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ORGANIC MATTER IN INTERSTELLAR SPACE

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To commence our deliberations on this subject let us first ask where within the universe do we find interestellar molecules? If we look at a picture of a spiral galaxy such as M33 (Fig. 1) we can discern a number of dust patches. These dust patches tend to occur along the inner parts of spiral arms or near the nucleus of the galaxy. Let us now consider the dust patches themselves rather more closely. Some dust clouds are associated with bright nebulae and make a rather attractive sight in a telescope (Fig. 2). The bright parts of the nebulae are ionised atomic gas and so are not of any direct interest to us from the point of view of interstellar molecules. However the remaining dust associated with the total nebula is much colder than the ionised gas, and it is here that interstellar molecules are found.

In addition to those dark nebulae that are part of a larger body and include ionised regions, there are others that are

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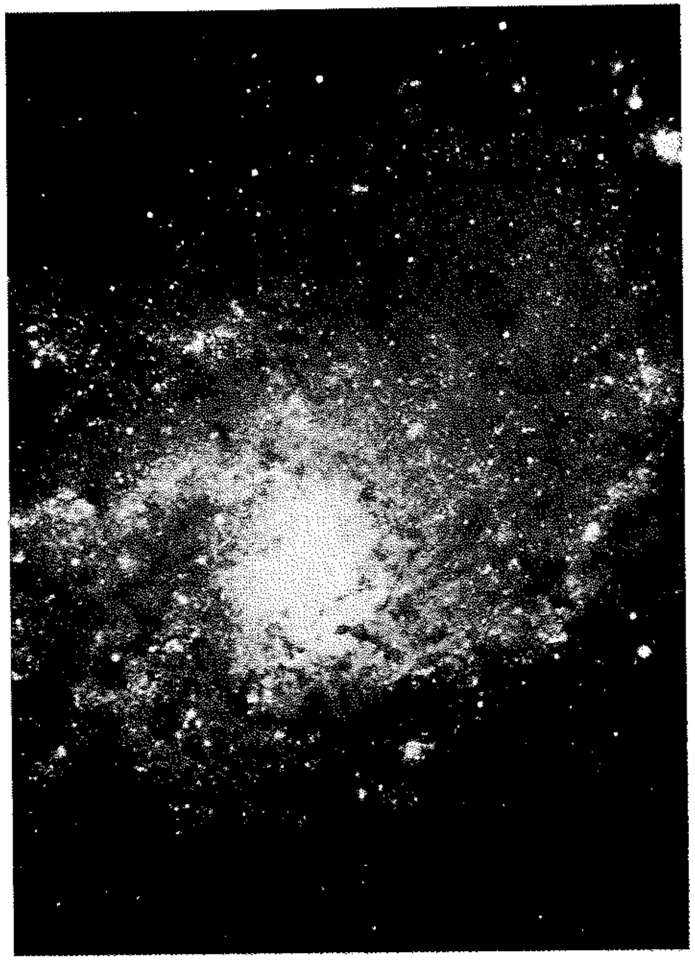


FIG. 1 — Spiral galaxy M33, showing presence of dust clouds.

FIG. 2 — The Trifid Nebula. The emission comes from ionized H and other atomic ions.

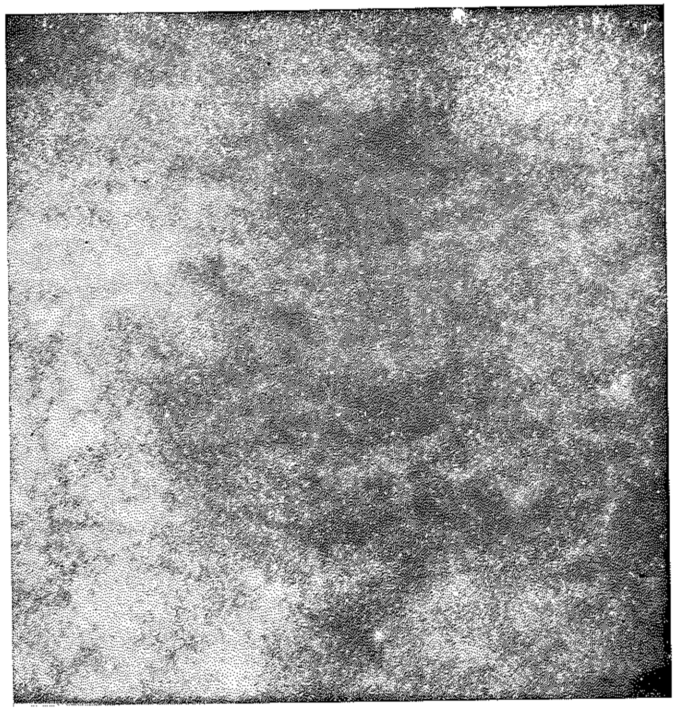


FIG. 3 — The southern Coal Sack, a dark nebula near the Sun.

isolated cold clouds of dust and gas. The southern Coal Sack (Fig. 3) is an excellent example of one of these. The two dark nebulae that are being most frequently studied in the search for interstellar molecules are the dark nebula that is immediately behind the bright nebula known as the Great Nebula of Orion (Fig. 4) and another dark nebula that is not directly visible to the eye but can be detected with radiotelescopes (Fig. 5). This is an enormous object, close to the centre of the galaxy, known as Sagittarius B2. It appears to be the most prolific source of interstellar molecules that we know and the Orion nebula is probably the next best source, not because it is the next largest dark nebula but because it is one of the nearest to

