds? Which is the largest?

A: Kinetic energy of random motion, potential energy of gravitational self-attraction, interstellar radiation and cosmic rays, magnetic fields, and chemical reactions. All are roughly equal in energy.

22

CHAPTER IV

SPECTROSCOPY: ATOMS, MOLECULES, AND LIGHT

Atoms are stranger than baseballs. Newton's laws of motion describe the motion of baseballs, but fail to describe the unfamiliar world of atoms. The behavior of matter on the atomic scale ($\sim 10^{-8}$ cm) is described by the theory of *quantum mechanics*, according to which, a particle's energy and position are quantized or divided into very small units measured in terms of Planck's constant h ($h \cong 6 \times 10^{-27}$ erg-sec.)

Let's consider the hydrogen atom. The single electron moving around the nucleus must occupy one of a fixed number of orbits or energy levels. Since the orbit is quantized, so is the energy of the electron in that orbit. In the lowest energy orbit (the *ground state*), the electron is closest to the nucleus. If sufficient energy is provided (e.g., heat, light, collision with another atom), then this ground state electron can be boosted (excited) to a higher energy level or state, into an orbit farther from the nucleus. In this process, the atom absorbs a definite amount of energy as the electron "jumps" (makes a *transition*) from the ground to the excited state. In the reverse process (*spontaneous emission*), the electron jumps from the excited state to a lower energy state as the atom emits a photon (quantum of radiation) whose energy precisely equals the difference in energy between the two states. These downward radiative transitions are very rapid. For example, excited atoms which emit photons of visible light only remain in the excited state for about 10^{-8} seconds. The energy of each electron orbit depends on all the other electrons circling the nucleus and on the charge of the nucleus.

Since this charge is different for atoms of different elements, each element has a unique set of energy levels and hence emits and absorbs a characteristic *spectrum*, a unique set of photon energies. The study of these electronic transitions in atoms is called *atomic spectroscopy*. The measured spectrum, a kind of atomic fingerprint, is a record of the amount of energy absorbed or emitted by a particular atomic species as the wavelength of the analyzing radiation is varied or "swept." When the energy of this radiation agrees with the difference in energy between two levels of the atom, the spectral record will show a sudden dip or peak (a "spectral line") depending on whether the atom has absorbed or emitted the radiation. The process of sweeping the wavelength of the radiation to find an agreement ("resonance") is exactly the same as sweeping a radio dial to find a station. Each kind of atom and molecule has its own "stations."

A molecule as a union of atoms also behaves in a quantum mechanical manner. What was said about transitions in atoms also applies to the more complicated motions possible in molecules. The bonding electrons in a molecule do not move in circles about a single nucleus as in atoms but rather in complex noncircular orbits about all the atoms in the molecule. As in the atomic case, the motions of electrons in molecules are quantized. Because molecules contain more than one atom, nuclear motions are also possible. The atoms in a molecule can vibrate against each other in the manner of balls on a spring, and the entire molecule can tumble end-over-end (rotate). Each of these different kinds of molecular motion (electronic, vibrational, rotational) is quantized and to each there corresponds a unique set of quantized

23

13

energy levels. Different molecular species absorb or emit characteristic photons of a well-defined energy when they undergo transitions from one energy level to another. The study of the structure of molecules by means of these transitions is called *molecular spectroscopy*. Careful laboratory measurements of the unique spectra of many different molecules have usually allowed astrochemists to decide which molecule is producing a detected interstellar "station" or spectral line.

The different types of molecular motion with the corresponding ranges of photon energy are presented in table IV. Also given is the typical lifetime of the molecule in the excited state and examples of interstellar molecules identified via their characteristic spectra in each energy range. Notice the variation in lifetime, from less than a millionth of a second for an electronic transition to more than ten thousand years for a transition in the radio range. These slow radio-frequency transitions occur between closely spaced energy levels in both atoms and molecules. Such fine splittings of energy levels can result, for example, from a magnetic coupling between an electron and the atomic nucleus, both of which behave like tiny magnets.

Table IV
Molecular Spectroscopy

Type of Motion	Energy Range	Wavelength λ(cm)	Lifetime (seconds)	Observed Species
Electronic	Ultraviolet-Visible	$10^{-5} - 10^{-4}$	10^{-7}	CH, CN, CH^+
Vibrational	Infrared	$10^{-4} - 10^{-1}$	10^{-2}	CO, SiO, dust
Rotational	Microwave	$0.1 - 1.0$	10^5	CO, HCN, H_2O
Fine Structure	Radio	$1.0 - 10^3$	10^{12}	OH, CH_3OH, H

The molecular transitions which give the most information about the interstellar chemistry are those in the microwave range, associated with changes in the rotational energy. For example, a rapidly tumbling molecule of carbon monoxide spontaneously emits a microwave photon and then tumbles more slowly since some of the energy of rotation has been converted to microwave radiation. One reason that rotational transitions of small molecules are a useful probe of interstellar clouds is that the energy spacing between rotational levels is roughly equal to the kinetic energy of molecules in the gas. This means that a molecule can be knocked into higher rotational states (made to tumble faster) by collisions with other molecules in the gas.

24

COMPREHENSION QUESTIONS

Q: Name the types of molecular motion that correspond in energy to (a) ultraviolet-visible, (b) infrared, and (c) microwave radiation. Give an example of an interstellar species observed in each of these energy ranges.

A: See table IV.

Q: Why are rotational transitions best for observing molecules in dust clouds?

A: The spacing between rotational energy levels is about equal to the energy of molecules in the gas.

25

CHAPTER V

MOLECULAR SIGNALS FROM SPACE

Interstellar space is criss-crossed by waves of radiation of all energies, from radio waves to gamma rays (figure 3). Most of this radiation is blocked by the Earth's atmosphere and never reaches us.
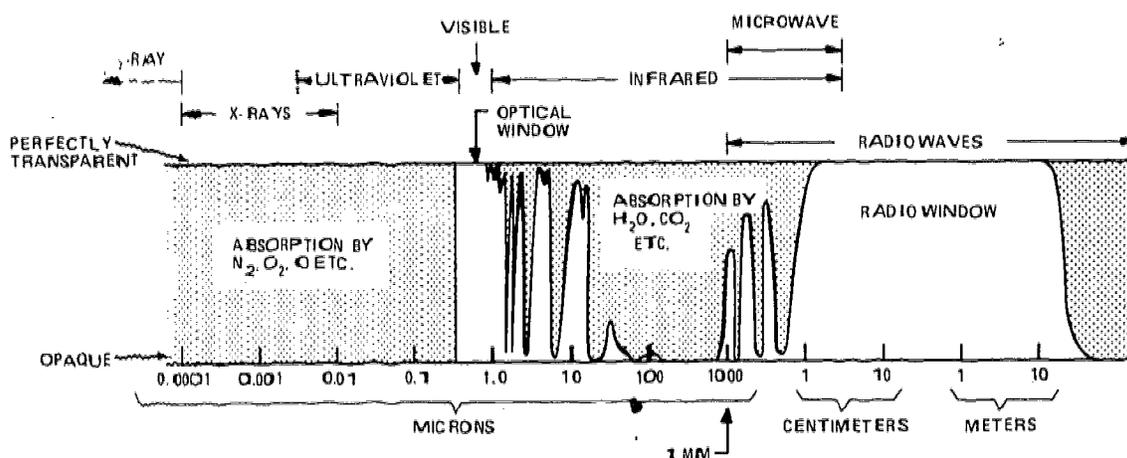
Figure 3 — The electromagnetic spectrum and the corresponding transmission of the Earth's atmosphere at different wavelengths.

Only in visible light and radio waves can we look out through clear "windows" in the atmosphere to the universe beyond (figure 3). From ancient times until the middle of this century, man's view of the cosmos was limited to wavelengths passing in through the "visible window" ($\lambda = 3000\text{-}10\,000$ Å) in our atmosphere. With the birth of the science of radio astronomy after World War II, astronomers began to assemble a picture of the heavens in radio waves ($\lambda \sim 1$ cm-10 m), which reach us through the "radio window." Except for a few narrow slits in the infrared range, the atmosphere gases block the radiation from space at all wavelengths outside the radio and visible windows.

Since the 1960s astronomers have begun to study the infrared and ultraviolet radiation from space by placing their telescopes above most or all of the Earth's atmosphere with the aid of high-flying jets, balloons, sounding rockets, and orbiting astronomical satellites. Since molecules emit radiation of wavelengths from radio through ultraviolet, these recent observations in spectral ranges outside the visible window, particularly those in the radio and microwave range, have provided a new understanding of the chemistry and the physical conditions in interstellar space.

17

Interstellar dust clouds could only be studied in detail after the development of the optical spectroscope at the beginning of this century. With this instrument at the focus of a telescope, collected starlight could be spread out (dispersed) into its constituent colors or wavelengths, as with a prism, allowing the identifying spectral features of different atoms and molecules to be distinguished (resolved). The first two interstellar species identified in this way were ionized calcium and neutral sodium atoms. Each was found absorbing its identifying radiation from the light of certain bright stars, located behind the cloud.

By spreading out the collected starlight even more finely into its separate colors, later measurements revealed that each broad absorption feature was usually a blend of several more narrow features, formed in several distinct interstellar clouds with different random motions along the line of sight from the Earth to the particular star observed. The slight increase or decrease in the frequency of received radiation with motion of an interstellar cloud toward or away from the Earth is an example of the *Doppler effect* (see Glossary). A more familiar example of this same effect is the dropping pitch of a passing train whistle. In the interstellar example, the Doppler shift in frequency is proportional to the velocity of the molecular cloud toward or away from the Earth. This motion is the combined effect of the rotation of the Earth about its own axis, the revolution of the Earth about the Sun, and the nearly circular motions of the Earth and the cloud about the center of the galaxy.

These optical measurements of interstellar atomic absorption spectra gave an early picture of the physical nature of interstellar clouds. The first clues about the nature of the interstellar chemistry came with the detection of the first three interstellar molecules: CH, CH^+, and the cyanogen radical CN. These three diatomic molecules were found in dusty regions of space, often in the same clouds and with the same random motion as the previously detected calcium and sodium, selectively absorbing their characteristic radiation from the light of bright stars behind these clouds (figure 4).

Each of these three molecules is a diatomic union of carbon with either hydrogen or nitrogen, and each is a highly reactive chemical species, either a *free radical* (CN, CH) or a *molecular ion* (CN^+). All three are found in the energetic environments of both candle flames and comet tails, as unstable fragments of larger molecules (table V).

The observed abundance of these three molecules relative to hydrogen is very low, even considering the relative cosmic abundance of the atoms. For example, the observed abundance of the molecule CH compared with hydrogen is $CH/H \leqslant 10^{-7}$, which means there is less than one CH molecule for every ten million hydrogen atoms. The relative abundance of carbon atoms to hydrogen atoms is much greater, $C/H \sim 3 \times 10^{-4}$. This means that only a small fraction of the available carbon is used to form these molecules. Where is the rest? And why do all three contain carbon?

