The successes achieved in mapping the spiral structure of the Galaxy and in elucidating the dynamics of galaxies in general from studies of the radio frequency line emissions from neutral hydrogen encouraged radio astronomers to look for radio emissions from other atoms in interstellar space. It was realized that recognition of any such signals would be difficult because other stoms would be present in much smaller numbers than those of hydrogen, and the probability of radio emission much lower than for optical lines. The energy of a quantum of radiation at radio frequencies is a million times weaker than for visible light, and so far radio emissions can only arise from rearrangements within an atom that involve very slight changes in its energy. Of the relatively few atoms likely to be present in space in which spin interactions may occur deuterium, or heavy hydrogen, H2, was chosen as the next most likely source of a radio frequency line. It was not very promising however since the emission was expected to be much weaker, and deuterium many thousands of times less abundant. A significant factor in selecting deuterium was that the frequency of its line emission had been measured with high precision in laboratory tests, at 327.3843 MHz.

Numerous attempts were made over several years to detect
the deuterium line. The world's most powerful radio telescopes
in the U.S.S.R., Great Britain and Australia carefully scrutinised
some of the strongest known sources, particularly that in the
constellation Cassiopeia, for signs of absorption at the deuterium
frequency. In the process techniques were improved to yield
some of the most refined measurements that have been made in
radioastronomy: Weinreb at the Massachusetts Institute of
Technology, for example developed correlation techniques which
were capable of detecting deuterium if the concentration were
less than 1/13,000 that of hydrogen. These efforts were
unsuccessful, however, and attention was turned to another possibility, the combination of hydrogen and oxygen, OH, which

chemists call the hydroxyl radical.

The internal energy of a molecule is normally made up of three components: electronic, associated with electrons in their orbits; vibrational, due to vibration within the nucleus, and rotational, associated with the "tumbling" of the whole molecule. Energy levels in molecules are generally more complex than in atoms. Changes in the electronic energy commonly resulting the chieffer of optical spectrum lines, and in the vibrational energy of infrared radiation. Transitions between possible rotational states for some molecules involve energy changes which result in emission at microwave frequencies, and hence are of special interest to radioastronomers. In the case of the OH molecule in its lowest or ground state the electron distribution can be either along the axis around which the molecule is spinning, or in the plane of the rotation. The difference in energy levels is such that emission (or absorption) occurs in the microwave region at a wavelength of about 18 cms. This is said to be due to "lambda-doubling". In either configuration however there are two other possibilities: the magnetic moment of one nucleus can be either mits aligned with or opposed to the internal magnetic moment of the molecule.

Each of the lambda-doublet states is thus split into two sublevels, so that the hydroxyl molecule has four energy levels. These are indicated schematically in Fig. 1, and the frequencies related to transitions from one level to another are shown in Fig. 2. Theory indicates that the flip from a to c is the most likely transition, with b to d the next most probable, followed by b to c and a-d: then relative probabilities, and hence intensities, should be in the ratio 9:5:1:1.

The first exploratory attempt to detect OH was made in 1958 by Barrett and Lilley of the U.S. Naval Research Laboratory. They looked for absorption at frequencies corresponding to the two strongest lines (1667 and 1665 MHz) in the spectrum of the strong radio source Cassiopeia A but were unsuccessful: at

that stage the frequency of the OH lines was not known to better an 10 MHz. An important step forward occurred in 1969 when Townes and his group at Columbia University succeeded in measuring the frequencies of the two main lines in the laboratory as 1667.34 and 1665.46 MHz, with an estimated probable error of 30 kHz. It was not until 1963, however, that OH was found in extraterrestrial sources, when Weinreb, Barrett, Meeks and Henry, using the highly sensitive correlation receiver which Weinreb had developed for studies of deuterium, achieved success at their first try. They used the 84 foot radio telescope of the Millstone Hill Observatory of the Massachusetts Institute of Technology and found significant absorption in the spectrum of Cassiopeia A due to the 1667 MHz line during their first evening's observations on 15 October 1963. Shortly afterwards they found absorption also at 1665 MHz, the other known OH line, the relative intensities being in the ratio of 9 to 5, in agreement with theoretical predictions. The absorption was small and indicated an average concentration of OH in that direction of about 1 molecule per 10 cubic metres: The absorption spectrum