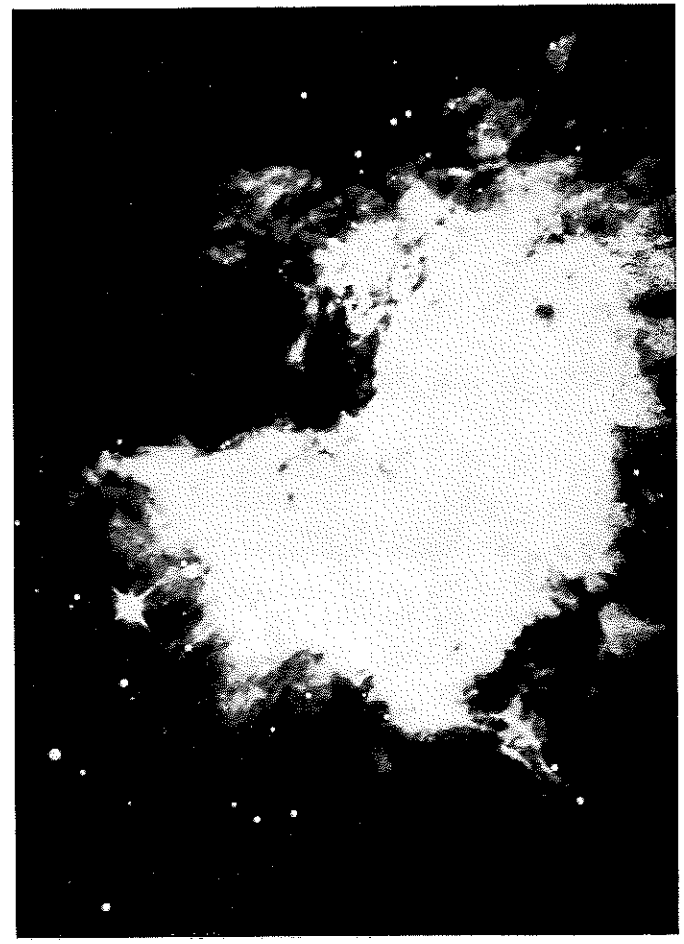


FIG. 4 — The Great Nebula in Orion (M42).

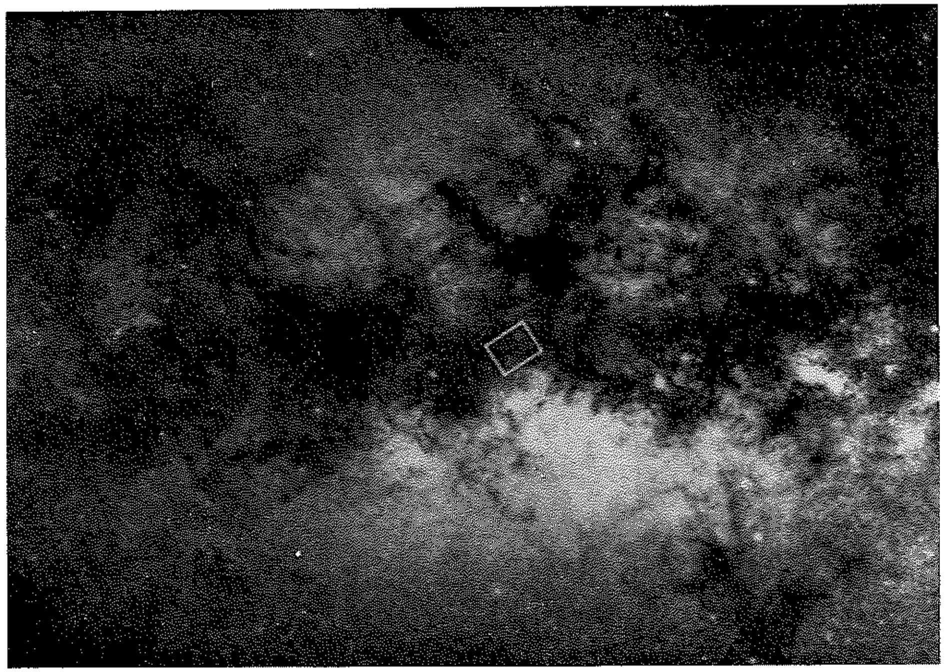


FIG. 5 — Looking towards the galactic centre and Sgr. B2 (within rectangle). Intervening interstellar dust obscures the view of Sgr. B2 in visible light.

the Earth. However, interstellar molecules have been found in a considerable number of other objects that are classified as either dark nebulae or, when they are rather more concentrated and so have a greater obscuration of visual light, they are now referred to as molecular clouds. The accompanying table lists typical properties of dark nebulae and molecular clouds that are of interest in the study of interstellar matter.