These chemical questions could not be answered from optical observations alone, which are limited to nearby clouds of moderate density by the blockage (extinction) of starlight by the interstellar dust. Only for radiation of wavelengths longer than one micron is it possible to "see" through the dust clouds to the far reaches of the Milky Way. Optical astronomers found that starlight passing through interstellar clouds is not simply blocked by the dust grains but also becomes redder in color (is "reddened"). Figure 5 shows how

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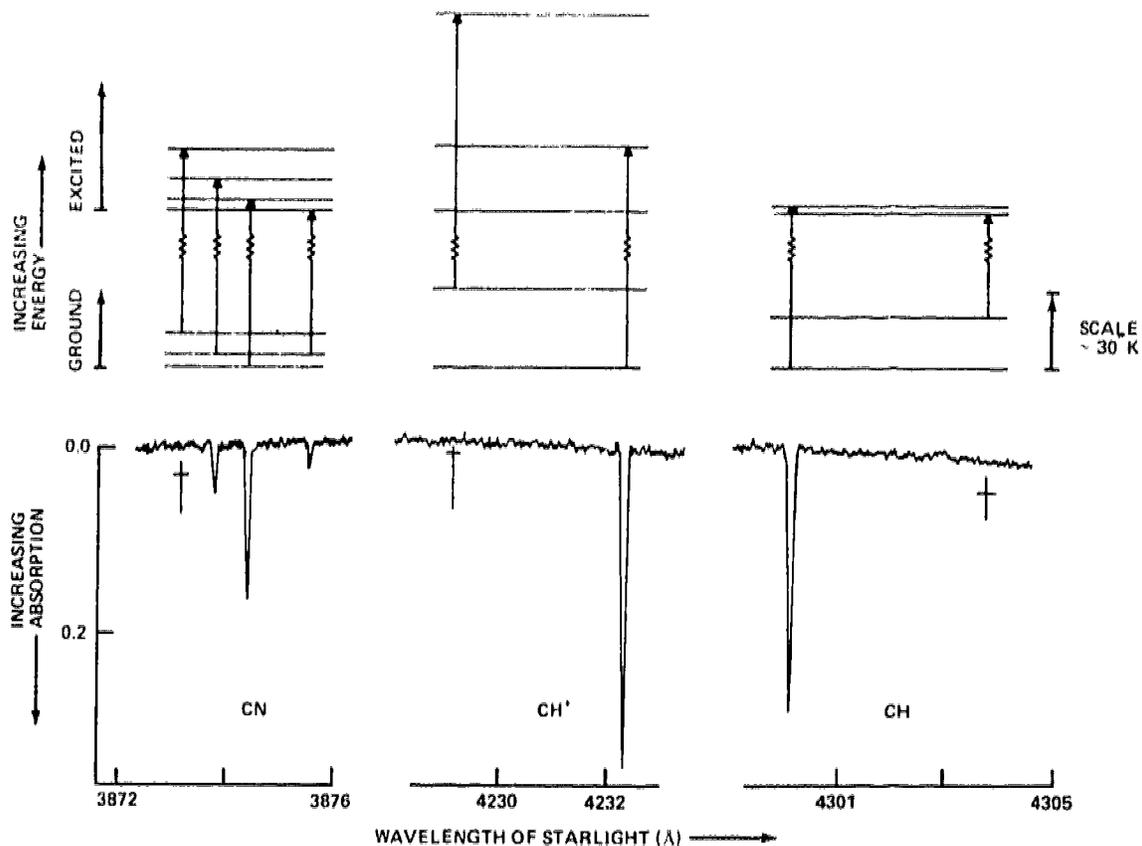
Figure 4 — The optical absorption spectra of interstellar CN, CH⁺, and CH. Above each spectrum is shown the corresponding pattern of rotational energy levels for the ground and excited electronic states of each molecule. Arrows mark the transitions. The crosses (+) in the spectra show the expected position of the unobserved lines from higher rotational states, indicating that these molecules are very cold (T ~ 3 K). The broken arrows (———ᴡᴡ→) indicate that the spacing between the ground and excited states has been reduced.

different wavelengths of starlight are blocked by the dust. From this graph, an average dust grain size of ~ 0.1μ can be determined. Notice the hump in the ultraviolet range (λ ~ 2200 Å). This feature (the "signature of graphite") may indicate that interstellar grains contain a sooty material like graphite. How much a certain cloud blocks the starlight also gives a measure of the gas density in that cloud, since astronomers find that there is a nearly constant ratio between the observed extinction and the abundance of gas in the same direction.

Molecules and dust go together. Dust clouds rich in molecules are found to be the darker ones, the ones from which the harmful ultraviolet starlight is almost completely blocked.

Interstellar Molecule (parent?)	Cometary Molecule (fragment?)[1]
OH, H_2O	OH, OH^+, H_2O^+
CO, H_2CO	CO, CO^+
	CO_2^+, N_2^+
NH_3	NH_2, NH
CN, HCN, CH_3CN	CN, HCN, CH_3CN
HC_3N, CH_3CCH, CH_3OH	CH, CH^+, C_2, C_3

NOTE: (1) The new comet Kohoutek, which rounded the Sun at the beginning of 1974, was a disappointment to the public but not to astronomers and chemists: in the visible light and radio radiation of this comet, several new cometary molecules were tentatively identified ($OH, HCN, CH_3CN,$ and H_2O^+).
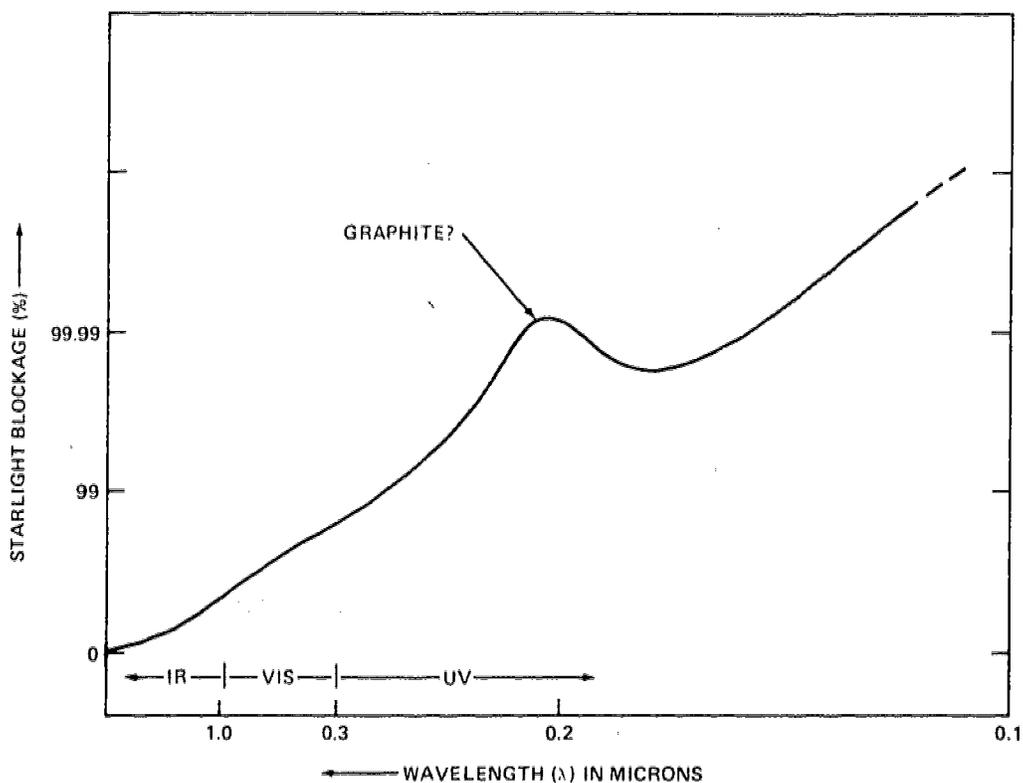

Figure 5 – The blockage (extinction) of starlight by the interstellar dust at different wavelengths. The bump at a wavelength of $\lambda \sim 2200$ Å has been called the "signature of graphite." Notice that ultraviolet light is mostly blocked, but infrared light is nearly unaffected by the dust.

20

About the same time that the sharp optical lines of CH, CH$^+$, and CN were first detected, several broad (diffuse) interstellar absorption features were also discovered, the most prominent at a wavelength $\lambda \cong 4430$ Å. Although first detected in the 1930s, these "*diffuse interstellar lines*" have still not been identified. Suggestions for the origin of these broad lines range from hydrogen molecules to the *porphyrins*, a class of very complex organic molecules like chlorophyll. Observations do suggest that these diffuse lines are produced by molecules in or on the dust grains, or by the grains themselves. We will know much more about the chemical nature of the grains when the diffuse lines and the "signature of graphite" are finally understood.

With the advent of rockets and orbiting astronomical observatories (OAO), celestial measurements in the ultraviolet spectrum ($\lambda < 3000$ Å) from above the Earth's atmosphere have become possible. Such observations are similar in principle to the Earth-based measurements at visible wavelengths: interstellar atoms and molecules are detected in absorption against bright background stars. Molecular hydrogen (H_2), the most abundant of all the molecules in space, was first detected in the early 1970s using an ultraviolet detector carried above the atmosphere by a rocket.

More recent ultraviolet observations of the interstellar gas and dust from aboard the unmanned satellites like the OAO "Copernicus" has shown that the gas in the regions between interstellar clouds is very "thin" ($n_H \sim 0.05$ cm^{-3}) and that the hydrogen is overwhelmingly in atomic rather than molecular form ($H_2/H < 10^{-7}$). In interstellar clouds of increasing density, the hydrogen is converted more and more to molecular form by the reaction, $H + H \rightarrow + 4$ eV, which takes place on the surface of the dust grains. Deuterium, a heavier isotope of hydrogen, was also detected in these denser clouds, in combination with the normal hydrogen (H) as the molecule HD.

The satellite measurements have shown that the interstellar grains scatter and absorb starlight more effectively in the ultraviolet than in the visible range (figure 4). For this reason the UV measurements are restricted to the interstellar clouds of lowest density and the hot regions between clouds. Only through these regions of low density can the ultraviolet starlight pass to Earth without being completely blocked by the dust.

Satellites have also been measuring X-rays and cosmic rays from space. Since this "hard" radiation can break all chemical bonds, it does not directly carry the "fingerprints" of interstellar molecules. However, interstellar cosmic rays and X-rays are important energy sources for heating and ionizing the depths of the denser interstellar clouds where no ultraviolet starlight can enter.

Ground-based astronomical observations at infrared wavelengths are severely limited by absorbing atmospheric gases, principally water vapor near the Earth's surface. Infrared astronomers have managed to get above some of this water vapor by placing infrared telescopes atop high and dry mountains (such as the Hawaiian telescope on 13,600-foot Mauna Kea), or by sending them aloft in high-flying balloons or on jet planes (like the NASA Galileo). The best infrared "windows" are really just narrow cracks compared with the radio and visible windows. These bands of partial atmospheric transparency occur at far-infrared wavelengths near 10, 20, and 100 microns (figure 3).

21

30

The visible window extending beyond 1μ is slammed shut by strong water absorption at 3μ. The 1-3μ band is called the "near infrared" and can be observed from the ground. Thermal radiation in this band is emitted by cool stars ($T \sim 3000$ K), and it is in the cooler outer layers of such stars that *circumstellar molecules* and dust have been most extensively studied. Vibrational motions in most molecules produce identifying spectral features in the 1-3μ band. Some of the molecules identified in the light of cool, luminous stars include H_2O, HCN, CN, CO, and TiO. Whether and how these circumstellar molecules can be safely carried from their parent star into distant interstellar clouds, where many of the same molecules have been identified by their radio spectra, is not yet known.

Infrared observations have been more helpful in determining the chemical composition of the dust than of the gas. A wide emission feature of heated circumstellar dust grains near 10μ is strong evidence for sand-like minerals called *silicates*. In general, the spectral features of solids are much broader and less definitive than those of free gaseous molecules or atoms. A very similar silicate feature has been seen in 10μ observations of the Orion Nebula (figure 6), the galactic center (figure 2), Comet Bennett, and a Martian dust storm. This silicate feature is not produced by quartz itself (SiO_2) but probably by a mixture of silicate minerals like those found in meteorites.

These sandy specks are believed to condense out of the oxygen-rich gases in the outer layers of certain cool and luminous stars. If the parent star has instead more carbon than oxygen, then circumstellar grains of soot or graphite are expected to form. Grains of carborundum (SiC) have been identified in the 10-micron spectrum of one star with about an equal abundance of oxygen and carbon.

As the circumstellar grain is blown away from its parent star by the *stellar wind* into interstellar space, it probably grows larger as heavy elements in the gas strike the grain and stick. The mineral core of the grain very likely becomes coated by a shell of condensed atoms or even large stable molecules (CH_4, NH_3, H_2O). (Remember that the Earth is a rock coated with life!) The size of grains has been found to increase with increasing distance into dense dust clouds. In addition, the 2.7-micron infrared "fingerprint" of ice has been seen in the spectrum of the dust in the Orion molecular cloud (figure 6).

In the future, infrared observations may be made from above the atmosphere with an orbiting infrared telescope of much higher sensitivity. With such an instrument, the infrared spectra of interstellar methane (CH_4) and carbon dioxide (CO_2) will very likely be detected. Infrared astronomers will probe deeper into the dark clouds to study the sites of star birth, already known as hot spots of intense infrared radiation ($\lambda \sim 100\mu$) from heated dust grains, and also as rich sources of interstellar molecules.

