

DR K. RANGADHAMA RAO MEMORIAL LECTURE—1979*

MOLECULES IN INTERSTELLAR SPACE

R. K. ASUNDI, F. N. A.

*Retired Professor of Physics and Spectroscopy, Banaras Hindu University,
Varanasi-221005†*

Although it was believed that at least simple diatomic molecules must exist in interstellar space, it was not until about 1940 that three diatomic species, CN, CH, CH⁺ were identified by their narrow, till then unidentified, absorption features in the continuous spectra of several bright stars. Molecular Hydrogen (H₂) which was expected to be abundantly present, was discovered in 1970 by its UV absorption bands only after rocket and satellite techniques were available.

The development of microwave and radio frequency spectroscopy in the 1950s, led to the discovery of the famous 21 cm radiation in interstellar space in 1951. This enabled a survey of atomic hydrogen (H) in our galaxy. This radiation represents the hyperfine splitting of the ground state of H.

Inspired by the successful laboratory observations of its Δ-doublet transitions, a calculated search for OH in interstellar medium led to its discovery at 18 cm in 1963.

Since then, a large number of di- and polyatomic molecules including organic molecules involved in synthesis of amino-acids has been discovered in interstellar medium by radio frequency spectroscopy techniques during the last decade. Particularly significant among them are vinyl-cyanide (H₂C = CHCN) having a double bond C = C and, the whole series of long chain linear molecules, HCN, HC₂N, HC₃N, HC₄N and HC₅N, the last being discovered in 1978 in interstellar space, but not yet on earth.

A detailed knowledge of the state in which molecules are found existing in different parts of interstellar space is expected to throw useful light on the origin of celestial bodies like stars, etc. and of life as we know it. The study of interstellar molecules has thus become an area with a hectic pace of discovery for several disciplines of Science.

The search for molecules has followed closely and depends heavily on the progress of spectroscopy and demands the most minute details of structure of molecules. Essential data of desired accuracy and resolution are not available for several molecules; *f*-values for most transitions are unknown. All this calls for continued research of the highest quality in all branches of spectroscopy.

Keywords: Molecules; Interstellar Space

TRIBUTES TO DR RANGADHAMA RAO

"The life of man is a long march through the night, surrounded by invisible foes, tortured by weariness and pain, towards a goal that few can hope to reach and where none may tarry long. One by one they march, our comrades vanish from our sight seized by the silent orders of omnipotent death."

— BERTRAND RUSSEL

*The lecture was delivered at Andhra University, Waltair on 30th March, 1980.

†Present address : 12 Om Shanti, 16th Road, Santa Cruz West, Bombay 400 054.

I AM deeply touched by the wish expressed by the promoters of Dr K. Rangadhama Rao Memorial Lectures that the first of these lectures should be delivered by me. At the same time, I appreciate the decision of the INSA in honouring the wish of the promoters and giving me the opportunity to pay my humble tribute to the sweet memory of our seniormost, unassuming, lovable spectroscopist. The first time that I met Dr Rangadhama Rao was more than 50 years ago in London. He was deputed by the Andhra University to extend his research experience; for, Rangadhama Rao was already a Doctor of Science of the Madras University and under the guidance of the late Dr A. L. Narayan, had made significant contributions to atomic spectroscopy and was recognised as an able spectroscopist. I remember very vividly my first meeting with him in Richardson's laboratory in King's College, where I was working. Those were early days of Molecular Spectroscopy, which I was trying to learn. This required a working knowledge of atomic spectra as a pre-requisite. There were no books on the subject and all necessary information had to be collected only from published papers in research journals — e. g., the derivation and designation of energy levels of atoms from their electron configuration. Rangadhama Rao explained to me in full detail how this is done, on this our first visit in the laboratory. I can thus claim him as one of my spectroscopy teachers. When I saw him in Visakhapatnam a few months before he passed away, I never could imagine that it would be our last meeting.