To study the chemical composition of molecular clouds we make use of spectroscopic techniques. Such techniques of course have dominated astronomy for the last century although until about the last decade or two it was atomic spectro-

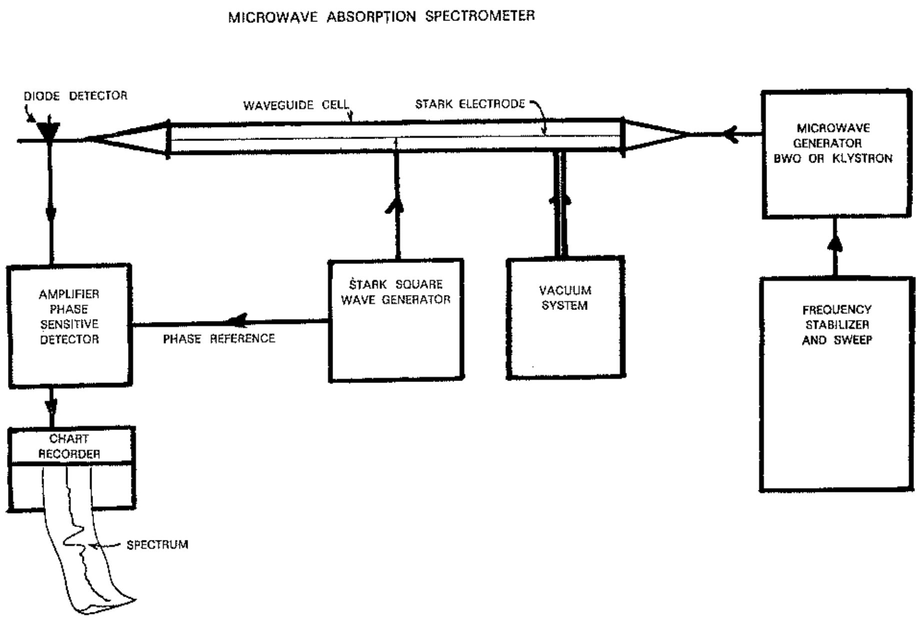
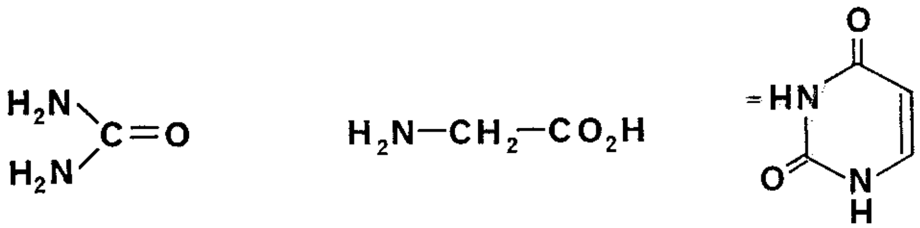


FIG. 6 — Block diagram of a microwave spectrometer.

scopy that was important. In the case of interstellar molecules it is the rotational spectrum of the molecule that proves valuable for its study. Rotational transitions occur in the microwave region of the spectrum for the great majority of molecules which means that it is microwave spectroscopy (Fig. 6) that must be pursued in the laboratory and then subsequently it is techniques of radioastronomy in the microwave region that are called for in the study of dark nebulae and molecular clouds.

Because one of the major interests in interstellar molecules is the question of their possible relation to the origin of life there has been a strong desire to search for organic molecules that have a particular biological significance. Such molecules are formaldehyde, urea, glycine — the simplest amino



urea glycine uracil

FIG. 7 — Urea, glycine and uracil.

acid, and uracil — one of the bases involved in the genetic code (Fig. 7). For spectroscopists all but formaldehyde present problems because the rotational spectrum must be studied with the compound as a low pressure gas. Urea, glycine and uracil are all normally thought of as involatile solids that decompose on heating. However we have managed to observe in turn the rotational spectra of all three of these molecules at Monash University by developing suitable spectrometer cells to enable the microwave spectrum of the vapours to be measured and analysed. Figs. 8 and 9 illustrate the kind of elaborate cells necessary to ensure that the material is heated in a highly controlled way to optimum temperature and that the effect of impurities and decomposition products is minimized by constant pumping, a dynamic vapour pressure being achieved by a balance of the vapourization and pumping processes.

In the case of glycine there was considerable interest in the particular conformation adopted by the molecule in the gas phase. Fig. 10 illustrates the six most plausible conformations indicated by studying the problem using molecular-orbital calculations. As a result of our analysis of the spectral lines

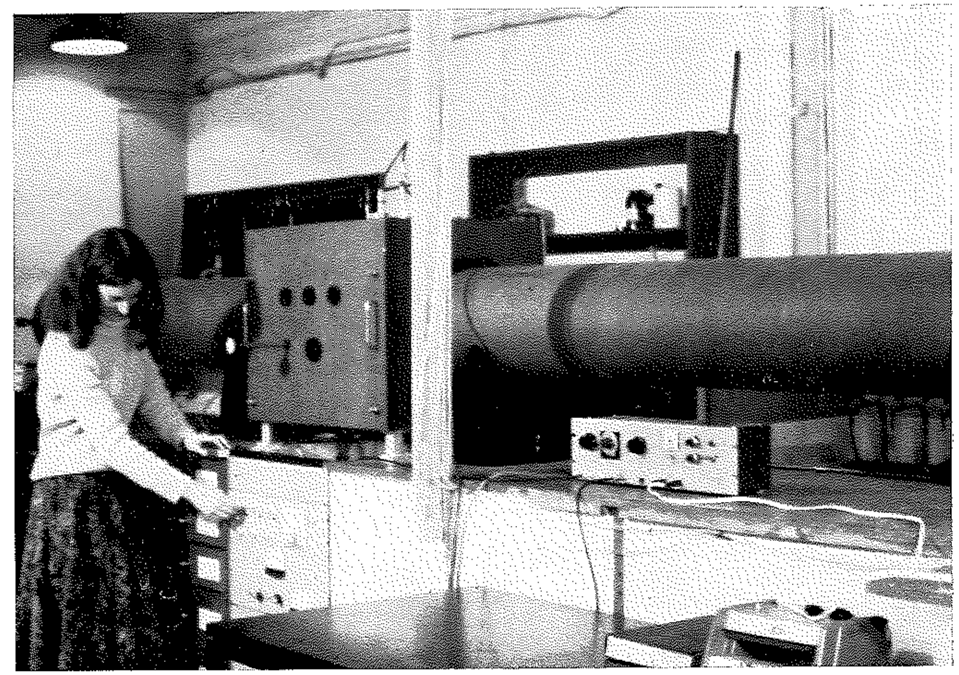


FIG. 8 — Special heated microwave spectrometer cell used to study urea and uracil.