Radio observations of molecules in dust clouds have dominated our emerging picture of the interstellar chemistry. The radio window of high atmospheric transparency stretches from the last water absorption feature ($\lambda \sim 1$ cm) out to the very long radio wavelengths ($\lambda \gtrsim 10$ m) which bounce off the Earth's *ionosphere*. Since photon energy is proportional to frequency ($E = hf$), a radio photon has much less energy than a photon of visible light. The detector at the focus of a radio telescope is similar in principle to your home radio set and can measure even the extremely weak radio signals from space. All the radio energy

22

Figure 6   The Orion Nebula, a bright region of swirling ionized gases about 1200 ly
away. Behind the visible nebula is an enormous black cloud of gas and dust
which contains several newly forming stars as well as a great variety of
different molecules. The observed sizes of strong emissions from water,
hydrogen cyanide, and carbon monoxide are indicated by the contour lines.
The HCN cloud is about 3 light years across. (Hale Observatory photograph)

collected by all the radio telescopes around the world since the beginning of radio astronomy as a science ($\sim$ 1945) is equal to the kinetic energy of one falling snowflake.

Although a working radio telescope had been developed in the 1930s, it was not until the end of World War II that the technical capability of radar was turned up to the heavens and the science of radio astronomy began. Even the densest interstellar dust clouds, totally impenetrable in visible light, are transparent to radio waves, which can "see" through the entire galaxy and beyond.

The cosmic predominance of hydrogen had been realized since the 1930s, about the time that the optical spectra of CH^+, CH, and CN were first observed. But it was not until 1951 that radio signals from hydrogen atoms in interstellar space were detected directly. This hydrogen "fingerprint," which occurs at a wavelength $\lambda = 21$ cm, was soon used to map out for the first time the vast pinwheeling spiral arms of the Milky Way in clouds of hydrogen gas.

No new interstellar molecules were discovered for over 20 years. In 1963, the radio spectrum of the hydroxy radical (OH) was detected at $\lambda = 18$ cm. OH is a reactive diatomic species (table V), and a reasonable one to expect, given the high cosmic abundance of oxygen and hydrogen (table I).

With the detection of OH, the theoretical viewpoint seemed confirmed that conditions in interstellar space were too harsh to permit any chemistry more complex than simple diatomic molecules. Within 5 years, this theory was overthrown by the detection of the $\lambda = 1$ cm radiation from the stable polyatomic molecule ammonia (NH_3) in the enormous dust clouds in the galactic center (figure 2). A few months later, strong microwave signals of water (H_2O) were picked up from across the galaxy, so strong in fact that astronomers soon realized that these signals could only be produced by a natural interstellar *maser*, the radio cousin of the powerful manmade *laser*.

The next year (1969) saw the first inkling of the organic nature of chemistry in space with the detection of interstellar formaldehyde (H_2CO), commonly known as embalming fluid. Since 1969, interstellar molecules have been detected so rapidly that the full list (table VI) already contains more than thirty different molecular species, detected in more than 100 different "radio stations" covering the wavelength range from $\lambda = 36$ cm to $\lambda = 1.2$ mm. Nearly half of these interstellar detections were made with the 36-foot-diameter radio telescope operated by the National Radio Astronomy Observatory and located on Kitt Peak, near Tucson, Arizona (figure 7).

The best places in the sky to find new species have been in the massive interstellar clouds located near the galactic center, in the constellation *Sagittarius* (figure 2), and in roughly the opposite direction, in the very dense dust cloud behind the relatively nearby (1200 ly) *Orion* Nebula (figure 6). The molecular signals of interstellar hydrogen cyanide (HCN), received from each of these sources by the 36-foot radio telescope, are shown in figure 8.

Look again at the list of detected molecules (table VI). Notice that most of the molecules in this list are *organic* (carbon-containing), polyatomic species, with as many as nine atoms (CH_3OCH_3). Also notice that most are made up of the atoms of highest cosmic

24

Table VI
Molecules Identified in Interstellar Space

Year	Name	Structure	Year	Name	Structure
1937		C H	1971	Carbonyl sulfide	O C S
1940	Cyanogen	C N	1971	Acetonitrile	N C C H / H
1941		C H+			
1963	Hydroxyl	O H	1971	Isocyanic acid	H N C O
1968	Ammonia	N / H H / H	1971	Hydrogen iso–cyanide	H N⁺ C⁻
1968	Water	O / H H	1971	Methylacetylene	H / H C C C H / H
1969	Formaldehyde	H / C O / H	1971	Acetaldehyde	H H / C C H / O H
1970	Carbon monoxide	C O	1971	Thioformaldehyde	H / S C / H
1970	Hydrogen	H H	1972	Hydrogen sulfide	S / H H
1970	Hydrogen cyanide	H C N	1972	Methylenimine	H / N C H / H H
1970	X–ogen	----?			
1970	Cyanoacetylene	H C C C N	1973	Sulfur monoxide	S O
1970	Methyl alcohol	H O C H H / H	1974	Dimethyl ether	O / H C C H / H H H H
1970	Formic acid	O C OH H	1974	Methyl amine	H / H C N H / H H
1971	Carbon monosulfide	C S			
1971	Formamide	O C N H H H	1974	Vinyl cyanide	H H / C C / H C / N
			1974	Acetylene radical	C C H
1971	Silicon oxide	Si O	1974	. . .	⁺N N H

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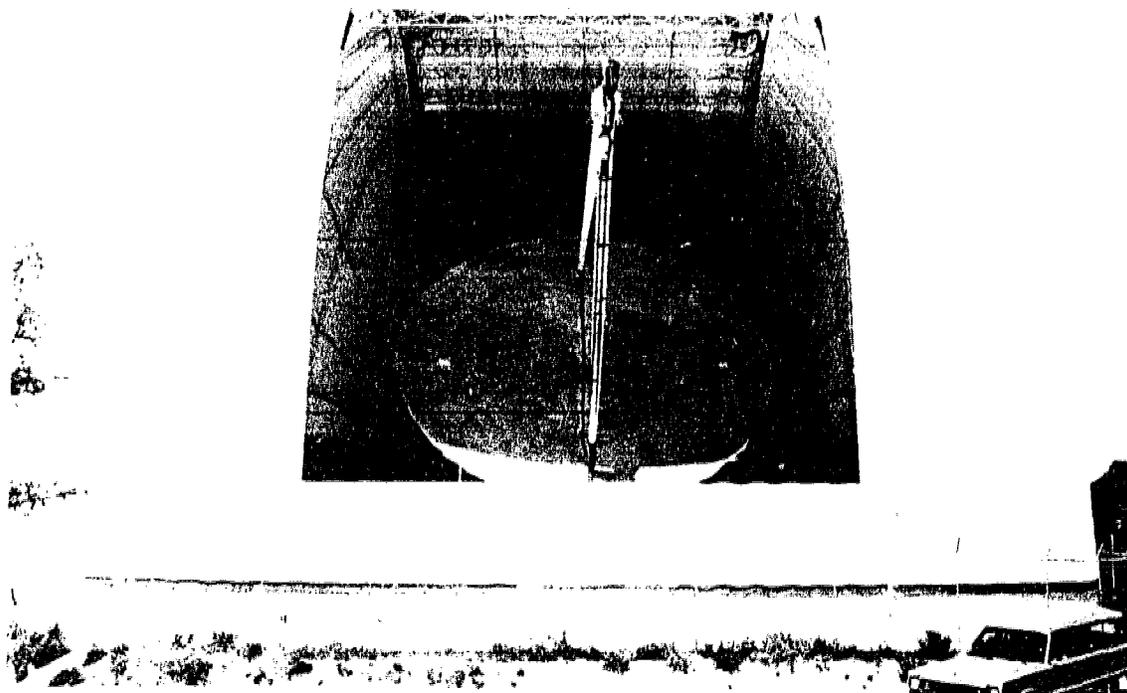
Figure 7 — The 36-foot-diameter radio telescope of the National Radio Astronomy Observatory, located on Kitt Peak, near Tucson, Arizona. Nearly half of the known interstellar molecules were first found with this telescope, which can focus and detect radio wavelengths in the range $\lambda = 1$ cm — 0.1 cm.

abundance (H, N, O, C), as is living matter, and that many are familiar on Earth: water, ammonia, formaldehyde, carbon monoxide, wood alcohol (CH_3OH), and formic acid ($CHCOOH$, the "sting" in a bee sting). Attempts to find even more complex compounds in space, like vinegar (CH_3COOH) and grain alcohol (CH_3CH_2OH), will likely be successful soon. Perhaps even the simpler amino acids, already identified in meteorites, may be found floating in interstellar clouds.

With the future development of larger and more sensitive radio telescopes, many more new interstellar molecules will certainly be found, not only in the Milky Way but in other galaxies also. At present, the only molecules found beyond the Milky Way have been OH and formaldehyde.

Just how big can interstellar molecules become? (Remember the suggestion of a chlorophyll-size molecule to explain the diffuse interstellar lines.) And how can astro-

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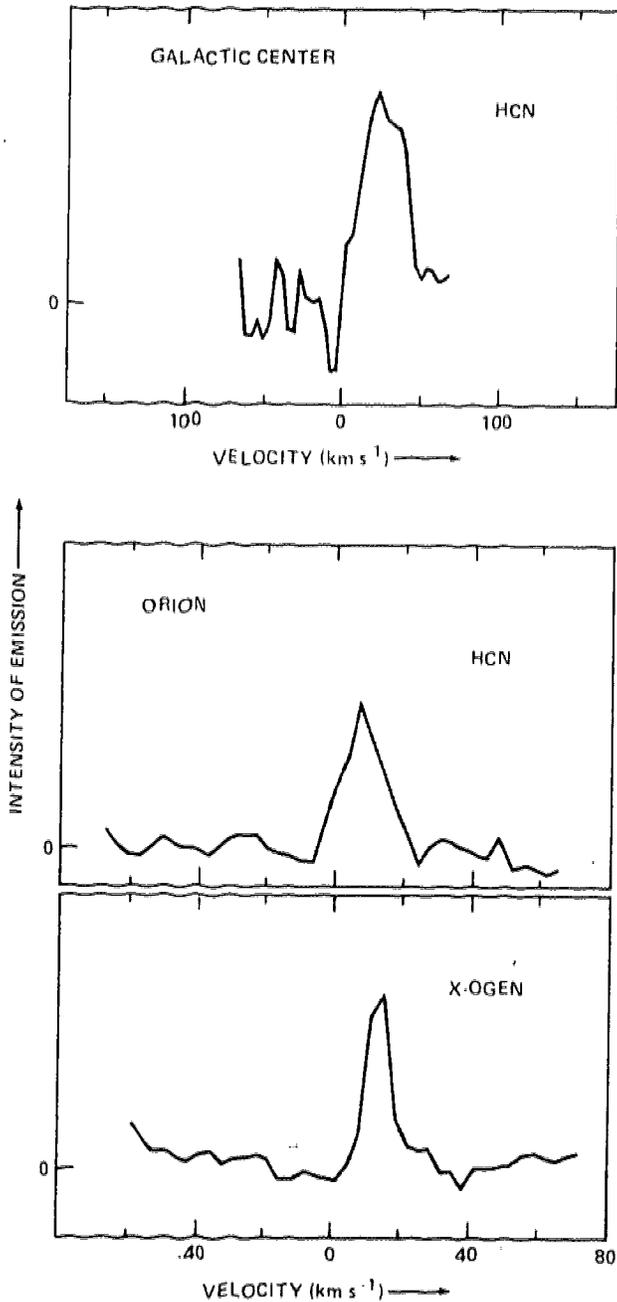
Figure 8 — Actual radio emissions from interstellar molecules. These signals were received by the Kitt Peak telescope (figure 7) at a wavelength near λ3 mm. Shown are the emissions of hydrogen cyanide received from the dust clouds in Orion and the galactic center. Also shown is the still unidentified spectrum of "X-ogen" in the Orion cloud, perhaps produced by HCO^+. The vertical axis is proportional to the intensity of the received radiation; the horizontal axis is frequency (like your radio dial), but converted by the Doppler relation to velocity in order to show the motion of the emitting cloud of gas.

27

chemists really tell what's out there and how much there is of each element? These chemical and physical questions lead us into the dark clouds where these molecules are formed and from which they send us their radio signals.

COMPREHENSION QUESTIONS

Q: Name the two main windows in our atmosphere. What happens to celestial radiation at other wavelengths? How are astronomers observing these other radiations?