This discovery came at an opportune time for radioastronomers, when an Extraordinary Administrative Radio Conference was sitting in Geneva to discuss the allocation of frequencies for Space Research and Radio Astronomy. Announcement of the discovery was received by telegram during the closing sessions of the Conference, which allocated a band from to for study of the OH lines. The allocation, however, was not on an exclusive basis but at least recognises the need of radio-astronomy for protection from "commercial" users of the radio frequency spectrum.

agreed generally with that of neutral hydrogen and this, in

Sociation with the close agreement between predicted and
observed frequencies and intensity ratios, indicated almost
beyond doubt that OH molecules were present in the interstellar
space between us and Cassiopeia A. It was perhaps fortunate
that this encouraging picture was not confused at this stage
by the anomalous and puzzling features which were to be revealed
later.

News of the discovery by Weinreb's group was conveyed to other radioastronomers in advance of formal publication and on 20th Movember 1963, a month after the first observation of OM, it was confirmed by Australian radioastronomers at Parkes.

Bolton, van Damme, Gardner and Robinson used the 210-foot dish with a rapidly improvised receiver to study the source at the centre of our Galaxy, Sagittarius A, and found absorption at the two hydroxyl frequencies ita 1667.357 and 1665.402 MHz. Three weeks later Ewen and Dieter at Harvard confirmed the presence of OH in both Cassiopeia and Sagittarius, closely followed by Heaver and Williams at the University of California. There was thus no doubt about the existence of OH as an interstellar molecule, but was it likely to be of any astrophysical significance?

As more information came in it became apparent that OH provided an excellent tool for probing the complex conditions at the galactic centre because the hydroxyl lines are narrower than the hydrogen lines. The width of a line is determined by the range of velocities in the line of sight of the molecules producing it, their metion being due partly to their temperature and partly to streaming, rotation or turbulence of the cloud as a whole. The thermal component is inversely propertional to the square root of the mass, and so in the case of OH contributes only about one quarter as much as H to the observed width of the line. Measurements of the line widths of both OH and H the from the same source thus enable/thermal component to be separated from that due to the motion of the cloud as a whole. In Cassiopeia A OH measurements showed that what looked to

be one cloud from H line measurements was, in fact a pair of louds moving with different velocities (see Fig. 3).

Some of the first surprises came as observations were spread over a wider range of frequencies. Bolton and his colleagues at Parkes were the first to show that strong OH absorption is sometimes found where there is very little hydrogen, and that the OH clouds are often moving in quite different directions. In Fig. 4 for example it can be seen that the two profiles have little in common. The hydrogen shows well-marked dips at radial velocities of 0, -30 and -53 km/s - representing gas in various spiral arms, the last two moving towards the solar system i.e. outwards from the centre of the Galaxy and these same features also appear but less prominently in the OH profile. The hydroxyl spectrum however shows mxamam pronounced absorption at a radial velocity of +40 km/s, indicative of a cloud or clouds moving inwards i.e. towards the Galactic centre. This feature has no such prominent counterpart in the hydrogen spectrum: it was completely unexpected, as was also the fact that the relative intensities of the lines at 1567 and 1665 MHz were almost equal instead of being in the ratio 9:5.

The absorption due to OH in the direction of the centre (>60%) was very much greater than in the direction of Cassiopeia (1.6%), and this encouraged Bolton and his colleagues to look for the OH satellite lines. At that stage their frequencies were known to only 12 MHz. The line at 1612.231 MHz was easily located and turned out to be at least three times stronger than anticipated: shortly afterwards its higher frequency companion was also detected, at 1720.53 MHz. In the meantime radioastronomers at Harvard had discovered an OH cloud toward the galactic centre which is moving outwards at a speed of 120 km/s, again with no associated absorption due to hydrogen. There is clearly a high proportion of hydroxyl radicals near the central regions of our Galaxy. Further observations showed that all four lines could be seen in absorption in a number

Cailed to agree with the predicted values, and thus could not be reconciled with the concept that the population of the various energy levels was in accordance with a Boltzmann distribution. It was clear that the OH was not in thermal equilibrium: radial velocity measurements in the general direction of the Galactic centre ranged between +200 km/sec and -200 km/sec so the gas was obviously in violent motion in this region.