observed in our microwave spectrometer we were able to conclude that the form of glycine that we had observed is glycine four. It is of interest that the elaborate calculation done on the two conformations had predicted that glycine three would be faintly more stable than glycine four, the other conformations being appreciably less stable than these two. The studies of urea and uracil have confirmed that the widely held belief that both would be planar molecules and that uracil is in the diketo form, are consistent with our analyses of the spectra of these two compounds.

Having established the rotational spectral frequencies of potentially interesting interstellar molecules the next step is

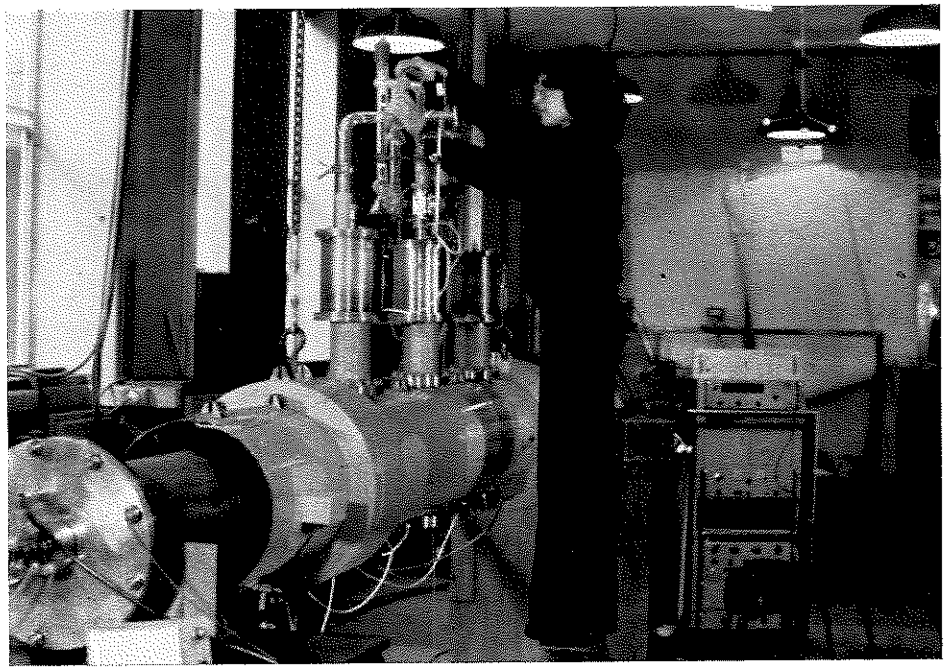


FIG. 9 — Special heated microwave spectrometer cell used to study glycine.

to make use of a radiotelescope. Figs. 11 to 13 illustrate some of the radiotelescopes that we and others have used in searching for and observing some interstellar molecules. Fig. 14 shows an example of a comparison of the spectrum observed in the laboratory and the corresponding spectrum observed on a radiotelescope. Most of the signals from interstellar molecules are so weak and are competing with rather substantial noise from the electronics of the radiotelescope and from space itself that it requires lengthy integrations to detect the signal above the noise. In the case of the methanimine signal, four days of integration on the telescope were required to observe the still rather noisy signal shown in the lower part of the diagram.

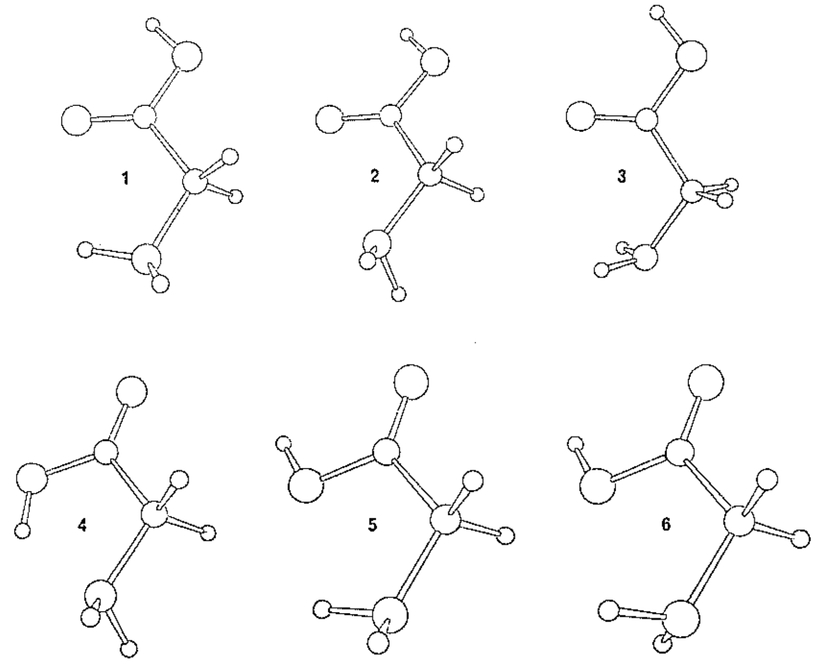


FIG. 10 — Possible conformations of the glycine molecule, $H_2N.CH_2.CO_2H$.