Dr I. Ramakrishna Rao who had taken the Ph. D. degree of Calcutta University, also came to London at the same time as Rangadhama Rao in 1928 and both joined the Andhra University after they returned to India. They were very close friends. I, therefore, requested Ramakrishna Rao to let me have an account of Rangadhama Rao's research career earlier to his work in the Andhra University. I thought such information will not be available in detail in the account that may be given of his total academic and research career and as I feel that such information will be a source of inspiration for our working scientists I reproduce pertinent extracts from his letter :—

“After taking his M. A. degree of the University of Madras in 1924, Dr Rangadhama Rao joined the Research Laboratories of Dr A. L. Narayan in Maharaja's College, Vizianagaram and registered himself for the degree of D. Sc. of the same University. Both Dr Narayan and Rangadhama Rao worked under great handicaps in their research on line spectra. The equipments they had were only three spectrographs, one Baby quartz, one medium quartz and one constant deviation. All of them were of low dispersion and low resolving power. Dr Narayan purchased them with the meagre grants for the Physics Department of a degree college. The grant was supplemented by funds from Narayan's pocket. They rigged up a small workshop and made arc stands and spark stands of their own. They had to do their own glass-blowing for making discharge tubes for gases. The high voltage required for these and for sparks was from an induction coil available for demonstration in the labs. Since there was no instrument of high dispersion, Rangadhama Rao went to Raman's labs. at Calcutta to take spectra with the 10 ft. concave grating available there. With this, he took photographs of line and band spectra which they analysed in conjunction with the data available with their own

equipment at Vizianagaram. High vacuum required for their discharge tubes could be got from a Cenco High-Vacuum pump. For higher stages of vacuum, they made their own glass mercury diffusion pumps which they themselves made and used with the backing of the Cenco pump.

"To make their analysis of spectra complete, they had to study the fine-structure of the spectral lines. For this they procured one Lummer-Gehrecke plate and a Fabry-Perot pair of plates. They made their own mounts for using them in conjunction with the constant-deviation spectrograph.

"For spectra in the vacuum region, they purchased a grating from Hilger and made their own mount for it, as they could not afford to purchase the mounted grating spectrograph. They made their own Schumann plates for this vacuum grating spectrograph.

"All the above show how they worked with meagre equipments and produced results which a best equipped spectroscopic lab. can be proud of. With this work, Rangadhama Rao got his D. Sc. of the Madras University.

"In 1928 Rangadhama Rao left for U. K. with a Madras University Fellowship to work under Dr A. Fowler in the Imperial College of Science and Technology, London, which had one of the best equipped spectroscopic labs. in the world.

"Dr Rangadhama Rao took his D. Sc. (London) in 1931 and returned to India in the same year. He joined the Andhra University Physics Department. Apart from his teaching work he began researches in Spectroscopy. The equipment he had, consisted of one small quartz spectrograph, one Littrow glass and one Littrow quartz spectrographs, and one 10 ft. concave grating. He took back the vacuum grating spectrograph from Vizianagaram. With this equipment, he extended his spectroscopic studies, with a band of research students, into band spectra, NMR and other fields in this line."

Professor S. Ramachandra Rao, F. N. A., another close friend, has kindly responded to my request for his reminiscences and has sent the following most fitting tributes to the personality of Rangadhama Rao :

"We first met in London in 1928. Dr I. Ramakrishna Rao introduced us to each other. From the moment we met till his last days, we were deeply attached to each other. He was an open-hearted, frank and delightful friend. I used to go to Andhra University often and he used to go to Annamalai University and Bangalore as often as possible.

"His whole interest was physics. We seldom talked about our private affairs. He used to tell me about his investigations, the trials and tribulations of working in a new university. Where facilities were restricted, he wanted to do much. I may go so far as to say that his family came only second in his attentions. He lived in his laboratory all the time and the heavy work he undertook far beyond his poor physical stamina was ultimately responsible for his death.

"In spite of his manysided interests in the University, he was essentially a shy individual. He opened himself only to the very few who were close to him; but for the others, he was a sealed book. He treated those around him with the utmost kindness and courtesy but nobody except very few knew what worries he had in his mind.

“He never wanted publicity. When I once told him that I would nominate him for the Presidentship of the Physics Section of Indian Science Congress, he positively told me he did not want the honour. Considering the vast amount of research he had done and the many brilliant students he had trained, he never sought any place in the administrative echelons of the different scientific bodies in India.

“However, I have known him to take quick decisions. If he felt that something was right, he would never hesitate to stand up for the cause. This has been of great help to many students of Andhra University. When he found that sometimes the rules of the University were not helpful to them, he was often willing to stretch a point in favour.