Except for the powerful source in Cassiopeia in whose spectrum OH absorption was first detected, there was no sign of OH in front of other strong sources. Wax Weaver and his colleagues at the Hat Creek Observatory of the University of California then turned their attention to HII regions for evidence of emission by OH - and found it, first in the nebula known as #49. The amazing feature was that the emission profiles were extremely narrow and the intensities again completely anomalous, 1665 being considerably stronger than 1667. This' factor and the lack of close agreement between profiles at these two frequencies suggested to the Berkeley group that some unknown' element may be responsible for the emission at 1665 MHz. named it "mysterium". The line profiles were made up of a number of narrow spikes, mostly less than 2 kHz wide, and the ratio of the intensity of each spike at 1665 and 1667 varied so much that the lines differed markedly in shape. Fig. 5 shows some of the initial results obtained by the Berkeley group. Observations at M.I.T. and at Parkes shortly afterwards removed any possible doubts: mysterium was none other than OH in an interesting new role. Fig. 6 illustrates the narrowness of the spikes in part of the 1665 MHz profiles. The Parkes group observed all four OH lines in emission in a number of sources and - as might have been expected from previous behaviour - with line intensity ratios which varied markedly from source to source. Meedless to say astronomers by this time had begun to take a keen interest in the new discoveries because they obviously

provided new light on the far from static state of affirs in the centre of our own Galaxy.

Polarization

The OH emission is almost invariably strongly polarized, mostly with a high degree of circular polarization. Individual spikes are often more than 90% circularly polarized, sometimes on all four lines: the left-hand sense predominates. A significant degree of linear polarization has also been reported for a number of sources. One of the few mechanisms which could produce circular polarization is the Zeeman effect which occurs when the source is located in a magnetic field. For a field in the line of sight the A-doublet lines 1665 and 1667 MHz should have circularly polarized components displaced on either side of their normal frequency while the satellite lines should split in to six a components. The observed profiles cannot readily be explained in this way and more extensive polarization measurements will be necessary before the mystery of the origin of the polarization can be solved. Typical OH emission profiles recorded in left and right-hand polarization are shown in Fig. 7.

Polarization has not been observed in any of the OH absorption features.

Size of the OH Sources

Attempts to resolve the OH sources were made at M.I.T.,
Owens Valley, Jodrell Bank and Parkes using interferemeters
with base-lines up to some thousands of wavelengths long, but
were unsuccessful. The HII region #49 began to be resolved
with a baseline of 300 km (nearly five million wavelengths),
but very long baseline techniques spanning continental U.S.A.
were needed to partially resolve some of the components in #3.
These observations were made between Greenbank, West Virginia,
and Hat Creek (California) (a distance of 1.95 x 107 wavelengths)
and showed that some of the emission was coming from elongated

regions about 0.01" long and less than 0.005" in width. The peasured intensity is such that for this size the brightness temperature of the source (at the assumed distance of W3, 1700 parsecs) must be about 1012. K. For regions which were not resolved at that spacing the brightness temperature must be substantially higher >10130K. Observations over an even longer baseline were made in 1949 between Parkes, Australia, Owens Valley California and Greenbank West Virginia. Several more sources were resolved indicating sizes less than .01 seconds of arc, but a number were unresolved and are thus very much smaller. Confirmation for the small sizes comes from the fact that the positions derived from measurements at 1665 and 1667 Miz, and from components of the profiles with a velocity spread of 5 km/s usually agree within a few seconds of arc. Strong scintillations were observed by Robinson and Goss at Parkes when the Sun passed within 5° of an OH source in Sagittarius in December 1967. Fig. 8. This provided an upper limit of 0.1 seconds of arc to the sizes of the two components of this source, which is at a distance of 10 kiloparsecs. Its linear dimensions must thus be less than 5 x 10-3 paragrap paragrap or 1.7 x 1011 km, i.e. they would easily fit within the solar system, and not extend much beyond the orbit of Jupiter.

Hany of the sources are double, at separations which are measured in tens of seconds of arc and thus resolvable with large dishes.

INMINIAL Identification of the OH Emission Sources

OH emission was first discovered near HII regions and roughly one third of the known HII regions have OH sources in or near them, mostly well to the side of the ionized areas.

Only three of the strongest sources are associated with well-known nebulae, namely W3, NGC 6334 and Orion: the source positions are known to within a few seconds of arc from interferometer observations and this accuracy is enough to show that

or the two firstnamed at least no familiar object is responsible to the emission. The location of the OH source in W3 (the nebula IC 1795) is shown in Fig. 8: it is well removed from the arc of nebulosity and from the positions of the continuum sources, but near a weak source which has been detected at ££ 6 cm. There are two OH centres of emission in the nebula NGC 6334, their position being indicated by circles in Fig. 9. The emission is strongly circularly polarized. The source B has components whose intensity has been observed to rise by as much as five times in a period of one or two days and then subsided over about a week. In the case of Orion the OH source is centred on the nebula and may be coincident with a source of infra red radiation which has been detected in this nebula.