From observations on the various radiotelescopes around the world it has been possible to detect fifty interstellar molecules. These are listed in Fig. 15. Several of the entries were in fact molecules detected not by their rotational spectrum but by their infrared spectrum or, in one case by the ultraviolet spectrum obtained from a spectrometer transported outside the Earth's atmosphere. Most of the detected molecules are organic compounds. Many of them are highly reactive species that would be very valuable starting materials in any laboratory synthesis of larger organic molecules, including biologically significant ones. You will notice that formaldehyde appears on the list. Of other biological molecules previously mentioned, urea, glycine and uracil have not yet

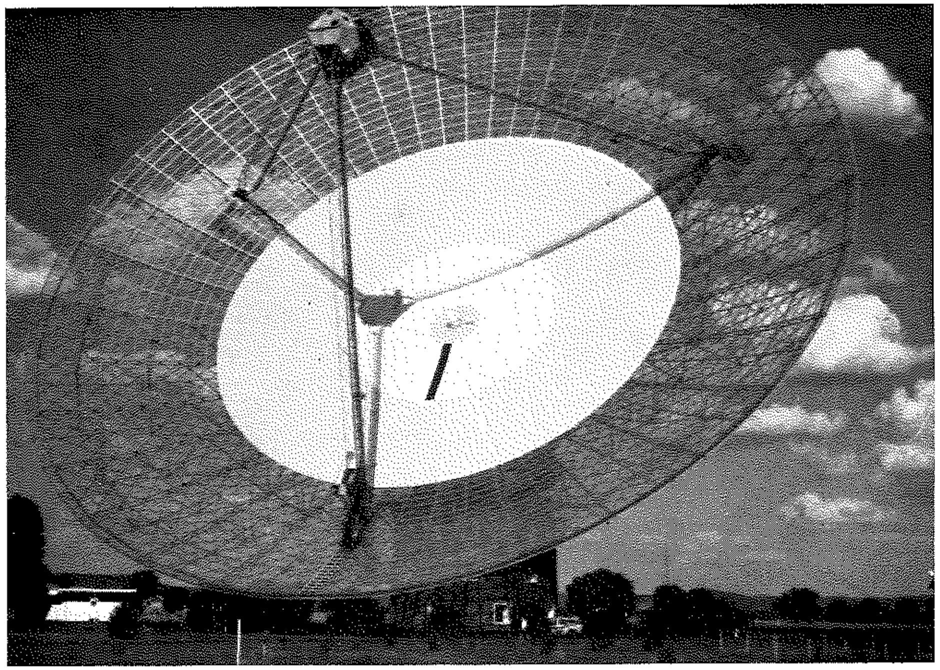


FIG. 11 — The 64m diameter radiotelescope at Parkes, N.S.W. Australia.

been positively detected, although my own group has made extensive searches on several telescopes for both urea and glycine. We know upper limits to the amount of these materials present in molecular clouds.

Once a number of interstellar molecules were detected it was natural to enquire how they came to be formed in dust clouds. It is easy to see why the molecules should be confined to the dust clouds. If they were not protected by dust then they would be rapidly photolysised by the ultraviolet light from the stars in the galaxy. Fig. 16 illustrates the results of calculations of the half life to photolysis of various molecules plotted against the protection afforded by a molecular cloud, expressed in the number of inter-

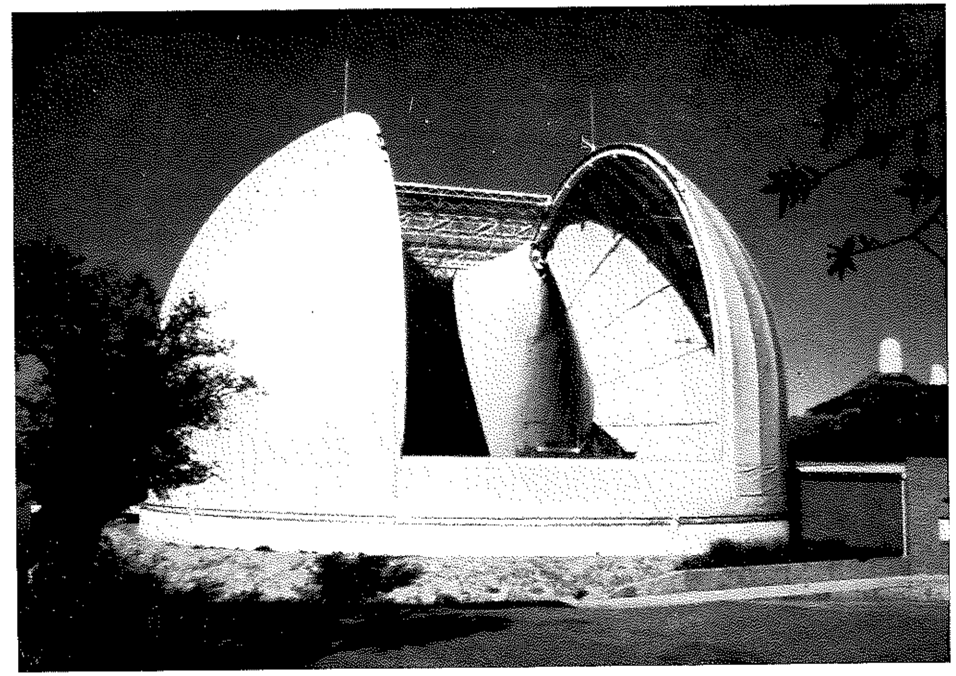


FIG. 12 — The 11m diameter radiotelescope at Kitt Peak, Arizona, U.S.A.

stellar magnitudes of visual extinction of the cloud. Even a cloud of very moderate density, i.e. a few interstellar magnitudes, provides very long lifetime protection against photolysis. Some of the molecular clouds that we are considering contain regions of fifty or one hundred stellar magnitudes of extinction and so offer essentially indefinite protection to molecules from photolysis by starlight.