“He was a strong nationalist at heart. He wore only khaddar and was simple and unostentatious in his habits. He was fond of his wife and children; it was a happy family. It was a pleasure to stay with him and partake of his hospitality and of his inimitable wit and humour. Very few knew that he could be extremely humorous and burst out into fits of laughter.”

Rangadhama Rao was working in Fowler's laboratory, where also Dr J. S. Badami, a brilliant young graduate and a foreign research scholar of Bombay University joined. As he had published some papers in collaboration with Rangadhama Rao, I requested Dr Badami to let me have his reminiscences of those days. I give below relevant portions of his reply :

“Jointly with Dr Rangadhama Rao, a paper was published in *Proc. R. Soc. London*, on the spectrum of Selenium (Se IV and Se V). Dr K. R. Rao, after his work in London and Uppsala was also at Professor Paschen's laboratory, Berlin, (which I had joined earlier) and from there three papers on Se III and on the Resonance spectrum of hydrogen were published in *Proc. R. Soc. London*, in our joint names” “Dr K. Rangadhama Rao was a very pleasant person to work with. Jovial by temperament, I have hardly known him to lose his temper. He was fond of listening to Indian music and in his leisure he was often humming songs — a particular one I remember was about Gajendra Moksha. Unlike many research workers, he was very liberal in giving credit for any work done by his colleagues and I must mention that the credit for our jointly published investigations is almost entirely his.”

I am sure everyone who has had the privilege of coming into contact with Rangadhama Rao shares this opinion. As a matter of fact, he would never consent to have his name associated as one of the authors even when the work was suggested and guided by him. Rangadhama Rao was a very quiet person, friendly, lovable and devoted to science. He had more downs than ups in his profession, but these or the few ups, little affected his equanimity and attitude towards work (न प्रहर्षत् प्रियं प्राप्य न उद्विजत् प्राप्य च अप्रियम्). The handicaps under which research had to be pursued in our days were of various types, financial handicap being the smallest of them. In spite of this, Rangadhama Rao succeeded not only in continuing research in spectroscopy, but also in training a good number of capable scholars. I believe this was mainly due to his tenacity of purpose and power of will which he so clearly exhibited in fighting out several earlier heart attacks. On such an occasion when our thoughts go out to him who was less of this earth, I thought it would be appro-

priate if I dwelt on a subject which is less earthly. I shall, therefore, try to give a brief account of the spectral observations of interstellar molecules in the optical and microwave regions.

MOLECULES IN INTERSTELLAR SPACE

“What a wonderful and amazing scheme have we hear of the magnificent vastness of the Universe. So many Suns, so many Earths.” — CHARISTIANUS HUYGENS

“बहूनि अदृष्टपूर्वाणि आश्चर्याणि परम भारत”

— *Bhagvad Geetha*

INTRODUCTION

During the 19th century, astronomers using the telescope supplemented by the aid of the spectroscope, mapped the spectra of celestial bodies and attempted to assess the mass, size, chemical composition, luminosity and temperature of surface layers of stars. Later, in the early part of the present century, when the spectra of atoms came to be definitely understood, several of the dark lines found in the emission spectra of hot stars were identified with spectra of atoms/ions known in laboratory experiments. In particular, the H and K lines which are due to Ca^+ do not show the periodic Doppler shift caused by rotation of the binary star (δ -orionis) in whose spectrum they are found (Hartmann, 1951). It was therefore concluded that the Ca^+ absorption lines are due to the gas that is pervading interstellar space rather than to the star's atmosphere. Since contemporary theories propose that stars are formed from condensation of the matter in the interstellar medium, a detailed knowledge of the contents and properties of the medium becomes necessary.

In addition to gas, dust came to be regarded in the 1920s, as another major constituent. The dust particles consist primarily of silicates of submicron size and are mixed in with gas molecules. They scatter light and cause the so-called ‘interstellar reddening.’ The gas and dust combine to form clouds both tenuous and dense. The dense clouds are dark and opaque. Later, in the 1940s, a few simple diatomic species CH , CH^+ , CN were identified in the medium.

