FROZEN FREE RADICALS IN INTERSTELLAR SPACE

by G. Wilse Robinson

The space between the stars is not an empty void but a region filled with dust and gas. To be sure, the number of atoms per unit volume is small—the average being only about 1,000 atoms per bucketfull of interstellar space. However, the concentration of atoms and dust tends to "bunch up" into clouds and is very uneven over space. Even in the clouds, however, the concentration of matter is not very high by ordinary standards. It is about 1/40th as dense as the best vacuums one can obtain in the laboratory by modern vacuum techniques, as can be seen by the comparisons below:

CONCENTRATION OF INTERSTELLAR ATOMS

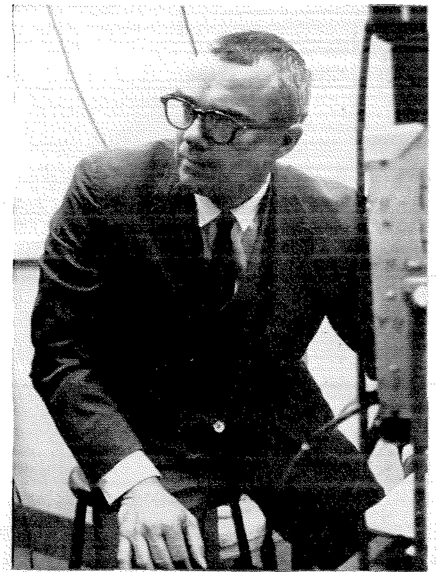
	atoms/liter
Average Value	100
Interstellar Clouds	100,000
Best Laboratory Vacuums	3,600,000

Even so, the space between the stars is so vast that the interstellar gas and dust comprise perhaps as much as 10 percent of the total amount of material in the galaxy.

Knowledge about the interstellar gas has been derived mostly from spectroscopic measurements. One finds that the white light from a very distant star, after passing through the immensity of space, has partially been absorbed because of the presence of the intervening gas. Each atom or molecule has a characteristic absorption color or wavelength which acts as a "fingerprint." In this manner, atoms and ions of the elements titanium, sodium, potassium, iron, and calcium have been found, as have the diatomic molecules CH, CH^+ (CH with one electron missing), and CN. Using radio frequency and microwave techniques, researchers have also detected hydrogen atoms and OH molecules. These atoms and molecular fragments are what I refer to as free radicals. (The use here of the term "free radical" to mean any atom or molecular fragment does not exactly coincide with the standard chemical definition.)

Many other kinds of whole molecules and molecular fragments, such as carbon atoms, hydrogen molecules, and water vapor, are believed to exist in interstellar space, but their absorptions are so weak at wavelengths of light presently possible for study that they have not yet been detected there. Rocket- and satellite-based spectroscopy has opened up new wavelength regions of the spectrum by eliminating atmospheric absorption, and, in the future, moon-based observatories will shed much more light on the problems of interstellar gas absorption.

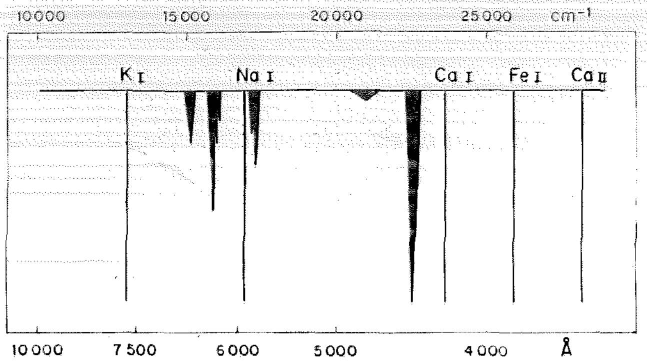
Our main concern here, however, is not with the individual atoms, molecules, and free radicals that form the interstellar gas, but rather with agglomerations of these—tiny, solid particles, many almost too



G. Wilse Robinson, professor of physical chemistry at Caltech, has been interested in "the space between the stars" for as long as he can remember. Only recently, however, has his work brought him very close to active participation in this field. While an assistant professor at Johns Hopkins University, Dr. Robinson discovered that atoms and small molecular fragments embedded in certain solids at very low temperatures absorb light in a manner resembling that by which light is absorbed by an isolated atom or molecule. However, differences in absorption between the isolated molecule and the "trapped" molecule cause difficulty in identification of such absorptions. Dr. Robinson reasoned that atoms and molecular fragments similarly frozen out in interstellar space could therefore be responsible for certain unidentified absorptions found there.