Having understood why any interstellar molecules are going to be confined to dust clouds we still have to understand how the molecules came to be formed, because they are constituted of material that earlier in the history of the universe was entirely in the atomic form. The first ideas were that molecules were formed by heterogeneous catalysis on

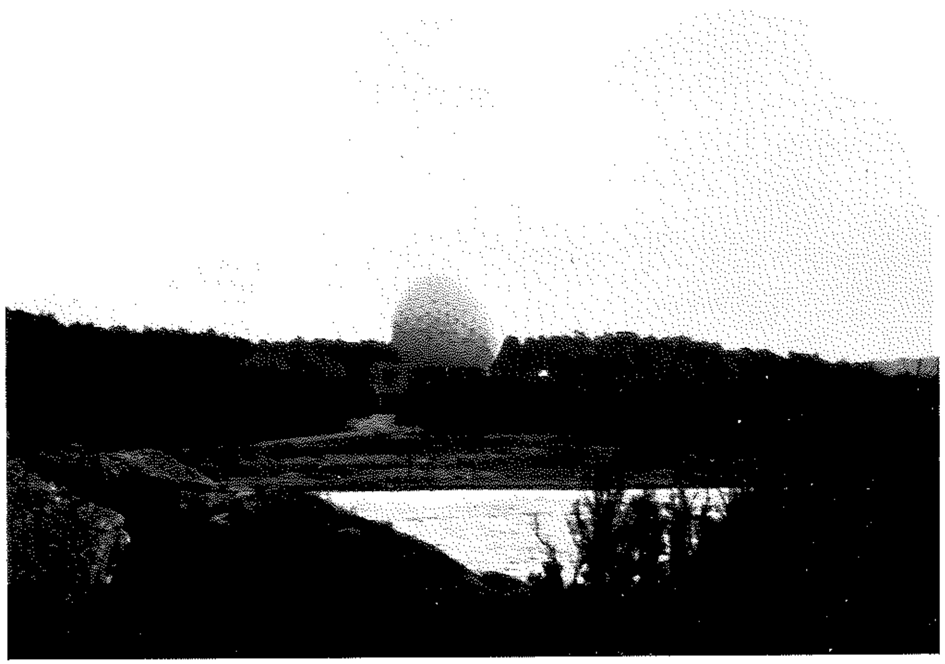


Fig. 13 — The radiotelescope at Onsala, Sweden.

the surface of the dust grains. However, this idea has the serious deficiency that the dust grains are so extremely cold — typically 10-15 K — that any molecule formed on the surface of the grain is likely to be trapped forever by physical absorption. It is only in the case of H_2 that the rate of evaporation from the surface of the grain at such low temperatures is sufficient to provide the quantities of interstellar molecules detected in these molecular clouds. Indeed we believe that this grain catalysis is the predominant mechanism by which molecular hydrogen is formed from atomic hydrogen. In the case of molecular clouds the hydrogen is overwhelmingly in the molecular form rather than in the atomic form, although

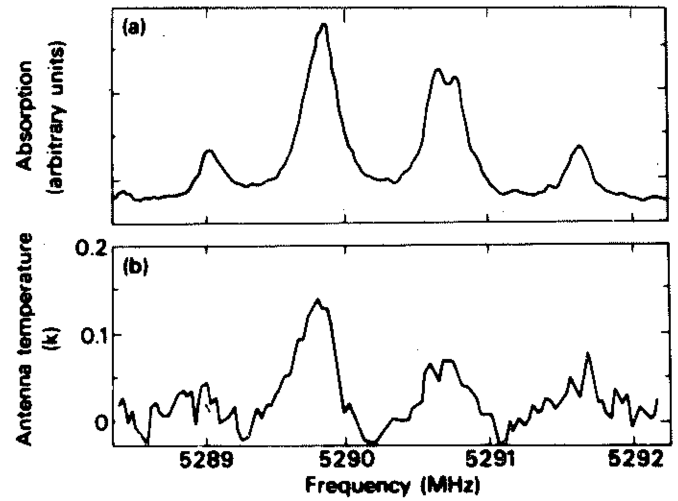


Fig. 14 — The $1_{10} \leftarrow 1_{11}$ interstellar line of methanimine in Sgr B2 (from P.D. Godfrey and R.D. Brown *et al.*, *Astrop. Letters* 13, 119-121 (1973)). (a) laboratory spectrum; (b) telescope signal.

elsewhere in the universe hydrogen occurs essentially in the atomic or ionised form.

For the remaining molecules, although several different suggestions have been made as to their origin, the most plausible is that based on a series of reactions between ions and molecules. These have the virtue of usually proceeding at the collision rate because such reactions normally do not require any activation energy provided that they are exothermic. On the basis of considering large numbers of elementary reactions between ions and molecules, it has been possible to account in a very superficial way for the kinds of interstellar molecules and their approximate relative concentrations.