Interstellar molecules provide an excellent tool to the study of the physical state, dynamics and chemistry of various types of clouds of gas and dust which are in the medium and are likely sites for star formation. Progress in such knowledge is necessary to discuss the evolution of stars and their grouping to form not only our galaxy, but also numerous other galaxies, which all together go to form the Universe. In this way man hopes to discover the most needed key to the solution of the mystery of birth, maintenance and death of the Universe.

GENERAL DESCRIPTION OF INTERSTELLAR MEDIUM

When one speaks of interstellar medium, it is the medium among the stars of our galaxy. During the early 30s of the present century, the concept of interstellar matter composed of gas, mostly hydrogen and helium, mixed with dust particles mainly silicates of sub-micron size, became generally accepted. The mass ratio of gas to dust is of the order 100:1 so that dust forms a trace constituent in the medium. The dust grains are built up by low energy collisions among atoms and

molecules of the gas in the medium, whereas high energy collisions with the dust grains produce the gas. Thus the grains are approximately of the same composition as the gas and primarily made up of molecules of atoms like hydrogen, carbon, nitrogen and oxygen. The sizes of the grains are limited by the relative numbers of low and high energy collisions among the atoms and molecules which form the gas of the medium. The mass of interstellar gas is approximately a billion times the mass of our sun; yet it is only about one per cent of the total mass of our galaxy, the remainder being made up by stars. 70 per cent of the interstellar matter is hydrogen (atom, molecule, ion). More than half of this is molecular and ionic. However, these species are found only in a tiny fraction of volume of interstellar space. The temperature of the gas is not uniform and depends upon the distance of the gas region from hot stars. Stars of spectral class O5, for example, will ionize nearly all gas within a radius of approximately 100 parsecs (3.08×10^{15} km \approx 2 million billion miles). Such regions are called HII (hydrogen ionized) or proton regions and their temperatures can reach 10,000 °K. When the matter is far away from hot stars, hydrogen is not ionized (HI regions) and the temperature of the gas may be as low as 100 °K or lower.

The interstellar mass of gas and dust is distributed irregularly and unevenly throughout the galaxy. There are dust clouds (or long filament loops) of various densities and temperatures, the denser ones dark and opaque to optical radiation. They are to be found moving with different velocities mostly in the spiral arms of the galaxy. In other regions, the density of the material gas is very low.*

Of the total mass of galaxy, approximately $2 \times 10^9 M_{\odot}$ is in cold molecular clouds and a considerable fraction of this mass is in complexes with mass $10^6 M_{\odot}$.

In short, it is presently believed that the interstellar medium consists of gas, dust grains, small and big, hot and cold and molecular clouds (or filament loops) in motion, thick and thin, hot and cold, dense or diffuse. Apart from matter, the space between stars is filled with photons, cosmic particles and magnetic fields.

Most of the above information has been gathered through spectroscopy and has grown systematically parallel to the progress of our knowledge of the structure and properties of atoms and molecules and, therefore, parallel to the progress and the manifold development of spectroscopy, whose usefulness to Astronomy and Astrophysics is beyond question.

OPTICAL OBSERVATIONS OF INTERSTELLAR MOLECULES

Absorption lines of interstellar gas have been known since the beginning of the century. Most of these could, however, be identified much later only when the spectra and structure of atoms came to be understood. Dunham and Adams (1937) recognised several sharp lines in absorption which included those of Na, Ca,

*The cloud model of the structure of the medium which is currently adopted, proposes that gas is clumped into individual clouds. Recent detailed observations including X-ray, *u-v*, *i-r*, and radio frequencies and in particular, the detailed map of the distribution of atomic hydrogen in space compiled at the wavelength of 21cm indicate that the gas in the medium loops through the space in long filaments rather than in tenuous clouds. The new model proposed is called the shell model.