In 1959 Dr. Robinson came to Caltech as associate professor of chemistry. In recent years he has concentrated his work in the fields of vibrational and electronic spectroscopy of molecules, low temperature chemistry, and energy transfer phenomena in chemical and biological systems.

During the past year he has been advisor for the honors work of two Caltech undergraduate students, Jim Marable and Mike Ruth, who have been conducting experiments designed to identify the composition of "interstellar dust," which Dr. Robinson discusses in "Frozen Free Radicals and Interstellar Space." This article has been adapted from a lecture given by Dr. Robinson on May 15, the last of Caltech's 1967 Spring Lecture Series in Beckman Auditorium.



Broad interstellar absorptions with lines of potassium, sodium, calcium, and iron as reference.

small to be seen under a high-powered microscope. These interstellar grains, as they are called, may be ejected from the cooler regions of stellar atmospheres by radiation pressure, or they may freeze out from the interstellar gas in the very cold parts of interstellar space, which are around 20 degrees above the absolute zero. Or perhaps they arise from a combination of dust ejection followed by condensation of interstellar gas.

In any case, from a chemical point of view, the grains are expected to be very complicated. It makes a chemist's head swim to think of all the possibilities that can arise from a mixture of atomic carbon, oxygen, nitrogen, magnesium, silicon, and sulfur, plus a dash of atomic sodium, calcium, iron, and other less abundant elements, freezing out at low temperatures in the presence of constant bombardment by electrons, hydrogen atoms, and ionizing radiation.

Because much of the hydrogen may boil off, the grains, unlike the rest of interstellar space, need not have a high hydrogen content. Most of the hydrogen that sticks is probably chemically bound to the grain. Even if these particles were formed from "dirty graphite cores" (i.e. cores made up primarily but not entirely of carbon) ejected from stellar atmospheres, as some scientists think, the accumulation of complex chemical substances on their surfaces would seem to be inevitable. A typical-size grain contains roughly a billion atoms. Such a grain undergoes about a collision per minute with a hydrogen atom and about a collision per day with some chemically reactive heavy atom other than hydrogen. At this rate it takes only about a million years for such a grain to undergo collisions in space with a billion other atoms, not including hydrogen. So, the equilibrium composition of a grain may be pretty much at the mercy of its gaseous interstellar environment, rather than dependent on the mode of its initial formation.

Information about the grains is derived, just as for the interstellar gas, mostly from spectroscopic measurements. Absorption of light by grains, scattering of light by grains, and polarization of light by grains are examples of problems that have been studied. The diagram at the left shows, schematically, some of the more prominent, discrete absorption lines thought to be caused by the grains. The complexity of the spectrum is consistent with the expected complex chemical composition of the grains. It is to be emphasized that no definite identification of these features has yet been made, although many speculations have been advanced. Thus a major mystery exists. This is a pity since we are, therefore, ignorant of a measurable fraction of the composition of the universe.

In addition to these relatively discrete absorptions, there could be an underlying, general, continuous absorption caused by substances embedded in the grains. This aspect of the problem has never been considered by astrophysicists. The presence of a continuous absorption could spoil the interpretation of the light-scattering experiments on which much of our present knowledge of the grains rests.

The mystery of the grains is as much of a chemical problem as a physical one. Laboratory experiments, trying to duplicate the interstellar absorptions, should be performed by chemical spectroscopists who are familiar with complicated molecules adsorbed on or embedded in solids. Actually some work along these lines has been carried out. Atomic sodium and calcium can be frozen out under certain conditions resembling those in interstellar space. It is noteworthy that the absorption spectra of these frozen atoms are very close to the spectra observed for the grains. The concentration of sodium and calcium atoms in interstellar space is not high, as seen in the above table, but their absorption is very intense. Besides, in the grains, the atoms probably have a higher concentration than in the interstellar gas.

RELATIVE STELLAR ABUNDANCES OF SOME ELEMENTS

Hydrogen	1,000,000	Magnesium	25
Carbon	500	Silicon	25
Nitrogen	100	Sulfur	25
Oxygen	1,000	Helium	150,000
Sodium	2		
Calcium	2		
Iron	2		

Further frozen free radical experiments are now being carried out at Caltech in a more directed effort to identify the grain material. Various mixtures of atomic carbon, oxygen, nitrogen, and hydrogen, together with the more prominent metal atoms, are allowed to impinge on a surface cooled to liquid helium temperature (4°K). The frozen material is then examined spectroscopically for the possible presence of the grain absorption lines.