Figs. 18 and 19 show some results of some unpublished calculations done at Monash University, in which the relevant kinetic equations were directly integrated using a large computer program. They illustrate two important points, *Interstellar Molecules*

September, 1978.

H_2	HCO^+	HCN	HCO_2H	CH_3-O-CH_3
CH	N_2H^+	HNC	HC≡C-CN	C_2H_5OH
CH^+	HCO	NH_3	HC≡C-C≡C-CN	CH_2=CH-CN
CN	C_3N	H_2O	HC≡C-C≡C-C≡C-CN	HCO_2CH_3
CO	C_4H	H_2CO	H-(C≡C)$_4$-CN	NH_2CN
CS	C_2H	H_2CS	CH_3-C≡CH	CH_3-C≡C-CN
SiO		H_2CNH	CH_3CN	C_2H_5CN
SiS		OCS	$HCONH_2$	CH_2=C=O
SO		H_2S	CH_3OH	
NS		SO_2	CH_3CHO	
OH		HNO	CH_3NH_2	
NO				
	HC≡CH			
	CH_4			

FIG. 15 — Interstellar molecules.

firstly that the kind of results obtained depend rather sensitively on the initial conditions assumed for the cloud. In one case we assumed that the hydrogen was all initially in the form of H_2 and the carbon all in the form of CO, in the other case we assumed that all material was entirely in the atomic form initially. The second point to emerge from these studies is that the relative proportions can vary extensively as the cloud goes through its life history. In principle if our model of the cloud were reliable enough we should be able to determine the age of a cloud by carrying out a measurement of relative concentrations of different selected molecules

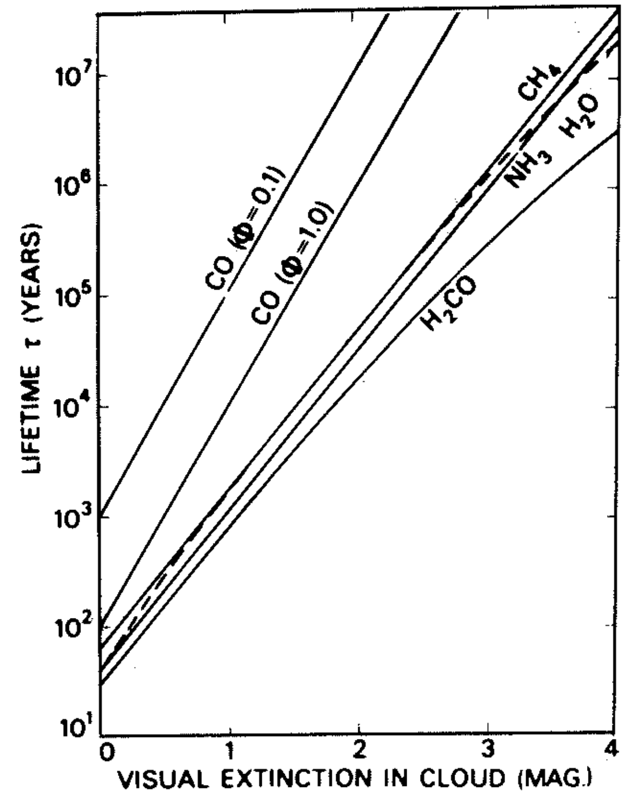


FIG. 16 — Half-lives for photolysis of molecules as a function of the optical extinction of the protecting dust cloud (from L. J. STIEF *et al.*, *Ap. J.* 171, 21 (1972)).

using a radiotelescope, but at present we are still a considerable way from this goal, partly because theoretical astrophysicists are still busily developing more relativistic theoretical models of molecular clouds. The corollary to this study is that as the cloud gets older its chemistry is going to get steadily more complex and on the physical side the cloud will usually be collapsing gravitionally. The result of this collapse will be the formation of new stars and, in many instances, new planetary

IONIZATION	$H_2 + p \rightarrow H_2^+$ (or H^+)
	$H_2^+ + H_2 \rightarrow H_3^+ + H$
	$He + p \rightarrow He^+$
ION-MOLECULE	$H_3^+ + C \rightarrow CH^+ + H_2$
	$H_3^+ + O \rightarrow OH^+ + H_2$
	$C^+ + OH \rightarrow CO + H^+$
	$C^+ + NH \rightarrow CN + H^+$
	$O^+ + H_2 \rightarrow OH^+ + H$
	$N^+ + H_2 \rightarrow NH^+ + H$
	$OH^+ + H_2 \rightarrow OH_2^+ + H$
	$CH^+ + O \rightarrow CO + H^+$
	$CH^+ + N \rightarrow CN + H^+$
PHOTO-RECOMBINATION	$C^+ + H_2 \rightarrow (CH_2^+)^* + h\nu$
DIELECTRONIC RECOMBINATION	$CH^+ + e \rightarrow C + H$
	$CH_2^+ + e \rightarrow CH + H$
PHOTO IONIZATION	$CH + h\nu \rightarrow CH^+ + e$
	$CH_2 + h\nu \rightarrow CH_2^+ + e$
NEUTRAL-NEUTRAL	$O + CH \rightarrow CO + H$
	$O + CH_2 \rightarrow OH + CH$
	$N + OH \rightarrow NO + H$
	$C + NO \rightarrow CO + N$

FIG. 17 — Some ion-molecule reactions and other processes thought to proceed rapidly in dark nebulae.

systems. It thus seems of great importance to attempt to trace the chemical evolution of molecular clouds through to the point at which one has reached the embryonic planetary system stage. Inevitably one asks where the organic molecules in the molecular clouds are likely to survive to the point where they arrive on the surface of a young planet of the