K, Ca⁺, Ti⁺ and could be identified because by then the spectra of such atoms were well understood. There were also a few unidentified lines around 4000 Å. The cosmic abundance of light atoms, e.g., H, He, C, N, O, suggests that if at all, only simple diatomic radicals such as CH, CN may also be present in interstellar space. Naturally, these were also the first to be identified but had to wait for identification until their spectra were well understood. Later, in 1941, CH⁺ was identified when its spectrum excited in the laboratory was analysed and established (Douglas & Herzberg, 1941). The R(0) lines at 3957.700 Å and 4232.539 Å of the (0-0) and (0-1) bands of CH⁺ were readily identified with the known catalogued interstellar absorption lines. OH was discovered in optical absorption, in rocket and satellite observations, only after a new absorption band near 1220 Å was discovered (Douglas & Lutz, 1970). Three lines R₁, Q₁, P₁ at 1221.166, 1222.071 and 1222.520 Å were predicted in 1971 as possible interstellar absorption lines. Several years later in 1976, OH was identified by its Q₁ line at 1222.071 Å. A similar prediction for identification of SiH⁺ by the R(0) lines of (0, 0) and (1-0) bands at 3993.400 and 3932.347 Å, has been made (Douglas & Lutz, 1970) but not yet identified in interstellar space. Similarly, identification of OH⁺ will also be possible, if and when for purpose of comparison, accurate values for the R(0) lines of the (0-0) and (1-0) bands of OH⁺ are established accurately by laboratory investigations. However, until 1963, CH, CH⁺ and CN were about the only diatomic species identified in interstellar medium.

From these absorption observations, it is seen that in interstellar space containing tenuous clouds, only the very lowest rotational levels of the molecules are populated. This, however, does not necessarily indicate that the environmental temperature is that low enough, for a thermal equilibrium distribution, such that there is no appreciable population at higher levels. Rather, the higher levels get depopulated by emission of far infrared radiation and due to lack of excitation of the molecules to the higher levels by collisions. Examples are now known in investigations in the microwave region, of several molecules existing in high rotational states.

As long as one was limited to observations from the earth's surface there could be no hope of detecting in optical absorption, the most abundant atoms viz., H, He, C, N, O, or simple molecules like H₂, CO, N₂ because their resonance lines lie below the ozone cut-off by earth's atmosphere. Identification of such atoms and molecules had, therefore, to wait until after the middle of the century when rocket-borne spectrometers could obtain and identify the vacuum *u-v* spectra of the interstellar medium with the known laboratory spectra, e. g. by the resonance Lyman bands of H₂ and fourth positive bands of CO. Satellite observations confirmed these results, not only finding H₂ in the spectra of many red stars but also discovering the isotopic molecule HD and indicating that the HD/H₂ ratio is approximately 10⁻⁶. These optical results relate to absorption through thin tenuous clouds but since hydrogen is believed to be the main constituent of the medium, this discovery of molecular hydrogen which was long sought after, strengthens the idea that it must be one of the major molecular constituents even in denser clouds. Here, however,

they cannot be detected either in optical absorption because the dense clouds are opaque, or in the radio region because H_2 being a non-polar molecule has no spectrum in that region.

From the observed intensities of the lines, in most cases the concentration and abundances of the species of atoms or molecules can be determined (exceptions are cases where the oscillator strengths (f values are known) and these abundances, as well as upper limits on a large number of additional species, are compared with the predictions of chemical models for diffuse clouds. Oscillator strengths are not known in a majority of cases, so that considerable activity in spectroscopic research has understandably revived in recent times to measure this parameter, which is important also for development of lasers. A recent paper (Snow, 1979) on optical observations of interstellar molecules read at the IAU Conference No. 87 held in August 1979 at Mount Tremblant, Canada, gives a list of 21 diatomic molecules including one isotope, 7 diatomic ions including one isotope and four triatomic species O_3 , CH_2 , CO_2 and H_2O , detected in optical observations.

DIFFUSE FEATURES IN THE OPTICAL REGION

In addition to the sharp lines of atoms and molecules, most of which are well understood and their assignment quite definite, there are several unidentified diffuse broad absorption lines known in the optical observation for over 40 years. 39 such diffuse features between 4400 and 6850 Å are recognised as of interstellar origin. A unique characteristic of these features which differentiates them from all identified interstellar lines is their line width which varies from 10 to 100 cm^{-1} . The origin of these features has been a long standing mystery. There has been no lack of interest in these bands and attempts at identification have ranged over almost every conceivable spectroscopic phenomenon with no convincing success so far. It is thought likely that the carrier of these diffuse lines is a polyatomic molecule or ion present in the interstellar gas and in view of the overwhelming preponderance of H in the interstellar medium and the relatively high intensity of the diffuse lines the molecules responsible must contain mostly hydrogen.