A: Visible window and radio window (see figure 3). Other radiation is absorbed or reflected by the Earth's atmosphere. Observations are made by going above the atmosphere with rockets, balloons, and satellites.

Q: What were the first three interstellar molecules discovered? How are they similar chemically?

A: CH, CH^+ and CN (see figure 4). All contain two atoms, all contain carbon, and all are reactive species.

Q: What evidence supports the sandy nature of the grains, the covering of frozen gases?

A: The 10μ silicate feature observed in spectra of the dust, the increase in grain size into dust clouds, and the 2.7μ "fingerprint" of frozen water.

Q: Name four interstellar molecules which are familiar on Earth.

A: Water, ammonia, carbon monoxide, and formaldehyde (see table VI).

37

CHAPTER VI

MOLECULES AS INTERSTELLAR PROBES

Look again at figure 8. What can these molecular signals tell us about interstellar space? The first task is to identify the sender of the signals. Each different molecular species has a unique set of energy levels and hence a unique set of spectral features ("lines") by which it can be identified. By accurate laboratory measurements of rotational lines, the size and shape of many different species have been determined. The geometries of several known interstellar molecules are presented in figure 9. The lines between the atoms represent chemical bonds of length ~ 1 Å.

The interstellar molecular lines are not observed in space at exactly the same frequency measured in the laboratory, but appear slightly shifted to higher or lower frequency by the Doppler effect. The shift is very small, less than 0.01 percent of the laboratory frequency, but can be accurately measured. This shift, together with the shape of the spectral line can be analyzed to give clues about the temperature and gas motions *inside* the molecular cloud.

These shifts also complicate the problem of identifying interstellar molecules. With more than 100 lines of dozens of different species already observed, the identification of new interstellar species is only sure when confirmed by a second line or isotopic form (e.g., ^{12}CO and ^{13}CO). Several radio interstellar lines have been observed for which no matching laboratory spectrum has been found, such as the $\lambda 3$-mm line of X-ogen (figure 8). These unidentified signals probably come from unstable molecular species not yet studied in the laboratory, suggesting that conditions in interstellar space lead to some unusual chemical compounds not known on Earth.

After an interstellar line is assigned to the molecule responsible, what else can be learned from the spectral "fingerprint" itself about the abundance of that species and physical conditions in the dust cloud? The intensity of absorbed or emitted radiation, as measured by the depth or height of the spectral feature, can often be directly related to the number of absorbing or emitting molecules in the line of sight to Earth. Typical *column densities* of interstellar molecules are found to be in the range n(molecule) = $10^{14} - 10^{16}$ cm^{-2}, which corresponds to a volume density of $\sim 10^{-2}$ cm^{-3} in a cloud of hydrogen density $n_{H_2} \sim 10^4$ cm^{-3}. To illustrate just how thin the molecular soup in interstellar clouds really is, imagine that on your journey through interstellar space you decide to quench your thirst with water collected from a nearby dust cloud. Even with a bucket two meters across, you would have to sweep through the cloud at the speed of light for a whole year just to collect a single drop of water.

Whether an interstellar molecule will emit or absorb the surrounding radiation depends on the temperature of the molecules compared with the temperature of the radiation. For example, the molecules observed in figure 4 are very cold (T ≈ 3 K) and hence absorb the light of hot stars (T $\approx 10,000$ K) shining through the thinner clouds. In the radio range, however, the molecules are usually detected in emission. This is because the molecular temperature in dense clouds is nearly the cloud temperature, which is always greater than the cosmic radiation temperature (3 K).

29

How do molecules get from one energy level to the next under interstellar conditions? The excitation of interstellar molecules is largely determined by the competing effects of collisions with the interstellar gas (mostly H_2) and the absorption and emission of radiation (mostly starlight and the cosmic microwave radiation). It is a tug-of-war between collisions and radiation for control of the molecules.

Since each molecular species has its own pattern of energy levels and rates of changing levels, each species is affected by the conditions in the cloud in its own way. This makes the analysis of spectra like those in figure 8 very difficult, but also means that each molecule serves as an independent probe of the cloud.
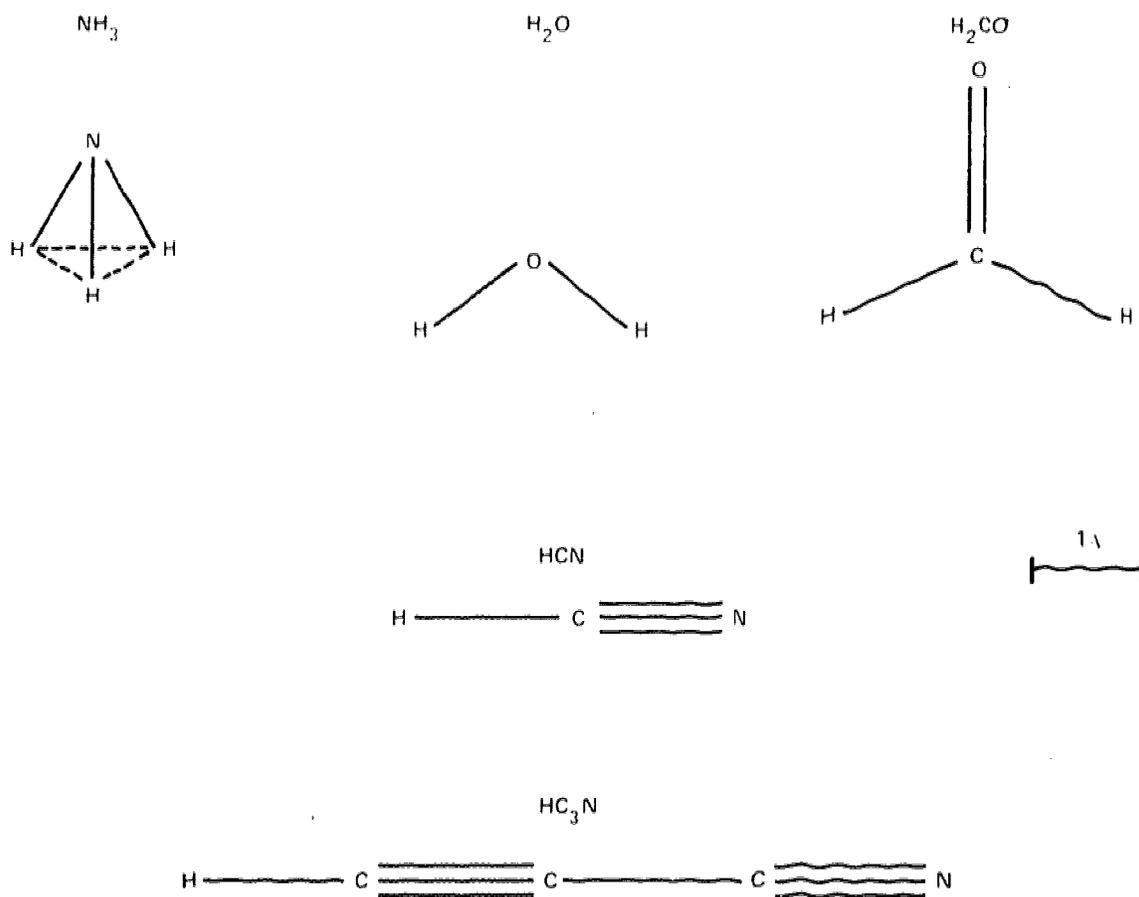

Figure 9 – The shapes of several of the known interstellar molecules. These geometries were determined by laboratory spectroscopic measurements. The lines between atoms represent chemical bonds of length about 1.5 Å. Extra lines represent the stronger double ($=$) and triple ($\equiv$) bonds of "unsaturated" species.

30

With increasing density, the collisions begin to win the fight with radiation for control of the molecules. In this case the temperature of the molecules approaches the kinetic temperature of the gas. For example, the λ2.4-mm emission signals of interstellar carbon monoxide are now being used as a "thermometer" for measuring the gas temperature in interstellar clouds. At sufficiently high gas density, collisions are frequent enough to make the molecular temperature equal to the gas temperature. This equilibrium case is common on Earth but quite rare in the interstellar clouds.

At the other extreme, in clouds of very low density, collisions with hydrogen are so rare that the radiation wins out and the molecular temperature comes close to 3 K. In this way the spectra of the molecule CN (figure 4) provided a direct measurement of the cosmic microwave radiation.

Most molecular signals correspond to the intermediate case in which the competing effects of collisions and radiation are about equal. A molecule in an excited rotational state spontaneously emits a microwave photon (typically once a month) in the downward transition to a lower energy state. Some molecules have longer lifetimes in the excited states than others, which means that less frequent collisions with the gas are required to keep them in the excited state. The gas density at which molecules are knocked into the first excited state just as fast as they spontaneously return to the ground state is about one thousand hydrogen molecules per cubic centimeter for carbon monoxide and more than one million per cubic centimeter for hydrogen cyanide.

Several interstellar molecules absorb and emit radiation in a very strange manner, as if their temperatures were far from equilibrium with either the temperature of the gas in the cloud or the surrounding radiation. The most spectacular examples of this weird behavior are interstellar water (H_2O) and formaldehyde (H_2CO). The water signals are very intense and probably come from the hot and dense cores of interstellar clouds, already collapsing to form new stars. While most molecular signals come from diffuse clouds light years across, the water emissions pinpoint hot spots often smaller in size than our solar system, flickering off and on from week to week, often brighter than the sun. All these properties mark the water emission as the result of a celestial *maser* (Microwave Amplification by Stimulated Emission of Radiation), the longer wavelength cousin of the *laser*. The water emission received from the center of the molecular cloud in Orion is shown in figure 10.

In contrast to these super-hot emissions, the λ6-cm absorption line of formaldehyde (H_2CO) is super-cold, less than the 3 K temperature of the cosmic background radiation. Formaldehyde is a cosmic refrigerator, trying to cool down the universe.

40

COMPREHENSION QUESTIONS

Q: What is the Doppler effect? What kinds of motion produce this effect in the spectra of interstellar molecules?

A: (See Glossary for definition.) Rotation of Earth, revolution of Earth about Sun, and rotation of the Milky Way produce the Doppler effect in the spectra of interstellar molecules.

Q: What are the two competing effects that determine the temperature of an interstellar molecule?

A: Radiation and collisions with H_2.

Q: Name a molecule which is a useful thermometer for measuring the temperature of interstellar clouds; one useful for measuring the cosmic 3 K radiation; and one useful for measuring a "super-hot" molecule.

A: Carbon monoxide; CN; H_2O.

41

CHAPTER VII

CHEMISTRY IN SPACE: TRYING TO EXPLAIN WHAT WE FIND

The discovery of vast interstellar clouds of ammonia, formaldehyde, and water in the late 1960s was totally unexpected by nearly all astronomers and chemists. Since that time, the pace of new discoveries of molecules in interstellar clouds has kept far ahead of any satisfactory theories which explain these observations. Before considering ways of making and breaking interstellar molecules, let's try to get a general picture of the nature of the interstellar chemistry directly from the astronomical observations: which kinds of molecules are found, which are missing?

Look again at the list of observed interstellar molecules (table VI). The predominance of carbon-containing species is clear. The organic molecules observed are generally more abundant than the inorganic molecules (figure 10). Although molecular forms of silicon (SiO) and sulfur (OCS, CS, H_2CS, and SO) are observed, such molecules represent only a tiny fraction of the available cosmic abundance of these elements. For example, less than one silicon atom in ten million is found in the gaseous form of silicon monoxide (SiO), compared with the silicon atoms bound as silicate minerals in the solid particles of interstellar dust. The different kinds of atoms making up the observed interstellar molecules include H, C, N, O, Si, and S. Attempts to detect molecules containing other heavy elements (Fe, Mg, and P) have not yet been successful. Ultraviolet measurements from orbiting satellites indicate that, even in the low-density regions between the dust clouds, these heavier elements are missing from the interstellar gas and probably have been captured by the dust grains.

The most abundant molecule in dense clouds is hydrogen (H_2), which is at least one thousand times more abundant than carbon monoxide (CO). Carbon monoxide, a very stable molecule in interstellar clouds, is about one hundred times more plentiful than the sum of all of the remaining interstellar molecules together (figure 11). This means that most species are very scarce relative to hydrogen. For example, there is about one formaldehyde molecule for every hundred million hydrogen molecules. Interstellar carbon is bound up in molecular form to a much greater extent than any of the other heavy elements in space. Nearly one tenth of the available carbon is observed as carbon monoxide. Comparable fractions may be in the form of methane (CH_4) and carbon dioxide (CO_2). However, these two molecules have no identifying radio "stations" by which they might be detected in dust clouds.