The conditions which lead to emission by the hydroxyl molecule are not yet fully understood. The OH clouds are most frequently found near regions of ionized hydrogen but do not appear to be associated with any particular feature of the visible nebulosity, nor with absorbing dust clouds since there are no traces of OH emission in the prominent dark lanes characteristic of nebulae such as NGC 6334. The radial velocity of at least one component of the OH emission usually agrees closely with that of the associated HII region. Emission has also been observed from other non thermal sources, in particular from the direction of two shell-type sources which are probably supernova remnants.

For a number of them a characteristic feature is emission on one of the satellite lines while the other lines appear in absorption only.

Mechanism of Emission

The outstanding properties which must be accounted for in any explanation of the emission from OH are the extremely high brightness temperatures, emission in the form of narrow a"spikes", high degree of circular polarization and departure from thermodynamic equilibrium indicated by the wide variation in intensity ratios at the four line frequencies.

Origin in any possible thermal process is ruled out on il four counts. The explanation which comes closest to satisfying some of the requirements is that here we have a maxima natural maser in operation (see page) i.e. due to some local "pumping" action more molecules are in higher energy states than is normal, and in returning to the ground state they emit radiation which strongly reinforces the continuum background at the OH line frequencies. The amplification factor needs to be very high (10") and at these high gains the lines would be expected to be very narrow, and to vary widely in intensity from line to line. It is difficult however to envisage a pumping mechanism which will replenish the higher am energy states at a sufficient rate to maintain emission from the OH condensations: the most efficient process appears to be by means of ultra violet radiation (from the associated HII region) at a wavelength near 3080A* but the efficiency of this procass is much too low to explain the high brightness temperatures observed. Purther absorption by OH itself would severely limit the distance to which the ionizing radiation could penetrate into a cloud. Apart from these factors none of the possible pumping processes - by microwave, infra red or ultra violet radiation could produce the predominantly high degree of circular polarization observed in all four lines, nor the preference for the left-handed sense.

The inadequacies of the radiation-pumped hypothesis has led to a search for other explanations and interest has been focused on chemical reactions which can occur in regions of high density and are capable of producing OH in an excited state. These processes cannot explain the high degree of circular polarization but at least operate more effectively as the density increases, where other pumping processes are unable to penetrate far enough into the cloud. The OH sources are observed to be on the outer edges of HII regions and are probably produced in the shock front shead of the expanding gas. Under

H in an inverted state, but considerably more data is needed before a decision can be made as to which of the possible maser mechanisms, or perhaps combinations of them, is acting.

Detection of Isotopic OH

The most common species of the hydroxyl molecule is 0^{16} H, the isotopic variation 0^{18} H having an abundance ratio on Earth of 1 to 490 the line frequencies to be expected from 0^{18} H were computed by Barrett and Rogers in 1964 and one line of the lambda-doublet was \$ first observed in absorption at Parkes in July 1965, the frequency being 1639.460 MHz. Shortly afterwards it was detected by Rogers and Barrett at Greenbank, their results being shown in Fig. Prom the depth of the absorption features relative to those for 0^{16} H the abundance ratio is about 1/500, close to the terrestrial value. Several attempts have been made to detect the second most intense line of the lambda doublet pair at 1637.4 MHz, but without success.

OH molecules as Tracers

The patchy distribution of the OH condensations, their small sizes, and the fact that they are embedded in HI regions and also among the continuum sources and yet, particularly near the Galactic centre, have their own peculiar motions (often with high components in the line of sight) means that they can be used as tracers to help in delineating the complex process in operation in that region. In these most interesting areas of our Galaxy which are forever hidden from optical view by obscuring dust clouds we are completely dependent upon the story released by the only radiation - of longer wavelength - which can penetrate these clouds. The addition of OH to what for years was believed to be the only possible probe, namely the 21 cm hydrogen line, has therefore been eagerly welcomed by astrophysicists. The revelation that such molecules can

exist in abundance in interstellar space has come as a complete and welcome - surprise, with its implication that other molecules
may also be detectable. As we shall see below several have
already been found, among them most surprising of all, water!