The strongest of these diffuse lines lies at 4428 Å with a half width of 20 Å. It is suggested that this is the Soret band of porphyrins (tetraphyrroles). But this suggestion has serious difficulties. Douglas (1977) has recently proposed that these bands could be due to absorption by long chain carbon molecules ' C_n ' where ' n ' may lie in the range 5–15. He suggests that their widths are due to radiationless internal conversion between levels of the excited electronic state which suffer possible overlapping by high vibrational levels of a lower electronic state. This can explain band widths by well understood concepts of spectroscopy. The argument proceeds as follows: — The simplest polyatomic carbon molecule, C_3 , is known to have a strong absorption band at 4050 Å and there is evidence that C_4 has absorption bands in the 5000 Å region. There if we examine the spectrum of a mixture of C_n molecules in which the abundance of C_n decreases as ' n ' increases, and ' n ' has a certain lower limit such as 5, we should expect to find a series of bands extending to the red from a strong band in the 4000–5000 Å region (Douglas, 1977).

The presence of HC_3N , HC_5N , HC_7N and HC_9N in interstellar medium

recently discovered (Avery *et al.*, 1976) and identified by their rotation lines of high quantum numbers in the microwave region, suggests that long chain polyenes which have no electric dipole moment and therefore cannot be observed in the microwave region, but can be observed in the optical region, are also very likely to be present. Investigation of the optical absorption of such molecules is necessary to test this hypothesis. Some of these molecules have to be prepared for the first time. This appears to be a challenge to chemists.

Recently, Sagan and Khare (1979) obtained a complex organic solid produced from cosmically abundant molecules, for which they propose the name tholins. According to them, tholins have a substantial absorption in the blue region, which is not due to S, and may be caused by conjugated polyenes, $H - (CH = CH)_n - H$, where $n \geq 6$. Pyrolysis fragments of tholins give good evidence for dienes and longer polyenes also seem to be present. Further spectroscopic and chemical work is necessary before the identification of the emitter of the diffuse bands is finally achieved.

MICROWAVE AND RADIO OBSERVATION OF INTERSTELLAR MEDIUM

The development of microwave and radio frequency spectroscopy in the 1950s gave another method to search for molecules whose rotation spectra are already known in laboratory investigations. Molecules which do not possess permanent electric dipole moment like e.g., N_2O_2 , H_2 have no rotation spectra and so cannot be detected by this technique. However, the method is suited for a large number of molecules particularly associated with dense clouds and those which do possess dipole moments and hence a rotation spectrum. The discovery in 1951 of the radio-frequency line, the well-known 21 cm h.f.s. line of atomic hydrogen predicted earlier in 1945, enabled an atomic hydrogen survey of our Galaxy. This revealed geometrical structure of our galaxy and led to a knowledge of the extent of H and the clouds that occupy the interstellar medium. This knowledge and a large amount of theoretical work based on it helped to construct a model of our galaxy. According to it, the medium has two basic components characterised by the neutral hydrogen atom region called HI and the ionized hydrogen region called HII. The optical spectral observations give information about tenuous clouds in HI region only since the denser clouds are opaque and no transmission of radiation through them is observed. It is thus known that each tenuous cloud consists of 10–50 atoms, has temperature roughly of 50–150 °K and an abundance ratio of the more abundant atoms of $He/H = 10^{-1}$, $O/H = 7 \times 10^{-6}$, $C/H = 3 \times 10^{-6}$ and $N/H = 1 \times 10^{-6}$. For the remaining atoms the ratios are much less than 10^{-6} . The ionized HII region surrounds the hot stars and is characterized by high temperature of the order of 10,000 °K. Low density and exposure to strong radiation make it unlikely for any polyatomic molecule to exist in either region without undergoing photodissociation.

However, the discovery and accurate measurements of the Δ -doublet transition of OH in the laboratory (Sanders *et al.*, 1953) in 1953 led to the identification in 1963 of the OH radical in interstellar space by its $\lambda = 18$ cm. doublet transition. This encouraged a search for polyatomic molecules like NH_3 , H_2O previously

thought unlikely to be present in space. However, the general view was that interstellar clouds were composed primarily of atoms with, may be, a limited number of simple radicals.