In contrast to carbon, less than one percent of the other heavy elements is found in molecular form. In particular, the fraction of cosmic nitrogen in observed molecular form is very low (e.g., $NH_3/N \sim 10^{-4}$). Perhaps some of this nitrogen exists as the stable molecule N_2, which also has no radio spectrum.

Another puzzle in the chemistry of nitrogen in space is that, unlike automobile exhaust, the interstellar gas is free of nitrogen oxides. Not one molecule containing a chemical bond between nitrogen and oxygen has been detected, although many different ones (NO, NO^+, NNO, NO_2 HNO, and HNO_3) have been looked for.

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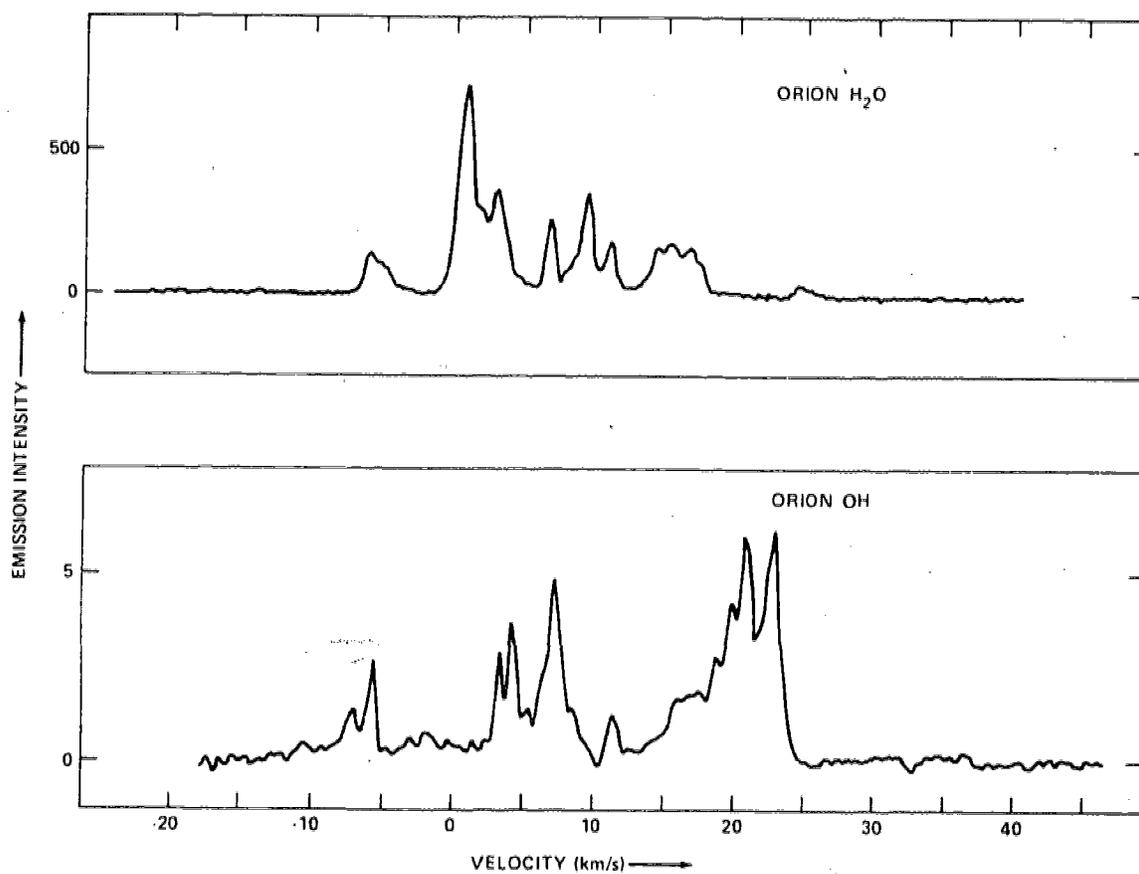
Figure 10 — The radio emissions of interstellar water (H_2O) and hydroxyl (OH) from the core of the Orion molecular cloud. These super-strong maser radiations pinpoint sites of starbirth deep within the cloud. Compare the complex pattern of H_2O and OH emission at different velocities with the simple velocity peak of HCN in the same source (figure 8).

43
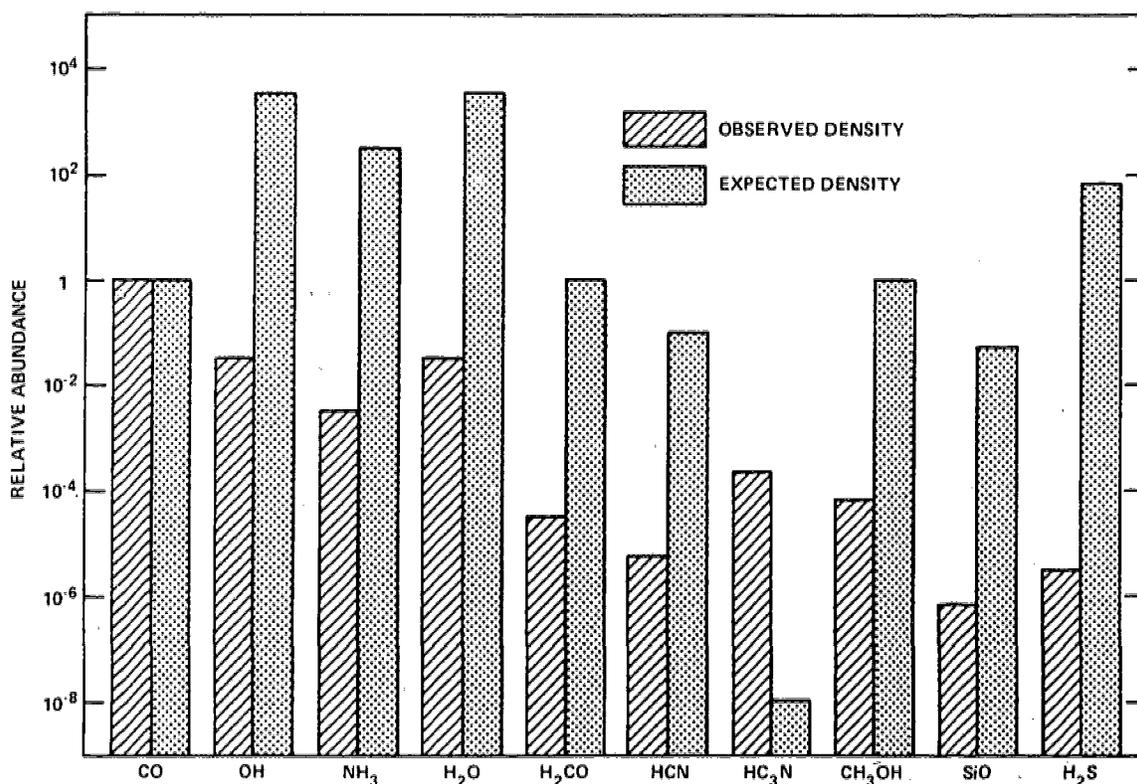
Figure 11 — The abundances of several interstellar molecules with respect to carbon monoxide. Also shown is the "expected" abundance if molecules formed in proportion to the product of the cosmic abundances of their heavy atoms.

Another clue to the way chemistry in space works is presented by the distribution of different species. Which molecules are found where? In general, the abundance of an interstellar molecule depends strongly on the conditions in the dust cloud: temperature, gas density, and the intensity of the surrounding radiation. Dust and molecules go together. Molecules are not found in the unshielded regions between clouds. The size of molecules depends on the density in the cloud. Simple, unstable molecules are observed in the clouds of lowest density; larger, more stable species are found in the darker, denser interstellar clouds. The densest clouds harbor the most complex species, some of which have only been detected in the massive clouds near the galactic center (figure 2). Molecules detected throughout the galaxy (OH, CO, and H_2CO), are found to lie closer to the thin plane of the Milky Way than does the hydrogen gas. In general, abundance decreases only slowly with increasing molecular complexity. Large molecules are nearly as abundant as simple ones. This suggests that even larger molecules will certainly be detected in the future.

Ways of making and breaking interstellar molecules can be divided into two types: (1) chemical reactions in the gas phase, and (2) reactions on the surfaces of the dust grains. Two comments apply to either type.

35

First, the only important reactions in interstellar clouds are those which can occur spontaneously at very low temperatures. For example, reactions between free radicals or molecular ions occur on every collision without requiring any starting (activation) energy, even at interstellar temperatures of less than 50 K. Second, the production of interstellar molecules must be "local." This means that species must be formed in the dust clouds where they are observed. Molecular formation occurs much more easily in the warmer, denser gas surrounding an emerging young star or in the outer atmosphere of the older stars where the dust grains are made. However, it's unlikely that molecules formed near stars could survive the million-year journey through the harsh ultraviolet rays of interstellar space to the shelter of the dust clouds where we find them.

Simple diatomic molecules can form directly when two atoms collide. Usually the two colliding atoms just bounce apart again without forming a molecule. One time in a million, the atoms stick together. In this process ("radiative association"), the new molecule is stabilized by sending off energy as a photon of light. In the thin clouds where this process is important, atoms collide with each other only once a year on the average. So the overall process is a very slow way to make molecules. An important molecule formed in this way is CH^+ ($C^+ + H \rightarrow CH^+$ + photon). The CH^+ molecule then collides and exchanges with other atoms in the interstellar gas to form more stable species ($CH^+ + O \rightarrow CO + H^+$).

How molecules are formed in dark dust clouds is not well understood. We do know that inside such clouds, the hydrogen is in the less reactive molecular form and that no ultraviolet radiation is available to promote chemical reactions. One theory is that high-energy cosmic rays passing through these dark clouds ionize the hydrogen ($H_2 \overset{C R}{\rightarrow} H_2^+ + e^-$). This ionized hydrogen is quite reactive and can lead spontaneously to the large molecules found in such clouds. ($H_2^+ + H_2 \rightarrow H_3^+ + H/H_3^+ + CN \rightarrow H_2CN^+ + H/H_2CN^+ + e^- \rightarrow HCN + H$). Reactions of this type, with at least one partner having an electrical charge (ionized), are called *ion-molecule* reactions.

Interstellar molecules may also be formed on the surfaces of dust grains, which sweep up atoms from the gas in sticking collisions. These captured atoms and molecules find each other on the grain surface, react to form new molecules, and eventually escape again to the gas. This process (grain-X + Y $\rightarrow$ grain + XY + energy) is probably responsible for the formation of interstellar hydrogen molecules (X = Y = H), and probably OH (X = H, Y = O). The great drawback in such a scheme is the almost completely uncertain nature of the grains, especially their surface properties (pitted or smooth?) and composition. Are the attractive forces between the grain and the attached atoms weak (physical adsorption) or strong (chemical adsorption)?

The grains may even act as *catalysts*, promoting reactions between interstellar species that would not otherwise take place. In laboratory experiments using a catalyst of ground meteorites (probably similar in composition to interstellar grains), simple molecules (CH_4, NH_3 and H_2O) have been converted into many of the same complex species observed in space.

An important problem with all reactions on grain surfaces is how to get the newly formed species off the grains again and back into the gas where the interstellar molecules are observed.

4 5

How are interstellar molecules destroyed? In unshielded interstellar space, most molecules would be destroyed by ultraviolet radiation within a few hundred years (for CO, a few thousand years). This "ultraviolet lifetime" increases rapidly with increasing depth into the protective dust clouds (figure 12). For dark clouds in which more than 99 percent of the starlight is blocked, molecules can survive more than a million years, close to the lifetime of the cloud itself. Molecules in the centers of such dense clouds can only be destroyed by the high-energy X-rays or cosmic rays, or by reacting to form new species.

Interstellar molecules can also be removed from the gas by sticking onto the grains. On the average, a molecule in the gas will collide with a dust grain every 10^5 years in a cloud of density $n_{H_2} \sim 10^5$ and temperature $T \sim 10$ K.