Perhaps the most exciting prospects are that the clouds of Oli that have been detected represent the culmination of the first few thousands of millions of years in the life of a gas cloud which is collapsing to form stars. We cannot yet determine the masses or the densities of these OH condensations but the indications are that they are quite massive though still only ten degrees or so above absolute zero. The densities are not high but adequate for the formation of other compounds, and the clouds may well have reached the crucial stage when condensation is about to or taking place at a much faster rate, i.e. the "proto-star" stage. This is the phase in the birth of a star which, until now, we have not been able to watch, when the temperature reached in the collapse of the original gas and dust is not high enough to produce optical emission. The possible contribution from studies of the puzzling and controversial 18 cm emissions from hydroxyl molecules as they are tossed about in the turbulent shock fronts of expanding HII regions is highlighted by the fact that some of these OH clouds are also the sources of strong infra-red radiation. The first of these to be located is within the Orion nebula, one of the most famous of the known stellar nurseries, and others are associated with very young stellar objects, one of them (NML Cygni) the strongest known emitter of the OH line at 1612 MHz.

Other Interstellar Molecules

The first of a series of discoveries in which the existence of further common molecules in interstellar space was revealed took place in December 1968, when C.H. Townes, Missessans discoverer of the maser, and his colleagues from the Departments of Physics and Radioastronomy at the University of Berkeley detected weak microwave emission from ammonia. They used a new 20-foot dish at the Hat Creek Observatory of the University

from a dense cloud of gas and dust in the vicinity of the Galactic centre - having first searched unsuccessfully in Cassiopeiae and the strong OH and infra-red source NHL Cygni. The volume-density of the ammenia was estimated to be about 10⁻³ per litre and its most likely origin to be by absorption of hydrogen and nitrogen on grains of interstellar dust, followed by pharmam photo detachment, bombardment by particles, or sublimation. A means for revealing the part played by nitrogen in the relatively cold areas where OH is also present and stars are in the making thus becomes available.

Water

Following proof of the existence of hydroxyl and ammonia molecules in space it was scarcely a mit matter for wender that the next to appear should be water: Townes and his group were again responsible for this discovery, which was also made at the Hat Creek Observatory, strong emission being found at a wavelength of 1.35 cm f22x224 (22.235.22 MHz) from the Orion Nebula where they had been unable to find any traces of amenia. It was located also in a number of other sources, the antenna tenperature being at least 55°K for W49. The high intensity plus the fact that line widths are very narrow suggests that the radiation may not be thermal in origin. The line was attributed to water because it coincides closely with the laboratory frequency and no other known atomic or molecular transition could account for it. The possibility that it might arise from water vapour in the Barth's atmosphere was easily ruled out by the fact that it occurred only in three highly localized directions in space, and showed a different Doppler-shift for each source: had it been located in terrestrial clouds its emission would have occurred at the frequency determined in the in laboratory.

Formaldehyde

The third in the series of discoveries was that of the organic compound formaldehyde (H.C.H.O.) which was found in 15 of 23 sources surveyed with the 140 foot radio telescope of the U.S. National Radio Astronomy Observatory at Greenbank in

the rest frequency being 4829.65 MHz (near 6 cms). It was also detected in 26 out of 40 continuum sources surveyed with the 210-foot telescope at Parkes. The lines, in general, are single and have velocities similar to those of the associated sources so the formaldehyde clouds are possibly associated with them. The profiles have a general similarity to those of OH. The formaldehyde is present in sources which have also been found to contain water but associate and formaldehyde have not been found to occur together.

Future Prospects

The detection in succession of OH, water, amaonia and formaldehyde suggests that such molecules are probably relatively common ingredients of interstellar space - contrary to an earlier belief that the intensity of ultra-violet light would be too great to permit the formation of complex solecules. feature of particular interest is that these compounds occur in some of the most interesting corners of our Galaxy, relatively cold regions of dust and gas in which new stars are in process of formation. It is too early yet to forecast the full bounties to be reaped from these discoveries but it is clear that the radio assurements will provide vital data on the temperatures and concentrations involved in such events. Formaldehyde is of special significance because it provides indirect evidence that methane is also present: methane is one of the basic compounds believed necessary for the commencement of life but there appears to be no possibility of its detection by direct means. We may reasonably hope that further observations will,

due course, shed some light on the composition of primeval atmospheres "in the beginning". andxitixxanxitaxans and thus on the origin of life itself.