In 1968, the first transition of a polyatomic molecule NH_3 was detected in various clouds. This was the first shock to the general view, that polyatomic molecules are not likely to be present in space. "Collisions in space are not too frequent," thought many. But then followed the discovery of H_2O and in 1969 the first organic polyatomic molecule, formaldehyde (HCHO) was detected. Further when *masers* were produced in the laboratory and the abnormal intensity and other optical properties of OH and H_2O radiations observed in some interstellar regions were traced to strong *maser* action, many exclaimed "*Good Lord! Think of it; there are giant water 'masers' in the sky!*" Three such cosmic *masers* are now known, OH , H_2O and SiO and evidence for weak *maser* action in the interstellar molecule cyano-di-acetylene HC_3N is recently reported (Brotten *et al.*, 1978). These led to a burst of activity in the field of radio-frequency detection.

ORIGIN OF LIFE, STELLAR EVOLUTION

The discovery of several simple organic molecules like HCHO (1969) CH_2CHCN (1975) etc. that occur in living things was yet another great surprise. More recently, starting from HCN , the detection by 1978 of molecules like cyanoacetylene (HC_3N), formamide, acetaldehyde, methyl-amine and dimethyl ether, has encouraged the search for biologically important molecules. The discovery of vinyl cyanide $\text{H}_2\text{C}=\text{CHCN}$, having a double bond $\text{C}=\text{C}$, proves conclusively that olefines the class to which this molecule belongs, do exist in interstellar space; these being very reactive, and chemically unstable, very easily form polymers and are important for reaction chemistry of interstellar space. This discovery supports the view that other hydrocarbons such as ethylene $\text{H}_2\text{C}=\text{CH}_2$ and similar long chain compounds must be inhabiting the interstellar medium.

Life till now is thought to have originated in the oceans of the earth. According to Charles Darwin's intuitional suggestion, "*in a 'warm little pond' (or J.B.S. Haldane's 'hot dilute soup')* with all sorts of ammonia and phosphoric salts, light, heat, electricity etc. present, if a protein compound was originally formed, chemically ready to undergo still more complex changes, life would evolve." But here was the evidence that chemical build up that precedes the development of the simplest elementary life-forms may be taking place in space on grains in dirty interstellar dark dense clouds or at the surface of stars.

Apart from the surprise regarding the origin of life, the initial excitement was due to the fact that the trend of stellar evolution is that stars have condensed from the gas clouds. In other words, stars are formed out of matter in interstellar space. The first step in star formation is, therefore, the formation of condensation of matter in the medium. The presence of molecules indicates the process of condensation of atoms taking place so that apart from H and He the medium does contain also matter in the form of molecules formed from various atoms.

On the other hand, the nature of condensation including formation of molecules from atoms, the distribution of absorbing and emitting molecules and their

excitation states are influenced by the energy distribution of stars in the form of Planck radiation, when they are in the quiet state and during their spectacular phases in the form of high energy X-rays, γ -rays and cosmic rays. Using molecular lines as probes, we can learn something about the nature of condensations and how they are influenced by the radiation field produced by the stars which in turn is produced by the process of condensation of matter in the medium. In other words, some light is expected to be thrown on the problem of stellar evolution and the origin of the Universe.

GENERAL OBSERVATIONS

Most of the molecular lines detected in the radio-frequency region are in pure rotational transitions. Other types of spectra are also observed for some molecules. These are due to interaction of rotation with other types of motion. Such interactions result in splitting of the rotational levels. Internal rotation (CH_3 , OH, CH_3NH_2 etc.), inversion doubling (NH_3), coupling of rotation with electronic motion (CH, OH, SO, ...) are some such cases. Rotational transitions are also affected by uneven nuclear charge distribution which gives rise to the so called hyperfine splitting of rotational lines. This is found in spectra of interstellar molecules containing ^{14}N , ^{17}O or D nuclei.

Identification of molecules has been possible only in those cases where their spectra (optical or radio-frequency) were well established by laboratory spectroscopy previously. In cases where data were not available, detection had to wait till such information was made available by laboratory experiments, and was accurate to a degree required for locating the exact spectral region for scanning. All this clearly indicates that a detailed and intimate knowledge of molecular spectroscopy in all its aspects is necessary to understand interstellar molecular spectra.