Which formation theory agrees best with the observations? One important difference between the theories is that molecules formed on grains are expected to be hydrogen-rich ("saturated"), whereas molecules formed in the gas by ion-molecule reactions are expected to be hydrogen-poor ("unsaturated"). We can arrange the interstellar molecules in families or sequences according to their hydrogen content (figure 13). Included in these sequences are molecules searched for but not yet found in interstellar space. The result is clear: interstellar space favors hydrogen-poor molecules, despite the overwhelming cosmic abundance of hydrogen. Sequences of chemically related molecular species (figure 13) show that *unsaturated* molecules (e.g., $H - C \equiv N$) seem to be favored over the corresponding saturated species (e.g., $CH_3 - NH_2$). This trend is surprising at first, since each molecule might be expected to grow by adding hydrogen stepwise (e.g., $CO + H \rightarrow HCO$, $HCO + H \rightarrow H_2CO$, $H_2CO + H_2 \rightarrow CH_3OH$), especially in view of the enormous overabundance of hydrogen. This chain, which saturates a multiply-bonded species with its full complement of bonds to hydrogen atoms, is predicted to be an important mechanism for the chemistry occurring on the surfaces of the dust grains. Most of the observed molecules are not saturated; this suggests that other mechanisms are more important. In particular, gas phase reactions of the *ion-molecule* type *do* predict the observed predominance of unsaturated species. Unsaturated bonds are stronger than saturated ones, which means that molecules like $H - C \equiv N$ can survive harsh radiation fields longer than can the corresponding saturated species, $CH_3 - NH_2$. The observed interstellar abundances must certainly reflect the balance of formation and destruction for each species, a kind of natural selection, or "survival of the fittest."

46

LIFETIME (YEARS)

10^8

10^6

10^4

10^2

CO

H_2O

H_2CO

OCS

0　　　　40　　　　80　　　　88　　95

STARLIGHT BLOCKAGE (%)
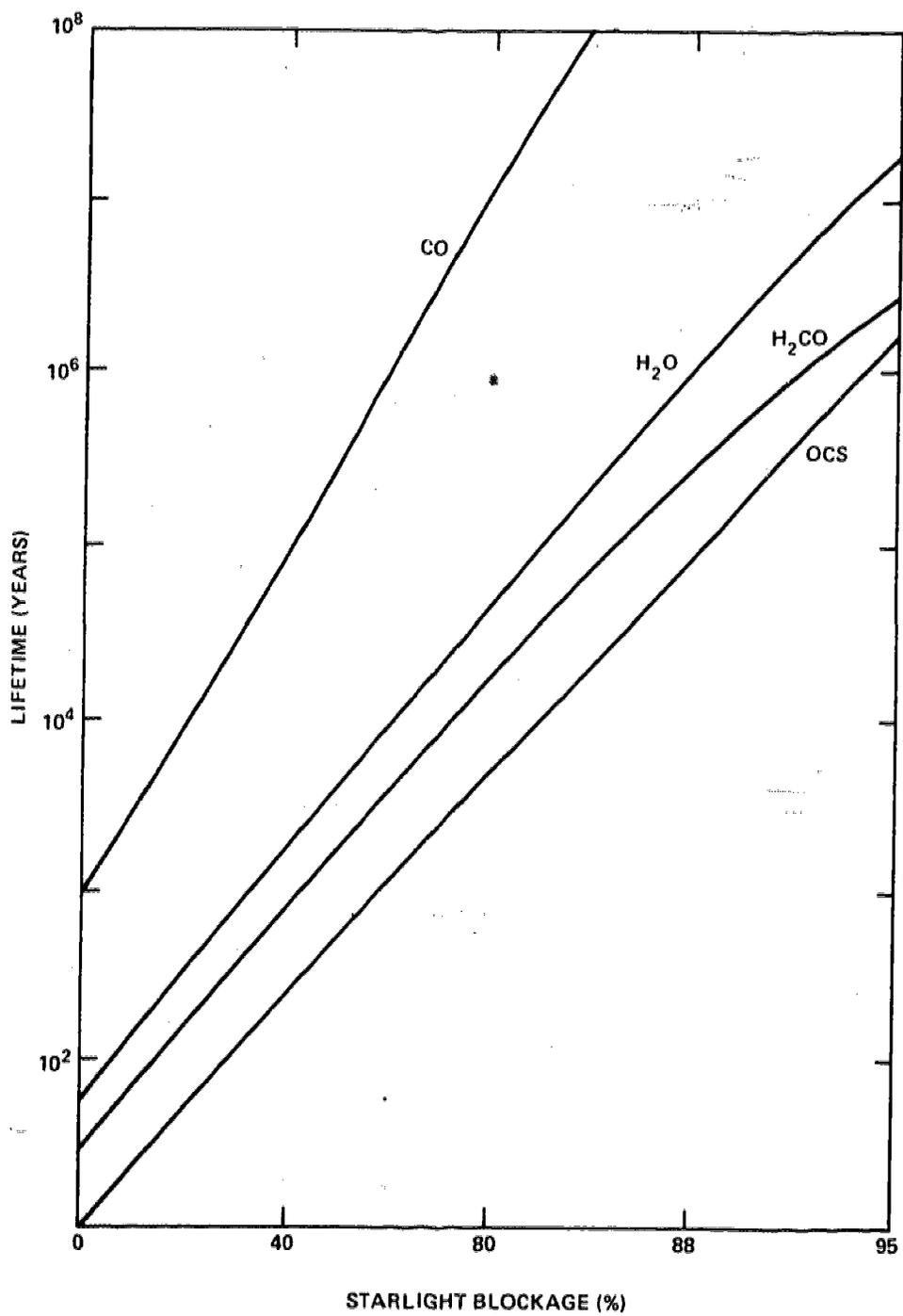
Figure 12 — The lifetimes of interstellar molecules before being destroyed by ultraviolet starlight. Notice that in unshielded interstellar space, most molecules would survive less than 100 years. In a dust cloud of moderate density, one in which the starlight is 95 percent blocked, the molecules might last more than a million years. Note the longer lifetime of CO, a molecule very abundant in clouds.

38

INCREASING TEMPERATURE OR ENERGY ⟶

$CH_3 \cdot NH_2$ $CH_2 = NH$ $HC \quad N$

$CH_3 \cdot CH_2 \cdot NH_2$ $CH_3 \cdot CH = NH$? $CH_3 \cdot C \quad N$

$CH_3 \cdot CH_2 \cdot CN$ $CH_2 = CHCN$ $HC \cdot C \cdot C \quad N$

$CH_3 \cdot CH_2 \cdot CH_3$ $CH_3 \cdot CH = CH_2$ $CH_3 \cdot C \quad CH$

$CH_3 \cdot CH_2 \cdot OH$ $CH_2 = CHOH$ $HC \quad C \cdot OH$

$CH_3 \cdot OH$ $CH_2 = O$ $C = O$

$CH_3 \cdot CH_2 \cdot OH$ $CH_3 \cdot CH = O$ $CH_2 = C = O$?

$NH_2 \cdot CH_2 \cdot OH$ $NH_2 \cdot CH = O$ $HN = C = O$
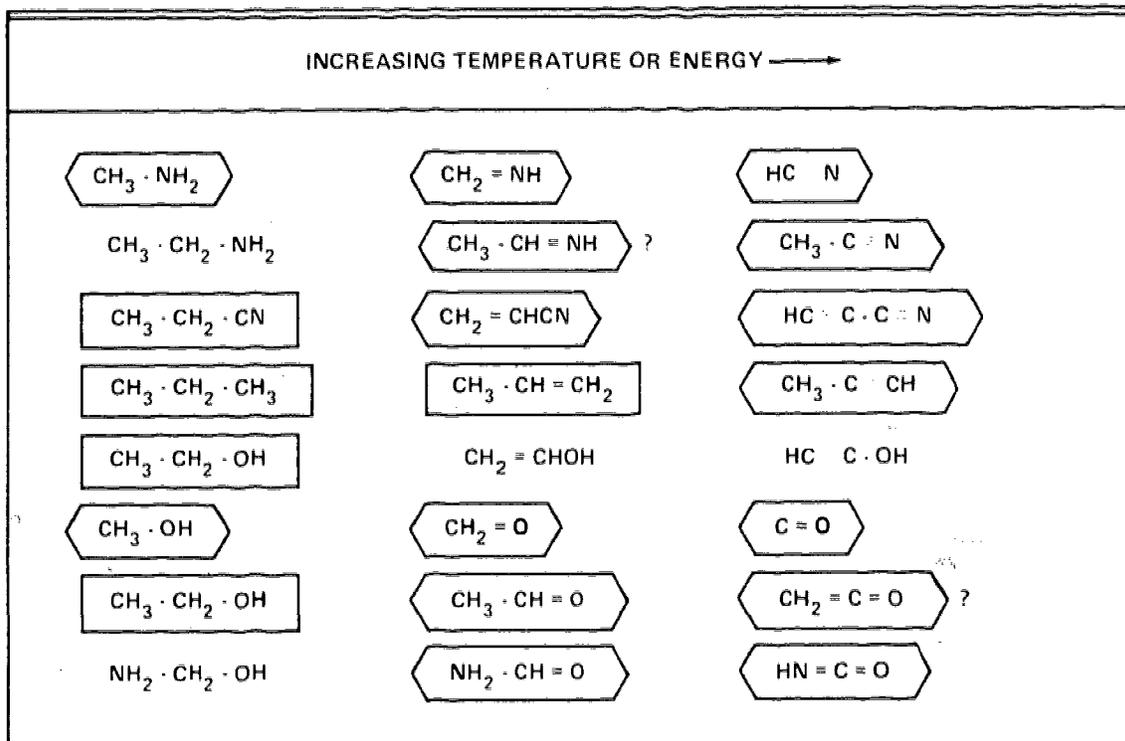
Figure 13 — The prevalence of "unsaturated" over "saturated" molecules in patterns of related species observed or not observed in interstellar clouds. Molecular species within the symbol ⟨⟩ are observed, those within the symbol ☐ have been looked for but not found. The trend is clear: for a given sequence of molecules, the unsaturated (hydrogen-poor) ones are favored over the saturated (hydrogen-rich) ones. Question marks indicate a possible detection and no symbol means that no interstellar search has been made.

48

COMPREHENSION QUESTIONS

Q: What are the two most abundant interstellar molecules? Which four elements occur most commonly in the observed molecules? In life?

A: H_2 and CO: H, C, N, and O, H, C, N, and O.

Q: What are the important physical conditions in interstellar clouds that determine the abundance of molecules?

A: Temperature, density, and radiation.

Q: Name three ways of making and three ways of destroying interstellar molecules.

A: Formation may be achieved by radiative association, ion-molecule reactions, or reactions on grain surfaces. Destruction may result from ultraviolet radiation, freezing onto grains, or chemical reaction.

CHAPTER VIII

INTERSTELLAR MOLECULES AND OTHER AREAS OF ASTRONOMY

One of the most interesting applications of our recent knowledge of interstellar chemistry has been the use of the molecular signals from interstellar clouds to study the birth of new stars. How does a dust cloud become a star? Before interstellar molecules were known, astronomers could only make theoretical models to describe the gravitational contraction of a cloud to form a pre-star ("protostar"). Now, with the aid of the molecular signals from the cloud, astronomers can watch the process of star-birth directly. By comparing the appearance ("line-width" and Doppler shift) of different molecular lines, astronomers can trace the growth of the densest cores of dark clouds, cores which will soon light up as new stars.

Interstellar molecules and new stars go together, since the densest clouds, where molecules are most easily formed and survive the longest, are also the regions most likely to contract gravitationally to form new stars. The evolution of thin clouds to dark clouds to protostars is paralleled by the evolution of molecules from simple diatomics to the larger polyatomic species found in the densest clouds.

The most diffuse interstellar clouds, those with temperatures near 100 K and gas densities from 10 to 100 hydrogen atoms per cubic centimeter, contain only simple diatomic molecules (figure 4). In the denser and darker clouds, which have lower temperature (5-20 K) and higher density ($n_{H_2} \cong 10^2 - 10^4$ cm^{-3}), radio emission from more complex molecules like NH_4 and H_2CO has been detected. These massive dark clouds are gravitationally unstable and already collapsing to form very compact condensations called globules (figure 14). It is thought that globules contract to form protostars, compact regions of greatly increased temperature and density, which appear as hot spots of infrared emission located within the cooler surrounding gas. These hot spots will soon become new stars. Within these protostellar cores, the temperature (T $\gtrsim$ 500 K) and density ($n_{H_2} \geqslant 10^8$ cm^{-3}) are great enough to produce the spectacular water maser signals, as, for example, in the Orion cloud (figures 6 and 10). Interstellar clouds where HCN has been observed have densities of more than a million hydrogen molecules per cubic centimeter and will probably become new stars within the next million years.