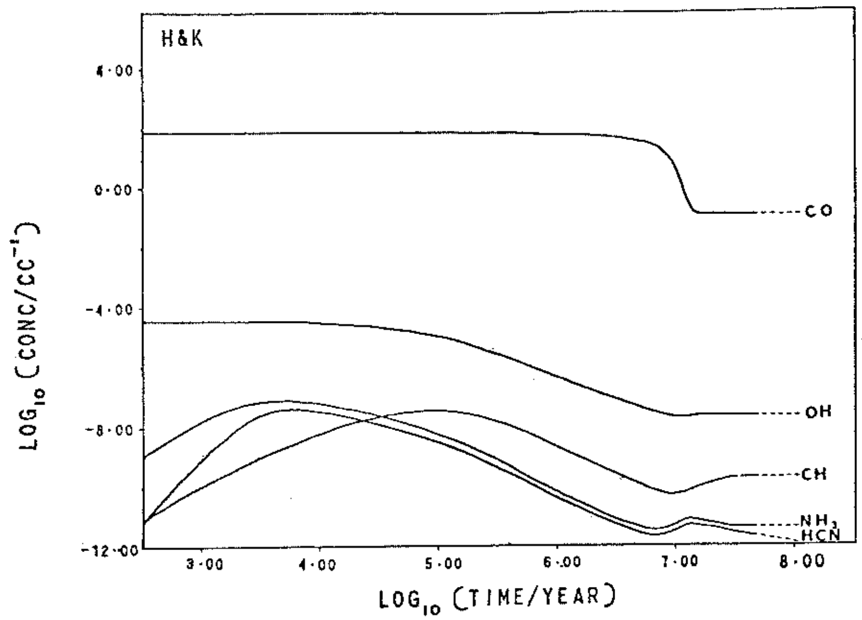


FIG. 18 — Results of direct numerical integration of a scheme of ionmolecules proposed by Herbst and Klemperer; initial condition: $(H_2) = 10^4$ molecules cc^{-1}, all carbon as CO, other constituents atomic.

terrestrial kind and, moreover, whether they are the chemical starting point from which biological material ultimately emerges.

Although the material that forms the new star and that forms the initial planetary condensation inevitably will heat up to high temperatures simply through the release of gravitational potential energy, the residual material that forms the minor bodies, i.e. meteorites and comets, will mostly not be heated appreciably above ordinary laboratory temperatures. We have direct evidence of this in the case of studies of a particular form of meteorite — the carbonaceous chondrites. The evidence is that the highest temperatures that they experienced were no more than 90C.

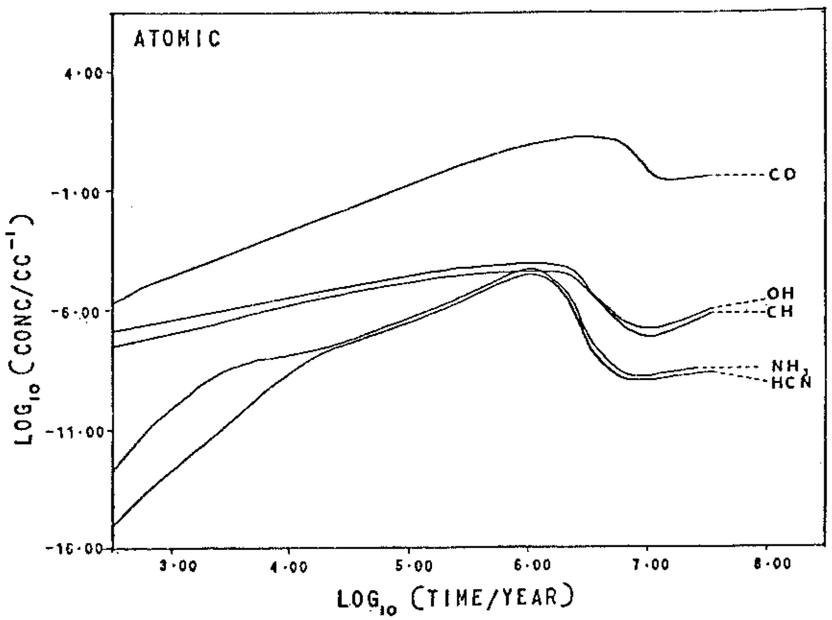


FIG. 19 — Same as Fig. 18 but all constituents initially atomic.

The particular interest in carbonaceous chondrites is that a chemical examination of their content has revealed the presence of amino acids and other biologically significant molecules. There is no doubt that these molecules have an extra terrestrial origin because they occur as racemic mixtures of asymmetric amino acids whereas all biological material contains just the L isomers. We are thus left with the intriguing possibility that material of this sort showered on the surface of the young Earth in the form of carbonaceous meteorites and by a series of processes such as moistening it ultimately emerged that some material assembled itself into a form of a primitive self-replicating package. This part of my story of course is extremely speculative and views differ considerably on the plausibility of it. However, some people at

least go further than this speculation. I instance the case of Hoyle and Wickramasinghe who have recently proposed that the interstellar organic chemistry proceeds so far as virus particles and that these survive in the heads of comets. Hoyle and Wickramasinghe have proposed that epidemics occur even today from the falling of the debris of comets on the Earth. I remain somewhat unpersuaded, but at least it illustrates to many of us that the study of organic matter in interstellar space is an important issue that could possibly bear on the vital question of the origin of life on Earth.