Scanning radio-frequency spectrum is a very involved technique. It is very laborious; it has not been possible to develop methods and apparatus necessary to just scan the full radio region throughout the entire microwave region for mapping whatever spectra may be present there, as is possible to do in the optical region. Therefore, unless one knows the exact rotational transitions of the molecules of interest and, thereby the exact spectral narrow band involved, it is almost impossible to detect them by this method. Detection and identification will therefore be possible only if the molecules are first produced in the laboratory and their spectra accurately measured. In this connection, it is interesting to know, that the following molecules HCN , HC_3N , HC_5N , HC_7N and HC_9N have been detected by their emission rotation lines involving high 'j' values (Avery *et al.*, 1976, 1979) in the dense clouds near the nucleus of our galaxy. Of these HCN is well known, but HC_3N , HC_5N , and HC_7N which were unknown previously were for the first time synthesized and their spectra accurately measured in the laboratory before they were successfully detected in interstellar space. HC_9N has not yet been synthesized in the laboratory. But an accurate method of extrapolating its molecular constants from the known values of HC_3N , HC_5N and HC_7N has enabled its discovery and identification (Broten *et al.*, 1978).

The subject of interstellar molecules (astro-spectroscopy) is presently attracting

the attention of physicists, chemists and biologists in their search for an understanding of the evolution of stars and the origin of the Universe (astrophysics), evolution of complex molecules including those that are biologically important (astrochemistry) and evolution of life in the Universe (astrobiology). The total number of interstellar molecules discovered is increasing rapidly; it was 23 in 1973, 48 in 1978 and more than 60 in early 1979. More than 200 transitions of many different molecules in several isotopic combinations have been discovered. These span a frequency range from 0.8 to 230 GHz in the radio region and the entire optical region including the near infrared and the vacuum ultraviolet. The observations in the radio region are being presently extended with the availability of radio telescopes to higher frequencies upto 300 GHz. The heaviest presently known polyatomic molecule is the 11 atomic HC_9N with a molecular weight of 123 amu.

CONCLUSION

The very existence of molecules in interstellar space has provided considerable insight into the physics and chemistry of our galaxy. The interstellar environment is not nearly as hostile to evolve a complex structure from simplest beginning as originally assumed. It gives birth and shelter to molecules like HCN, H_2O , NH_3 , CHCO, $\text{H}_2\text{C}=\text{CHCN}$, which are known to take part in reactions that synthesize amino-acids. There is, however, no quantitative theory for the formation of polyatomic molecules. Reaction on grain surface and absorption processes indicate that polyatomic molecules in large numbers could form on grain surface. But since such reactions and nature of grain surfaces are not well understood, new insights into the basic understanding of chemical reactions are called for. Finally, enough has been said in this discussion of interstellar molecules, to accept with Einstein the inescapable fact that *'the most incomprehensible fact of Nature is the fact that Nature is comprehensible.'*

REFERENCES

- Avery, L. W., Broten, N. W., Macleod, J. M., Oka, T., and Krofe, H. W. (1976) Detection of the heavy interstellar molecule cyanodiaacetylene. *Astrophys. J.*, **205**, L173; (1979) **231**, 48.
 Broten, N. W., Macleod, J. M., Oka, T., and Avery, L. W. (1976) *Astrophys. J.*, **209**, L143.
 ——— (1978) *Astrophys. J.*, **223**, L105.
 Douglas, A. E. (1977) Origin of diffuse interstellar lines. *Nature*, **269**, 130.
 Douglas, A. E., and Herzberg, G. (1941) *Astrophys. J.*, **94**, 381.
 Douglas, A. E., and Lutz, B. L. (1970) *Can. J. Phys.*, **48**, 247.
 Dunham, T., and Adams, W. S. (1937) *Publ. Astron. Soc. Pac.*, **49**, 26.
 Hynek, J. A. (1951) *Astrophysics* (as observed by Hartmann), p. 67.
 Sagan, Carl, and Khare, B. N. (1979) *Nature*, **277**, 102.
 Sanders Jr., T. M., Schawlow, A. L., Dousnanis, G. C., and Townes, C. H. (1953) A microwave spectrum of the free OH radical. *Phys. Rev.*, **89**, 1158.
 Snow, Jr., Theodore, P. (1979) *IAU Conf. No. 87, on Interstellar Molecules*.