Some regions of the Milky Way are found to be "star factories," places of active and continual star formation. These regions of star birth contain interstellar clouds with densities of thousands or even millions of hydrogen molecules per cubic centimeter, and have a total mass of more than a million Suns. The temperature and density within these superclouds are sufficient to allow the formation of a great variety of complex molecular species (CH_3OH, HC_3N, and CH_3CN). These massive molecular clouds are often next to giant "HII regions," hot regions of glowing ionized gas surrounding bright young stars. Examples of such massive molecular clouds are Orion (figure 6) and the molecular source near the Cone Nebula, NGC 2264 (figure 15).

50

Figure 14 – M16, a complex region of ionized and neutral gas. The small, sharply defined clumps are dense, compact dust clouds called globules. (Hale Observatory photograph)

42

Figure 15   The cone nebula, NGC 2264. Near the tip of this cone, radio astronomers have
found a dense molecular cloud with a protostellar core. This region is similar to
the Orion cloud (figure 6) and is likewise rich in interstellar molecules. (Hale
Observatory photograph)

43

The richest molecular source known is a gigantic cloud of gas and dust near the very center of the Milky Way (figure 2). Nearly every known interstellar molecule can be observed in this cloud, and some have been detected only in this cloud.

Interstellar molecules are helping us learn not only about the life cycles of stars, but also about the shape and motion of the Milky Way itself. The massive dust clouds, unknown before the discovery of interstellar molecules, provide some of the "missing mass" needed to explain the observed speed at which the Milky Way spins about its center. The widespread distribution of some molecules (OH, CO, and H_2CO) throughout the galaxy is now allowing astronomers to make molecular maps of the structure of the Milky Way. These maps measure regions of high density and low temperature which complement the maps made in the $\lambda21$-cm radiation of hydrogen atoms. Molecular signals are also being used to probe the unusual motions of dense gas at the very center of the galaxy, where fantastic explosions may be occurring.

The molecular observations also have improved our understanding of the nuclear history of the interstellar matter. All the heavy elements and their isotopes are produced in the recycling of the interstellar material through stars every billion years or so. The isotopic ratios, especially $^{13}C/^{12}C$ and $^{15}N/^{14}N$, tell us which kind of star processed the matter most recently. The interesting result of measurements of isotopic pairs of molecules (e.g., ^{12}CO and ^{13}CO) is that the isotopic abundance ratios all around the Milky Way are about the same as here on Earth (table VII). This means that the stellar history of the interstellar matter is very similar throughout the galaxy or that the Milky Way is very well stirred, quite an unexpected result.

Table VII
Comparing the Chemical Isotope Ratios Found on Earth and in Space

Element	Ratio of Isotopes	Relative Abundance		Observed Molecule
		Earth	Space	
C	12/13	89	89 ± 15	H_2CO, CH^+
O	16/18	488	~ 500	H_2CO, CO
O	16/17	2700	~ 2700	OH
N	14/15	270	230 ± 70	HCN
S	32/34	22	24 ± 5	CS
S	32/33	125	> 100	CS

The last application of interstellar molecules we discuss involves a question that has brought together astronomers, chemists and biologists, namely, what do the observed interstellar molecules say about the origin of life in the universe?

The kinds of molecules observed in interstellar space are strikingly similar to those produced in laboratory experiments designed to simulate the conditions of the early Earth

53

before life began about 3.5 billion years ago (table VIII). In the famous *Miller-Urey* experiments (1953), amino acids were produced by an electrical spark in a mixture of simple gases (H_2O, NH_3 CH_4, and H_2). Since then, an impressive array of "prelife" molecules have been found to form under conditions designed to simulate the early Earth and the *presolar nebula* (the early dust cloud which later formed our Sun). In 1970, chemists synthesized amino acids in the laboratory by simply heating a solution of NH_3 and H_2CO!

Table VIII
Comparing the Kinds of Molecules Identified in Interstellar Space with
the Kinds Produced in Laboratory Experiments of Pre-Life Chemistry

Molecule	Space	Laboratory	Molecule	Space	Laboratory
CO	✓	✓	HC_2CN	✓	✓
H_2CO	✓	✓	HC_2CH_3	✓	...
CH_3COH	✓	✓	NH_2CHO	✓	✓
HCN	✓	✓	HCOOH	✓	✓
CH_3CN	✓	✓	CH_3COOH	...	✓
HNCO	✓	...			
			Amino acids	...	✓
CH_3OH	✓	✓	Sugars	...	✓
CH_3CH_2OH	...	✓	Porphyrins	...	✓

Of the interstellar molecules observed, the species most important for "pre-life" chemistry include water, ammonia, formaldehyde, hydrogen cyanide, and cyanoacetylene. Formaldehyde (H_2CO) is known to polymerize to form various sugars essential for life. The molecules hydrogen cyanide (HCN) and cyanoacetylene (HC_3N) are the key starting materials in the spontaneous formation of the basic building blocks of the *nuclei acids*.

Most of these "pre-life" syntheses have two essential features in common: first, simple molecular forms of C, N, and O as starting materials in a *reducing* (hydrogen-rich) atmosphere, and, second, a source of energy. Despite the vastly different ranges of density and temperature, these same conditions apply to the interstellar dust clouds. One important difference is *liquid* water, usually included in these laboratory experiments as representing the oceans, but missing from the interstellar environment. Remember that the early atmosphere of the Earth was different before life arose — rich in hydrogen, with no molecular oxygen and no ozone (O_3) layer to keep the Sun's ultraviolet rays from penetrating to the ground. Conditions are similar in upper layers of the present-day atmosphere of Jupiter, which probably contains many of the same molecular species observed in interstellar clouds.

It's also interesting to compare the kinds of molecules found in interstellar clouds with the kinds of molecules produced in the dust cloud which contracted to form our own solar

system. Perhaps the best record of this pre-Earth chemistry is in the form of meteorites and comets. Some meteorites, especially those of the carbon-rich type called *carbonaceous chondrites*, have been found to contain many important pre-life molecules. Among those recently found in meteorites are most of the amino acids, liquid formaldehyde, and large porphyrin-like molecules. Comets, which come from very far out in our solar system, may contain the purest record of the chemical nature of the presolar dust cloud. Many of the molecular species observed in comets are the same as those found in interstellar clouds (table V). Other cometary species look like reactive fragments of larger molecules, blasted to pieces by the Sun's radiation.

The similarity of molecular species found in interstellar clouds, meteorites, and comets, and in laboratory experiments in "pre-life" chemistry, is striking. It seems that interstellar clouds contain the starting materials for life even before they contract to form new suns. The chemistry which leads to life on Earth appears to be the natural and probable chemistry throughout the Milky Way. If life has evolved elsewhere in the galaxy, it must be based on a similar chemistry.

COMPREHENSION QUESTIONS

Q: What is a protostar and how can it be identified in space?

A: A protostar is a new star just forming at the center of a contracting interstellar cloud. It is usually seen as a hot spot of infrared radiation and molecular emission, especially when it produces the water maser.

Q: Name three applications of the study of interstellar molecules to other areas of astronomy.

A: The early stages of star formation; the structure and motion of the galaxy; and the history of the recycling of interstellar matter through stars.

Q: Name five interstellar molecules considered by biochemists to be important for the origin of life.

A: H_2O, NH_3, H_2CO, HCN, and HC_3N.

55

EXERCISES AND PROJECTS

DEMONSTRATIONS AND PROJECTS

1. **Conducting a field trip to a nearby planetarium.**

2. **Finding the interstellar dust clouds for yourself.** On a clear, moonless winter night, the Milky Way and the clouds of interstellar gas and dust can be easily seen with the unaided eye (figure 2) (Why is the dust in the plane of the galaxy easier to find that that out of the plane?). The region near Cygnus the Swan is especially favorable for observation. In the dust clouds in this direction radio astronomers have found H_2O, OH, H_2CO, CO, and NH_3, each identified by its characteristic radio radiation. Another important and nearby (1200 ly) molecular cloud is behind the Orion nebula (figure 6). Locate the Orion nebula in the winter sky; this is possible with the unaided eye, but is easier with binoculars or a small telescope. Behind the glowing gases is an enormous, dense, and cold dust cloud, which has been found to contain an abundance of different molecules as well as several new stars just starting to form.

3. **Constructing crossword puzzles.** Have students construct crossword puzzles of unfamiliar words in this unit.

4. **Illustrating interstellar clouds.** Show film-loop or time-lapse sequence of development of clouds in our atmosphere. Have discussion, comparing atmospheric clouds with interstellar clouds.

5. **Illustrating density of interstellar space.** Let the classroom represent one cubic centimeter of interstellar space. Then let a fine pencil dot (or width of one hair) represent one hydrogen atom. This comparison, one dot per classroom, represents a very dense interstellar cloud ($n_H \sim 10^3$ cm^{-3}), about 1000 times more dense than average interstellar space.

6. **Tracing interstellar clouds.** Have students draw in the spiral arms of the Andromeda galaxy by tracing the dark dust lanes (figure 1); they may also trace the outline of the obscuring dust clouds in Sagittarius (figure 2); and find the black specks ("globules") in M16 (figure 14). More advanced students may try the laboratory exercises (see references to H. Kruglak, Chapter X) on dust cloud distance.

7. **Playing a game to make molecules in space.** In a box, place at least 100 white marbles (hydrogen), 7 blue marbles (oxygen), 3 black marbles (carbon), and one green marble (nitrogen). Mix well. The "atoms" in the box represent the relative abundances of H, N, C, and O in interstellar space (except that we have reduced hydrogen 10^2 times to save marbles). The game is designed to show what kinds of molecules would form in random collisions in a gas of this mixture. Have a student draw two marbles from the box, representing the formation of diatomic molecules. Notice that two white marbles (H_2) are drawn almost every time, and very rarely do molecules without hydrogen form (CO, CN, etc.). If the class has a chemistry background, the game can continue by

allowing each molecule formed (pair of marbles drawn) to continue to grow (draw more marbles) until "stable" molecules are formed (CH_4, NH_3 H_2O, and H_2). Compare the list of game molecules made with the observed interstellar list (table VI).

8. **Making ball-and-stick models of interstellar molecules** (see table VI and figure 9).

9. **Illustrating "activation" or starting energy for chemical reactions.** Collect hydrogen and oxygen gas by electrolysis of water. Mix the gases and note that nothing happens. Apply spark. Discuss. For another example, strike a match to make it light.

10. **Illustrating the potential energy between atoms and the change from potential to kinetic energy as the atoms approach each other.** Two balls (or better air-carts on a track) attached by a spring may be used to represent gravitational attraction. Separate and release. Relate to contraction of interstellar clouds. To show how the energy of motion becomes heat, measure temperature change in a bag of lead shot, dropped several times from a height of several meters.

11. **Discussing the conversion of radiation into heat.** Conduct the discussion in the context of (1) warming yourself near a campfire, and (2) cooking with a microwave oven. For an analogy of the change in the rotational motion of molecules by absorbing radiation, shine light on a radiometer. Discuss.

12. **Illustrating the resonance behavior of two tuning forks.** Discuss in relation to maser action of water molecules in space.

13. **Discussing how a radio works.** Explain how different channels (e.g., rock, classical) are "tuned in" at different wavelengths. Relate to the "radio stations" of different molecules.

14. **Demonstrating how interstellar dust blocks starlight.** Fill a bell jar with smoke to simulate an interstellar cloud. Shine a narrow beam of white light through the smoke in a darkened room. Note the change in color of the emerging light. The effect is even better when viewed first through red and then blue filters. Another way to make "smoke" is to put a few drops of silver nitrate in a beaker of tap water.

15. **Explaining the Doppler effect.** Discuss the change in pitch of passing car horns. Use a ripple tank and vibrator to make water waves, or alternatively, a pyrex tray of water on an overhead projector.

16. **Describing the nature of interstellar space** (creative writing exercise). Imagine you are a hydrogen atom drifting through an interstellar cloud. Describe your experience.

17. **Relating interstellar molecules to life.** Make a wall chart comparing molecules important for life with those already found in space. Discuss the nature of life and implications of the discovery of "prelife" molecules in space for the possibility of life elsewhere.

57

EXERCISES WITH ANSWERS

1. Give the electromagnetic spectrum from gamma rays to radio waves, the wavelengths in each energy range, and the corresponding kinds of molecular motion. How well does the radiation at each wavelength penetrate the Earth's atmosphere or an interstellar dust cloud?

2. Compare the interstellar dust grains (size, shape, temperature, and chemical composition) of (1) meteorites, (2) comets, and (3) the Earth.

3. Write a report on U.S. ("Viking") and Soviet planetary probes, emphasizing the life-sensing experiments.

4. Read the science fiction novel, *The Black Cloud*, by the astronomer Fred Hoyle. On the basis of what you now know about the physical and chemical nature of interstellar clouds, discuss why you think life could or could not exist there.

5. A gas molecule in a typical interstellar cloud (radius 10 ly ($\sim 10^{19}$ cm) and gas temperature 50 K) is moving with a velocity of about 1 km s. How long will it take to go across the entire cloud?

6. The energy levels of simple diatomic molecules like CO are given by the formula

$$E = BJ (J + 1)$$

where E is the energy, B is the rotational constant of the molecule, and J is the rotational quantum number which labels the various levels – the lowest or ground state (J = 0), the first excited state (J = 1), etc. The molecule CO was first found in interstellar space by the radiation emitted in the transition from the J = 1 to J = 0 level. If B = 1.0 cm^{-1}, what is the energy of this transition in cm^{-1}, in terms of degrees Kelvin (1 cm^{-1} = 1.4 K)?

7. Consider an ideal molecule with only two energy levels. The dots represent relative numbers of molecules in each level.

$$\Delta E = \begin{cases} & \end{cases}$$

upper
lower

A   B   C

$\Delta E = E(upper) - E(lower)$

   (a) Which distribution of molecules represents the lowest temperature?

   (b) Which will appear in maser emission, which in absorption?

   (c) Which population indicates a temperature closest to ΔE?

   (d) Name an interstellar molecule whose spectrum indicates a population like A, and one whose spectrum indicates a population like C.

58

8. As an example of the Doppler effect, consider that we are located at position (B) in an ideal galaxy in which all the matter moves in perfectly circular orbits about the galactic center (A). If we detect an interstellar molecule in a gas cloud in the center (A), what would be the measured velocity of cloud (A) with respect to our position (B)? Answer the same question for the measured velocity of a source (C) located farther from the center than we are, but so that A, B, and C form a straight line.

SIDE VIEW   TOP VIEW
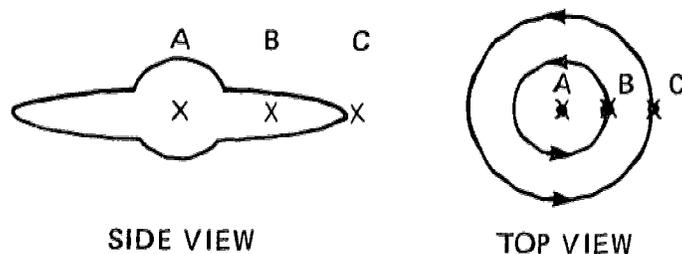
ANSWERS:

1. Refer to figure 3. Radiation of wavelength $\lambda > 1\mu$ can penetrate dust clouds. Radiation with wavelength decreasing from the visible is increasingly blocked by the dust (figure 5). Only when the energy becomes very high ($E \gtrsim 100$ MeV) can radiation and cosmic ray particles penetrate the densest dust clouds.

2.

	Dust Grains	Meteorites	Comets	Earth
size	$10^{-6} - 10^{-4}$ cm	$10^{-4} - 10^{2}$ cm	$1 - 10$ km	$\sim 2 \times 10^{4}$ km
shape	(?) Irregular	(?) Irregular	(?) $\sim$ Round	Round
temperature	10-20 K	--		300 K
composition	? Silicates, Fe organic shell	Silicates, Fe organics	Ice ball, organics	Rock core organic shell

The outer layers of meteorites become quite hot ($> 10^3$ K) during their fall through the atmosphere; inner parts remain cooler. Comets are cold (< 50 K) until they approach the sun, which heats them and evaporates material to form the tail.

3. -- -- --

4. Despite organic molecules observed, life is unlikely in dust clouds, which lack liquid water (essential for life as we know it) and which last only 10^6-10^7 yrs, too short a period for self-replication under interstellar conditions.

59

5. Distance = rate $\times$ time

$$\text{time} = \frac{10^{19}\,\text{cm}}{1\,\text{km s}^{-1}} = \frac{10^{19}\,\text{cm}}{10^5\,\text{cm s}^{-1}}$$

$$t \cong \frac{10^{14}\,\text{s}}{3 \times 10^7\,\text{s/yr}} \cong 3 \times 10^6 \text{ years}$$

which is about the lifetime of the cloud. Of course, collisons with other molecules would occur in a much shorter time.

6. $E = BJ\,(J + 1)$

$$E(J = 1) = B(1)(2) = 2B$$
$$E(J = 0) = 0$$
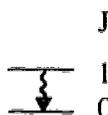
$$\Delta E = E(J = 1) - E(J = 0) = 2\,(1.9\text{ cm}^{-1})$$
$$\Delta E = 3.8\text{ cm}^{-1} \cdot 3.8\,(1.4) = 5.3\text{ K}$$

This energy spacing is about equal to the temperature in the coldest of the interstellar dust clouds.

7. **(a)** A is coldest.

   (b) C is a maser, A will absorb.

   (c) B has a temperature $T \sim \Delta E$.

   (d) A: H_2CO or the optical lines of CH^+, CH, CN.
   C: H_2O maser.

8. Both sources (A) and (C) would show the same velocity, zero, since for the purely circular motion, all positions on the line ABC have no motion along that line, only perpendicular to it. In this case the Doppler shift is zero and the observed frequency of the molecular transition will agree with that measured in the laboratory. For an example in the real world, look at figure 8; notice the measured velocities of interstellar HCN in the galactic center (which corresponds to ideal position A) and in Orion (which in fact lies nearly in the idealized anticenter position C). The velocities are not exactly zero or equal because (a) there are non-circular motions in the Milky Way, and (b) the Earth and these two sources are not exactly on a straight line passing through the center of the galaxy.

$$60$$

REFERENCE MATERIALS

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62

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63

GLOSSARY

activation energy— (see chemical reaction).

angstrom (Å)— a unit of length equal to 10^{-8} cm, the scale of atoms.

carbonaceous chondrite— a particular type of nonstony meteorite, rich in carbon and carbon-containing chemical compounds.

catalyst— a substance which promotes a chemical reaction, without itself undergoing chemical change.

chemical reaction— a process, involving atoms, in which a chemical bond is broken or formed. If the final *products* of the reaction are more stable than the initial *reactants*, the reaction is "exothermic" and energy is given off in the process. Exothermic reactions take place spontaneously unless inhibited by an energy barrier. The energy that must be supplied to overcome this barrier and cause the reaction to take place is called the *activation energy*. Important types of reactions are *association* (A + B → AB), the reverse — *dissocation* (AB → A + B), and *exchange* (AB + C → AC + B). If one of the reactants is an *ion*, the reaction is called an *ion*-molecule (AB + C^+ → AC^+ + B).

circumstellar— around a star, as opposed to *interstellar*, between the stars.

column density of molecules— the total number of molecules within a box of cross sectional area 1 cm^2 stretching along the line of sight from the Earth to the celestial source (see number density).

cosmic microwave background— the thermal radiation (3 K) which bathes all space and which astronomers interpret as the Doppler-shifted remnant of the primordial fireball from the explosive beginning of the universe.

cosmic ray particle— the bare nucleus of an atom, stripped of all its electrons, and moving at speeds approaching the velocity of light. The energy of such a particle is very great, up to 10^{20} electron volts.

Doppler effect— the apparent increase or decrease in the received frequency of an oscillating signal due to the relative motion of the source of the waves and the observer. For electromagnetic radiation of velocity c, the fractional change in frequency (f) for a relative velocity (v) is given by $\Delta f/f \sim v/c$.

electromagnetic radiation— a combination of electric and magnetic field distrubances with a given frequency, which travels through empty space at the speed of light.

electron volt (eV)— the energy an electron receives in being accelerated across a voltage difference of one volt.

exothermic — (see chemical reaction).

extinction— the absorption and scattering of starlight by the interstellar dust grains.

extragalactic— outside our galaxy.

galactic— within our own galaxy, the Milky Way.

interstellar— between the stars.

ion— an atom or molecule (*molecular ion*) which has more or fewer electrons than protons, and which therefore is negatively or positively charged. Ionization, the loss of electrons by an atom or molecule, produces positive ions (e.g., C^+, CH^+).

ion-molecule reaction— (see chemical reaction).

ionosphere— layer of charged particles (ions and electrons) at the top of the Earth's atmosphere.

isotope— two atoms of the same element which have different atomic weights are called isotopes of that element.

Kelvin— the temperature scale so calibrated that absolute zero temperature is 0 degrees Kelvin, which is $-273°$ Centigrade or $-459°$ Fahrenheit. A difference of one degree Kelvin is the same as one degree Centigrade.

light year— distance traveled in one year at the speed of light, about 10^{18} cm.

maser— the self-amplification of the characteristic microwave radiation of a particular molecule or atom. For visible light, the same effect produces a *laser* (*light* amplification by *stimulated emission of radiation*). In both cases, the effect is the same. Just as one tuning fork can make an identical fork resonate, some molecules (atoms) emit resonant radiation that stimulates other molecules to do likewise. In this way the intensity of the radiation is greatly amplified. One requirement for a maser to occur is that molecules (atoms) must be "pumped" into the upper state, from which they pass to the lower state by emitting the resonant radiation.

micron (μ)— one millionth of a meter.

Milky Way— our own galaxy.

molecule— chemical union of two (*diatomic*) or more (*polyatomic*) atoms. Organic molecules contain carbon; inorganic molecules do not. A free radical is a molecule in which one or more electrons are "free" or available to form additional chemical bonds. Free radicals are therefore very reactive.

NGC— *New General Catalogue*, a list of non-starlike objects compiled by the astronomer Dreher in 1888.

number density— the number of atoms (molecules) per cubic centimeter.

nuclear synthesis— the nuclear process in which atoms of one element are transformed into atoms of a different element.

nucleic acids— the molecules DNA and RNA, which are the building blocks of the genetic code in living matter.

65

photon— a quantum of electromagnetic radiation with energy (E) given by $E = hf$, where f is the frequency and h is Planck's constant.

porphyrin— a class of large organic molecules with a complex ringlike structure surrounding a central metal atom. Porphyrins have high stability and are important in living systems (e.g., hemoglobin (Fe) and chlorophyll (Mg)).

protostar— a newly forming star, usually observed as a pointlike source of intense infrared (but not visible) radiation at the center of a contracting interstellar cloud.

resonance— (in spectroscopy) the agreement in energy of a photon of radiation with the difference between two energy states of an atom or molecule. In this case the photon is called "resonant."

saturated— a condition of hydrogen-rich molecule that has each carbon, nitrogen, or oxygen atom bonded to the maximum number of possible hydrogen atoms. If this is not the case, the molecule is called "unsaturated" or hydrogen-poor.

silicate— mineral containing silicon, oxygen, and metal atoms, such as sand.

solar wind— (see stellar wind).

spectrum— the unique set of wavelengths of radiations which an atom or molecule characteristically absorbs or emits. The record of one such wavelength is also called a spectrum, spectral "line," or "feature."

stellar wind— the flux of radiation and fast particles which stream outward from a star. The stellar wind of the Sun is called the *solar wind*.

spectroscope— an instrument used to spread out (*disperse*) electromagnetic radiation into its components at each frequency (as a prism disperses sunlight into colors), and to record the *spectrum* of this dispersed radiation.

temperature— the measure of thermal energy (see Kelvin).

transition— change from one energy state of an atom or molecule to a higher or lower state, with an absorption or emission of resonant radiation.

turbulence— swirling or streaming motion, as shown, for example, in storm clouds or rushing water in a mountain stream.

unsaturated— (see saturated).

wavelength (λ)— the length of a wave, measured from crest to crest.